Sonolysis of Pharmaceutical and Personal Care Products as an Advanced Oxidation Process for the Remediation Treatment of Wastewater Effluents

by

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A thesis submitted in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE
in
CHEMICAL ENGINEERING

UNIVERSITY OF PUERTO RICO
MAYAGÜEZ CAMPUS
2007

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Abstract

Pharmaceutical and Personal Care Products (PPCPs) are a diverse group of chemicals, also known as xenobiotics, treated like potential environmental pollutants. Recently, PPCPs have been detected in trace amounts in surface and ground water resources especially those receiving wastewater effluents. Sonolytic irradiation, an Advanced Oxidation Process (AOP), had received increased attention lately as a possible remediation treatment for these pollutants. This research intends to study the sonolytic degradation of selected PPCPs model compounds, at an ultrasonic frequency of 20 kHz. At this frequency, water molecules generate $OH^{\cdot}$, whose formation was monitored by measuring the formation of H_2O_2 during the reaction. These radicals along with the cavitation phenomena are believed to be the main basis for the sonolytic degradation of these chemicals.

For caffeine, up to 34% was degraded resulting in a pseudo first order degradation rate constant of 1.68×10^{-3} min^{-1} after 4 hours of irradiation at 35°C. Comparable results were obtained for acetaminophen under the same reactive conditions (23% and 1.09×10^{-3} min^{-1}). Also, the addition of H_2O_2 into the reaction increased the degradation rate for both compounds resulting in higher decomposition percents. These results suggest combining sonochemistry with other existing AOP for larger scale applications. In addition, we captured water sonoluminescence and studied some particular higher frequencies, which increased acoustic pressures. This last finding could lead to an optimized frequency selection to achieve complete and more cost effective removal of these emerging and/or other existing pollutants.

Resumen

Los Productos Farmacéuticos y de uso Personal (PPCPs*) son un grupo diverso de químicos que son tratados como potenciales contaminantes ambientales. Recientemente se han detectado pequeñas concentraciones de estos compuestos en fuentes de aguas superficiales y subterráneas, mayormente en aquellas áreas que reciben descargas de aguas residuales. La degradación sonolítica, un Proceso de Oxidación Avanzado (AOP*), ha recibido un interés actual como un posible tratamiento de remediación para estos contaminantes. Este trabajo pretende estudiar la degradación sonolítica de compuestos modelos de PPCPs a una frecuencia ultrasónica de 20 kHz. A esta frecuencia, las moléculas de agua generan $OH^{\cdot}$, cuya formación fue monitoreada mediante la determinación de H_2O_2 durante la reacción. Estos radicales junto con el fenómeno de la cavitación, parecen ser la razón principal de la degradación sonolítica de estos químicos.

Para cafeína, hasta 34% fue degradado resultando en una constante de degradación de seudo primer orden de 1.68×10^{-3} min^{-1} luego de 4 horas de irradiación a 35°C. Utilizando las mismas condiciones de reacción, se obtuvieron resultados comparables para acetaminophen (23% y 1.09×10^{-3} min^{-1}). También, la adición de H_2O_2 a la reacción aumentó la rapidez de degradación para ambos compuestos resultando en mayores por cientos de descomposición. Nuestros resultados sugieren la combinación de la sonoquímica con otros AOP existentes para aplicaciones a macro escala. En adición, la sonoluminescencia del agua fue evidenciada y el incremento en presión acústica a ciertas frecuencias mayores fue

* Por sus siglas en inglés

estudiado. Este último hallazgo pudiera ser utilizado para seleccionar una frecuencia de irradiación ultrasónica optimizada y remover estos contaminantes emergentes de una forma más costo efectiva.

To my parents Francisco and Irma,

my family,

my niece Alondra,

and my love Lidiany. . .

"In the confrontation between the stream and the rock,

the stream always wins…

not through strength, but through persistence"

H. Jackson Brown

Acknowledgements

During the development of my graduate studies, there was this special people and entities that supported me. First of all, I would like to thank God for giving me the health, knowledge and dedication to continuously pursue and achieve my dreams. Many thanks to Dr. L. Antonio Estévez's CNY-PR AGEP program and scholarship for their encouragement, brotherhood, and financial support. My gratitude to Dr. José Colucci for giving me the respect and trust to conduct my research. It was his advices and supports what guided and taught me the way of a professional. Thanks to my graduate committee, Dr. Briano, Dr. Vega, and Dr. Castro for their considerations and suggestions to this work. Specially, Dr. Carmen Vega for your kindness and for being such a special human being.

I want to recognize the collaboration in this work of the undergraduate students D. González, J. Rovira, S. Sierra, M. Sánchez, E. Huertas, A. Flores and R. Defendini, who were friends and members of our research group. Specially, my lab partner Monica for all her help. Also, Zapata, Wilma, Angeles, the Chem. Eng. Dept. workshop staff, Waters Co., and EQ Analytical for their technical support.

To Abbott Pharmaceuticals P.R. Ltd., specially, Eng. L. Morán and the EHS Staff for the tremendous opportunity they gave me in the company. Also, many thanks to Eng. M. Moreno who gave me a day visit to their WWTP.

Last but not least, I would like to express my most sincere appreciation to my family and a special person who completely understood and encouraged me in the most difficult times of my graduate studies: Lidiany. She taught me the importance of achieving happiness not only in work but also in live.

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List of Symbols and abbreviations

Symbols

PPCP	Pharmaceutical and Personal Care Products
AOP	Advanced Oxidation Process
STP	Sewage Treatment Plants
WWTP	Wastewater Treatment Plants
HPLC	High Performance Liquid Chromatography
LC-MS/MS	Liquid Chromatography-Mass Spectrometry/Mass Spectrometer
SPE	Solid Phase Extraction
RR	Removal Rates
DAD	Diode Array Detector
IR	Infrared
DMP Method	2,9-dimethyl-1,10-phenanthroline
Rayleigh Plesset	RP Equation
EDC	Endocrine-Disrupting Chemical
MTBE	Methyl tert-butyl ether
SBSL	Single-Bubble Sonoluminescence
VOC	Volatile Organic Compound
TOC	Total Organic Carbon

1 INTRODUCTION

Most of today's emission sources of pollutants from manufacturing waste streams have long been subjected to controls and regulated by the corresponding authorities. However, the use of chemicals by the population in general and its implication or effects to the environment are more difficult to appraise. One of the up-and-coming water quality concerns is the release of small amounts of pharmaceutical and personal care products (PPCPs) into the environment. The denominated PPCPs include a wide range of prescription and non-prescription drugs, nutritional supplements, skin care products, cosmetics and cleansing agents.

PPCPs have a tendency to be "bioactive", are extensively used all over the world, and there are thousand of different products which falls into this classification. Almost exclusively these products enter the ecosystem through treated and untreated sewage and wastewater, either excreted by humans or animals, washed off the skin or decanted down the drain. These chemicals have the potential to be hazardous to many species of live organisms, including humans. However, even with the increasing efforts of the Environmetal Protection Agency (EPA), still there is not enough awareness or prevention to deal with the sources of this environmental problem.

Consequently, given the previous expertise acquire from former members of our laboratory in the utilization of ultrasound waves to enhance the synthesis of biodiesel, sonolysis of water oxidizing capabilities, another branch of sonochemistry, was studied as a novel mean to eliminate these micropollutants. Therefore, the feasibility, optimization and

kinetic parameters of this technique were evaluated in a 20 kHz ultrasonic reactor and sonoluminescence measuring equipment using caffeine and acetaminophen as PPCPs model compounds.

1.1 Justification

Puerto Rico, similar to other developed countries, is undergoing a transformation towards an ageing society. Specifically, an ageing population will result in higher concentrations of PPCPs and their respective metabolized byproducts in the environment. These pollutants are only recently recognized and present in small amounts. Additionally, they seem to be very stable, and their residence time through the bacterial sludge is not enough to destroy them in conventional sewage treatment facilities. Even though most of them are organic compounds, their difference with respect to the agrochemicals is the presence of multiple functional groups. This fact greatly complicates their transport and degradation, as well as the analytical techniques to be used for their monitoring.

In recent years, the number of articles reporting the presence, potential effects and possible removal or transformation of these compounds is increasing leading to the need of more comprehensive research. Also, there are other studies that focus on the behavior of these compounds in wastewater treatment facilities. It is suspected that some of these facilities are not operating at conditions that will destroy these compounds effectively, resulting in the need to seek for an effective way to remove PPCPs from wastewater.

As we all know, conventional techniques to remove contaminants from soil include land filling, air stripping/carbon adsorption, incineration, biological activity, and chemical treatment. Regarding the chemical treatments, recent methodologies involving the use of chemical oxidation have the potential to treat all types of organic and inorganic contaminants. These methods are commonly named Advanced Oxidation Process (AOPs), which generates hydroxyl radicals in enough quantity to improve water treatment.

Current advances in AOPs, which involves the application of ultrasound waves to induce cavitation to destroy or promote the destruction of liquid phase contaminants, include environmental sonochemistry. Some researchers are working in the application of sonochemistry in environmental remediation by using cavitation to improve other treatments (i.e. advanced oxidation), to reduce the amounts of chemicals required for conventional treatments, and as a clean energy source.

This work focuses on the detection, correlation and treatment of selected PPCPs. This will create awareness of their presence in the environment, and to study the chemical effects of ultrasound due to the phenomenon of acoustic cavitation and its possible mechanism(s) in the break-up of the mentioned compounds. The conditions (i.e. reagent concentrations, etc.) and parameters (i.e. temperature, ultrasound wave frequency, etc.) will also be varied and studied.

1.2 Objectives

- Select a model compound(s), among the most common PPCPs in Puerto Rico (i.e. caffeine, acetaminophen, clofibric acid, ibuprofen, and naproxen), that best fit our goals.
- Create awareness especially among undergraduate students of the potential impact of Pharmaceutical and Personal Care Products (PPCPs) in the quality of potable, ground and superficial water
- Develop expertise on UV-VIS Spectrophotometer and High Performance Liquid Chromatography (HPLC) techniques for the elaboration of calibration curves and treatment strategies of the model compound(s).
- Develop expertise on Sonoluminescence to study the driving pressures that result in light emission through the bubble collapse during the cavitation phenomena.
- Study, understand and develop Sonolytic Irradiation as a possible treatment process for wastewater effluents.

2 Background and Literature review

2.1 Pharmaceutical and Personal Care Products (PPCPs)

2.1.1 Origins and uses of PPCPs

For over 20 years, certain pharmaceutically active compounds (i.e. caffeine, nicotine, and aspirin) have entered the environment by a variety of routes, mostly via treated and untreated sewage effluent. Adding to it, the certainty about the environmental occurrence of these pollutants along with the wide array of other personal care products and drugs had created more awareness and interest in the scientific community. But it was not until 1999s when the topic of PPCPs in the environment had its more relevant origins after several compendia and reviews started to appear. But, in the literature, this topic is across numerous unrelated disciplines, disorganized and imbalanced in its coverage, and, when compared to conventional pollutants, it is more difficult to trace and to analyze in a common and broad manner [2].

In recent years, newly and/or improved pharmaceuticals enter the marketplace adding to the already existing and large display of chemical classes, each with different modes of biochemical action, many of which are not too well understood. These products are disposed or released into the environment on a continual basis via domestic/industrial sewage system and wet-weather runoff. The excreted metabolites and unaltered parent compounds from the

bioactive ingredients can then be subjected to further transformation in Sewage Treatment Plants (STPs) or further survive biodegradation before being discharged into receiving waters [20]. A summary of these events is illustrated in Figure 2-1.

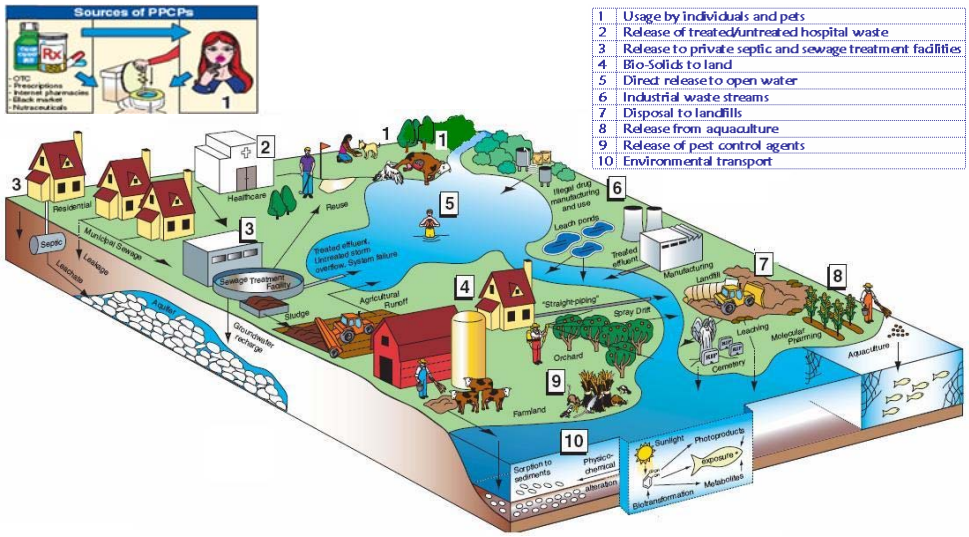


Figure 2-1 Origins and fate of PPCPs in the Environment [21]

Actually, in the United States and some countries of Europe, nearly 100 pharmaceutically active compounds from various therapeutics classes have been found in surface waters, groundwater, sewage, effluent from wastewater treatment plants, and even tap water at concentrations up to 1000 ng/L [1]. These findings agree with the ones mentioned by Daughton et al. [2], from USEPA, in which they state that more than 50 distinct compounds, including steroids and antimicrobial products, have been found in water resources (see Table 2-1). Daughton et al. also noticed the fact that there were at least 200 known and frequently used compounds that fall into this classification as PPCPs (see Table 2-2). While some authors have listed the PPCPs more likely to cause environmental problems

based on sales and human metabolism of these drugs in their respective countries, most of them agreed on certain PPCPs as the most common (see Tables 2-1 and 2-2).

Table 2-1 PPCPs found in the aquatic environment (Daughton 2001) [2]

Therapeutic Use	Generic Compound	Commercial Name
Analgesic/non-steroidal anti-inflammatories (NSAIDs)	Acetaminophen, diclofenac, ibuprofen, ketoprofen, naproxen	Tylenol, Voltaren, Advil, Oruvail, Naprosyn
Antimicrobials	sulfonamides, fluoroquinolones	many
Antiepileptics	carbamazepine	Tegretal
Antihypertensives	Bisoprolol, metoprolol	Concor, Lopressor
Antineoplastics	Cyclophosphamide, ifosfamide	Cycloblastin, Holoxan
Antiseptics	Triclosan	Igrasan DP 300
Contraceptives	Estradiol	Oradiol
Bronchodilators	Albuterol	Ventolin
lipid regulators	clofibrate (active metabolite: clofibric acid), gemfibrozil	Atromid-S, Lopoid
Musks	Polycyclic musks	Celestolide
anti-anxiety	Diazepam	Valium
sun screen agents	methybenzylidene	Eusolex 6300
X-ray contrast agents	Diatrizoate	Hypaque

Table 2-2 Some of the most frequently used PPCPs for which concerted environmental surveys have not been performed (Daughton 2001) [2]

Therapeutic Use	Generic Name
Anticoagulants	Warfarin
antidiabetic agents	insulin sensitizers, sulfonyluereas
histamine (H-2) blockers	Famotidine
Decongestants	Ephedrines
Diuretics	hydrochlorothiazide
Expectorants	Guaifenesin
gastrointestinal agents	omeprazole, lansoprazole, cimetidine
Vasodilators	lisinopril, enalapril, quinapril, benazepril

2.1.2 Occurrence and fate of PPCPs

As the concern to asset the occurrence, fate and environmental impact of these exogenous chemicals has increased, so too the need of exact, reliable and precise analytical equipments or methodologies to detect its presence. Recently, new and improved analytical methods have been developed resulting in some advances in this field. Castiglioni et al. [3], with a Limit of Quantification (LOQ) as low as 1 ng/L, used HPLC-MS/MS, along with other separation and extraction methods, to perform mass balances on selected pharmaceuticals in order to assess Sewage Treatment Plants (STPs) removal efficiencies and the subsequent environmental attenuation of this compounds.

Sometimes these contaminants are dissolved in such complex matrixes that complicate and even prevent reproducible and precise analysis, even with LC-MS/MS systems. Motivated by these problems, Vanderford et al. [22] used isotope dilution to correct for matrix suppression, as well as Solid Phase Extraction (SPE) losses and instrument variability. Their sampling recoveries in different and complex matrixes, such as wastewater influents and effluents, surface water impacted by wastewater, surface waters and drinking water ranged from 72 to 116%. Such findings could be an important tool in the development of new more strict guidelines to monitor and/or update environmental compliance reports from WWTPs and STPs, whose maximum allowable concentrations for some of these micro pollutants, in some way, are derived from older analytical techniques with higher detection limits.

Not only the analytical method used plays a significant role in the measurement of the PPCPs impact, but also the seasonal stages of the year in which the monitoring is being

conducted. Apparently, there are some factors like the attenuation and patterns of use by consumers, which should be considered before any analysis conducted on the removal rates (RR) or presence of these drugs. Recent studies performed in six different STPs plants in Italy receiving both domestic and industrial wastes, revealed these findings. All six STPs were equipped with primary and secondary treatment facilities, for example, primary setting and activated sludge processes. According to them, the removal rates could be divided into three seasonal groups: one with RR higher in summer than in winter, the other with similar RR both in summer and winter, and the last group with RR close to zero in both seasons. The last group consisted of pharmaceuticals of different therapeutic classes such as antibiotics, steroids (bronchodilator) and estrogen, whose environmental occurrences are known to cause some effects on aquatic biota. These pharmaceuticals that were not removed by in any means by STPs were carbamazepine, clarithromycin, erythromycin, lincomycin, spiramycin, and estrone. These results are depicted in figure 2.2 [3].

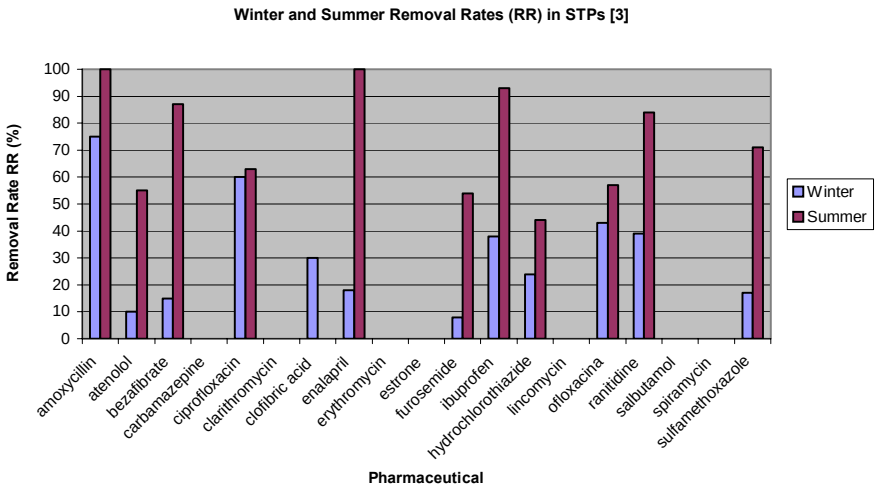


Figure 2-2: Effect of Earth Seasonal Stages on Removal Rates (RR) in STPs [3]

Not all the chemicals that are not removed from STPs end up in surface waters. There are attenuation rates produced by sorption, degradation, or a combination of both within the path length of the rivers receiving STP effluents. Moreover, the abundance in surface waters and consequent environmental concerns due to the presence of several pharmaceuticals, which can overcome STPs removal and environmental attenuation, like ciprofloxacin, ofloxacin, sulfamethoxazole, atenolol, ibuprofen, furosemide, hydrochlorothiazide, ranitidine, and benzafibrate are of particular concern. Apparently the residual loads of these pollutants to the rivers can range from 25-280 mg/day/1000 inhabitants [3].

Natural action in rivers, which occurs over time and distance, can attenuate the presence of pharmaceuticals and hormones. Mechanisms such as dispersion and dilution, sorption, photolysis, and biodegradation and biotransformation are among these low-cost and ecologically beneficial water polishing means that are currently being study to treat bioactive compounds contaminated WWTP effluents. Researchers have found that removal during flow of a regional river, where they conducted their studies, was more efficient than removal in engineered treatment wetlands. Their reports were 100% removal for gemfibrozil, a cholesterol-modifying drug, in the river and 58% in the wetland. As for ibuprofen, the reduction was 83% and 47% for the river and wetland, respectively. Further detailed results using microcosm studies backed up their findings suggesting that the attenuation mechanism for ibuprofen and gemfibrozil was not by means of photolysis but biotransformation.

Meanwhile, even though if any or some PPCPs are removed from STPs there is the possibility that it wont biologically transform in the aerobic or anaerobic microbial metabolized medium resulting in accumulation. Heidler et al. [4] focused on the retention of

the topical antiseptic triclocarban (TCC) during sludge treatment by performing a mass balance in both the liquid phase (i.e. influent and effluent) and solid phase (sludge). Their studies in a standard STP suggested that TCC was removed from the aqueous phase with an overall efficiency of 97 $\pm$ 1%, from which most of it were adsorbed into the sludge (78 $\pm$ 11%) without any further significant anaerobic digestion or transformation resulting in the accumulation of three quarters of the mass of the antiseptic compound disposed of by consumers. TCC could potentially end up in the environment by the remediation plan to reuse municipal sludge in lands partially used for agriculture (biosolids).

2.1.3 Ecologic Exposure and Effects

For some researchers, even though the measured concentrations of these compounds do not appear to be a significant risk to human health [25], the vision of a natural indirect potable reuse system to deal with water scarcity, could go wrong if caution and removal strategies are not taken when dealing with these micro pollutants [24]. Some scientists believe that the potential risk associated with the presence of low levels of these compounds in aquatic environment is limited to influence aquatic life only [5]. However, other investigators [1, 4, 6] believe that humans can also be affected.

The estrogen hormone (particularly 17β-estradiol, estrone, and estradiol) has properties of endocrine-disrupting chemicals (EDCs) and has been found to disrupt the endocrine system of many species, including humans even at ng/L [44,45]. Aquatic organisms might be chronically exposed to these bioactive substances, and because of their

continuous introduction in surface waters, exposure even to the environmental nonpersistent compounds may be significant. A recent report linked the feminization of Pacific Ocean coastal fish with wastewater effluent discharge from the city of Los Angeles, California [46]. Other species of aquatic organisms, for example, turtles, trout, frogs, and minnows, may have been sexually inhibited or reversed by the presence of these natural estrogens [47].

In other set of studies performed by Halden [4], triclorocarban (TCC) was suspected to enhance antibiotic resistance in bacteria in the sludge of STPs and/or somewhere else in the environment. Moreover, Pomati et al. [1], using a mixture of 13 drugs and at concentrations in the range of ng/L to mimic Italy's environment, reported a maximum 30-40% inhibition in growth and morphological changes in HEK293 human embryonic cells at the mentioned environmental exposure levels, attributing these effects not as individual but possible synergetic ones.

Also, simulating one of the most common tertiary types of wastewater treatment (chemical) in the U.S., Bedner et al. [6] proved that acetaminophen reacted to form the two toxic compounds 1,4-benzoquinone and N-acetyl-p-benzoquinone imine (NAPQI), which is a lethal toxic associated in human acetaminophen overdoses, among 9 other noticeable byproducts of chlorination. Their results proved that acetaminophen is likely to be transformed significantly during wastewater chlorination into these two compounds that are approximately 58 (1,4-benzoquinone) and 25 (NAPQI) times more toxic than their parent compound (acetaminophen).

These results are very recent, which is of concern due to the fact that it appears that the wastewater treatment plants are not capable of removing this kind of rising contaminants.

Any future large-scale implementation of our technique under study, whether it is the use of ultrasound waves alone or its coupling with any other AOP, should be made in that mentioned region (tertiary) of the wastewater processing facility. A schematic of a typical wastewater treatment plant, that uses UV rays as tertiary treatment, is included in the Appendix. This kind of treatment is rarely used, according to Metcalfe et al. [7], because of its high costs but still it is under extensive investigation due to its feasibility to deal with the presence and potential hazard of PPCPs.

2.2 Ultrasound Waves

The application of ultrasound for water treatment, have also been questioned because of energy costs, but recent papers point toward the optimization of specific conditions or the combination with other treatments. Ultrasonic irradiation can be used for the treatment of turbid solutions and slurries, and is reagent free unlike most other AOPs, which require the addition of reagents and/or photolysis. A number of large-scale water and sewer treatment plants are under development and sonolytic water purification systems have entered the marketplace [8]. The following subparts, contains the theoretical aspects and previous uses of the chemistry behind ultrasound waves, which provided the essential tools for this research.

2.2.1 Fundamentals

Even if it is the bang of an explosion or the steady sine-wave tone of a whistle, an underwater sonar pulse or the output of a clinical fetal scanner, “sound” is a waveform

consisting of density variations in an elastic medium, propagating away from a source [32]. For the majority of chemists an interest in power ultrasound springs from the fact that it provides a form of energy for the modification of chemical reactivity, which is different from that normally used e.g. heat, light and pressure [36].

By itself, ultrasound has no direct action on chemical bonds. Under the usual conditions of most sonochemical experiments, the energy density of an acoustic field is only about 10^{-10} eV per atom. There is no possibility for the occurrence of an interaction between the waves and the matter, which leads to the idea of the existence of an indirect phenomenon acting as a relay to induce reaction. This phenomenon is called cavitation, by which bubbles produced in a liquid as the waves propagate, pulsate non-linearly. After an expansion forced by the acoustic field, the bubbles undergo a violent collapse during which they focus mechanically the low energy density of the sound field by more than 11 orders of magnitude. The energy extends of this collapse is so energetic that it causes the emission of a faint light visible to the naked eye after some adaptation to the dark [30].

The mechanical and chemical effects of cavitation occur in three distinct regions:

- Within the bubble itself which can be thought of as a microreactor
- In the liquid region immediately adjacent to the bubble where the temperatures are so great and
- In the immediate vicinity of the bubble where the shockwave produced on collapse will create enormous shear forces.

The two most immediate properties of alternating pressure waves are frequency and amplitude. A simplified form of the temporal evolution of the pressure P(t) at a given point of a elastic medium (solid, liquid, gas) is given by:

$$P(t) = P_A \sin 2\pi ft$$ **Equation 2-1**

where: P_A is the maximum pressure amplitude

f is the frequency of the ultrasound waves

t is the time

Sound frequencies are recorded in units of Hertz (Hz) and ultrasound itself is defined in terms of human hearing and is sound having a frequency higher than the human hearing range, which correspond to those above 20 kHz. Figure 2-3 displays the different sonic regions and some of its most common applications.

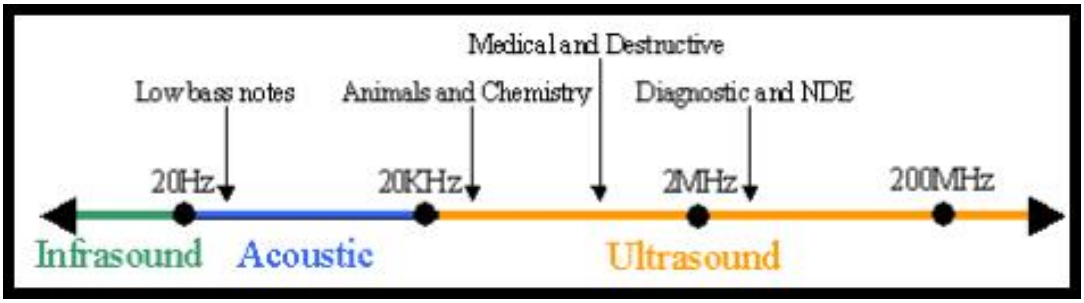


Figure 2-3: Sound Frequency Ranges

Our area of interest corresponds to the low frequency waves, known as power ultrasound, which lies between 20 and 100 kHz. Its uses are more relevant in cleaning, plastic welding and more recently, for sonochemistry [36].

2.2.2 Effect of Energy and Temperature

The effects of energy, directly associated to the wave amplitude, are easy to investigate despite the difficulty in measuring this parameter. There is an energy optimum for many examples. It seems that no sonochemical reaction occurs below the cavitation threshold, which will be discussed in section 2.2.3. When the energy is increased, the rate of the reaction increases as well as the amount of cavitation bubbles, reaches a maximum, and then decreases significantly. The pressure applied to the sonicated medium is directly involved in the resonance between the bubble vibration and the acoustic field, and modifies the cavitation threshold. When the pressure is increased, cavitation becomes more difficult, but there is also an increase in the energy release after the collapse of the bubble [30].

In a similar way, the temperature also has an optimum in sonochemical reactions. The presence of excessive amounts of vaporized liquid in the bubble makes the collapse less energetic, by the so-called “cushioning effect”, showing the relation between the nature of the medium and the temperature. The rates of sonochemical reactions can be increased, at least within some limits, by lowering the vapor pressure of the solvent or by choosing a less volatile one. Table 2-3 contains the cavitation characteristics of some of the most common

solvents, where I_{max}, T_{Imax}, and T_1-T_2 represent the maximum cavitation intensity relative to water, the temperature at which T_{Imax} is achieved, and the temperature range over which cavitation intensity is higher than 70% of I_{max}, respectively.

Table 2-3: Cavitation parameters of some organic solvents [49]

Solvent	Boiling Pt (°C)	I_{max}	T_{Imax} (°C)	T_1-T_2 (°C)
Water	100	1	35	+20+50
Toluene	111	0.71	29	+10+40
Benzene	80	0.43	19	+10+32
Chloroform	61	0.5	-3	-11+15
Methylene chloride	40	0.38	-40	-60-25
Carbon tetrachloride	77	0.35	8	0+22
Methanol	65	0.52	19	+4+23
Ethanol	78	0.46	21	+15+27
1-Butanol	118	0.43	32	+10+45
2-Butanol	97	0.42	27	+8+44
2-Propanol	82	0.38	16	0+30
Ethyl Acetate	77	0.45	9	-5+16
Acetone	56	0.44	-36	-50-20
Triethylamine	89	0.21	1	-12+14
Acetic acid	118	0.06	48	+20+60

Their measurements of these parameters were made using a cleaning bath delivering 46 kHz ultrasound waves at constant intensity. When they lowered the frequency to 22 kHz, the absolute intensity of cavitation was modified, but not it relative scale [49].

In environmental sonochemistry of organic compounds in aqueous solutions, the temperature effect was studied for Methyl tert-butyl ether (MTBE) by Neppolian et al. More than 95% degradation of 2.84 x 10^{-2} mM of MTBE was observed when the initial temperature of the reactor was at 30ºC, whereas 84% degradation was observed at 20ºC.

Likewise, the pseudo-first-order rate constants increased with temperature in a range from 10ºC up to 30ºC [18].

2.2.3 Bubble Dynamics and Mechanical Aspects

The Rayleigh Plesset (RP) equation has been solved to estimate the radius and pressure-pulse magnitude and history of bubble oscillation for a variety of conditions and is also used to analyze the sonochemical and sonoluminescence effects of cavitation [31-40]. This equation is expressed as:

$$\frac{d\dot{R}}{dt} = \frac{1}{\rho_L}\left[P_{go}\left(\frac{R^{3\alpha}}{R^{3\alpha+1}} \right) + \frac{P_V}{R} - \frac{2\sigma}{R^2} - \frac{\left(P_b - P_A \sin \omega t\right)}{R} \right] - \frac{3\dot{R}}{2R} \qquad \textbf{Equation 2-2}$$

with the initial conditions at t = 0, R = R_o, and $\dot{R} = \frac{dR}{dt} = 0$

where: R is the instantaneous radius of the bubble or cavity

$\dot{R}$ is the bubble wall velocity

P_b is the atmospheric pressure (P_h)

P_v is the vapor pressure in the bubble

P_{go} is the initial gas pressure inside the bubble

α (= κ) is the polytropic index of the saturated gas, which varies from

γ (C_p/C_v) for adiabatic conditions to 1 for isothermal conditions

Solutions to the RP Equation have been used to predict the maximum pressures and temperatures reached during the collapse of transient cavitation bubbles. Equation 2-3 and 2-4 displays these approximate results [37, 38]:

$$T_{\max} = T_o\left[\frac{P_m(\gamma-1)}{P}\right] = T_o\left[\frac{R_o}{R_{\min}}\right]^{(3\gamma-1)}$$

Equation 2-3

$$P_{\max} = P\left[\frac{P_m(\gamma-1)}{P}\right]^{\frac{\gamma}{\gamma-1}}$$

Equation 2-4

where: T_o is the temperature of bulk solution

R_{min} is the bubble radius upon collapse

P is equal to $P_v + P_g$

P_m is equal to $P_h + P_a$

As with transient cavitation, high temperatures and pressures are also produced in stable bubbles as they oscillate in resonance with the applied acoustic field. The ratio T_o/T_{max} is given by Equation 2-5 [34, 39]:

$$\frac{T_o}{T_{\max}} = \left\{1 + Q\left[\left(\frac{P_h}{P_m}\right)^{\frac{1}{3\gamma}} - 1\right]\right\}^{3(\gamma-1)}$$

Equation 2-5

where: Q is the damping factor, which is the ratio of resonance amplitude to static amplitude of the oscillating bubble usually assumed to be 2.5

Another parameter, the maximum size of a cavitation bubble is dependent on the applied frequency, the acoustic pressure, the density of the liquid medium, and the hydrodynamic pressure as expressed in Equation 2-6 [36]:

$$R_{\max} = \frac{4}{3\omega_a}\left(P_A - P_h\right)\left[\frac{2}{\rho P_A}\right]^{0.5}\left[1 + \frac{2}{3P_h}\left(P_A - P_h\right)\right]^{0.33} \quad \textbf{Equation 2-6}$$

where: ω_a represents the applied acoustic frequency

The maximum radius is associated to the collapse time of an acoustical bubble under constant pressure. Equation 2-7 gives a picture of this relation.

$$\tau = 0.915 R_{\max}\left[\frac{\rho}{P_m}\right]^{0.5}\left(1 + \frac{P_v}{P_m}\right) < \frac{T}{2} \quad \textbf{Equation 2-7}$$

where: τ is the time of collapse of the cavitation bubble

T is the ultrasonic period

Equations 2-3 through 2-7 show that at high acoustic pressures (P_A), the cavitation bubbles are able to grow in size during a rarefaction cycle such that there is not enough time for complete collapse of the bubbles during a single compression cycle. As a result, there is

an optimum power density (acoustic intensity) that can be applied during sonochemical irradiation to achieve maximum reaction rates [42].

Ultrasonic frequency also has an effect on the resonant size of an acoustically cavitating bubble. This relationship can be numerically described using Equation 2-8 [43] as follows:

$$R_r^2 = \frac{3\kappa P_h}{\rho \omega_r^2}$$

Equation 2-8

where: ωr is the resonant circular frequency (2πf)

As the frequency increases there are more cavitation events per unit of time and the bubble surface area-to-volume ratio is increased, but the bubble lifetime is shorter thus increasing the transport activities across its interface. In general, lower frequency sonication enhances pyrolysis due to the high temperatures that are achieved during the bubble collapse, while higher frequencies increase the formation of $OH^{\cdot}$ radical. However, at even more higher frequencies, there is a limiting point in which the resonant bubble size is not large enough to produce sufficient energy upon collapse to generate sufficient hydroxyl radicals from water [43]. This condition varies depending the dimensions, conditions and the system under study or treatment.

There is a critical or minimum rarefaction pressure, which must be applied in excess of hydrostatic pressure to create a bubble. In other words, it is possible to obtain a numerical idea of the minimum value of acoustic pressure P_a necessary for the growth of an acoustical bubble through the Blake threshold pressure (P_B):

$$P_B = P_h - P_v + \frac{4}{3}\sigma\sqrt{\frac{2}{3}\times\frac{\sigma}{\left(P_h + 2\frac{\sigma}{R_o} - P_v\right)R_o^3}}$$

Equation 2-9

where: R_o is the equilibrium or resonance radius of the bubble

Therefore, these microbubbles can be either stable about their average size for many cycles or transient when they grow to certain size and violently collapse or implode during the compression part of the wave. The critical size depends on the liquid and the frequency of sound. For example, at 20 kHz the bubble size ranges from 100-170 μm. But their implosions are the spectacular part of sonochemistry.

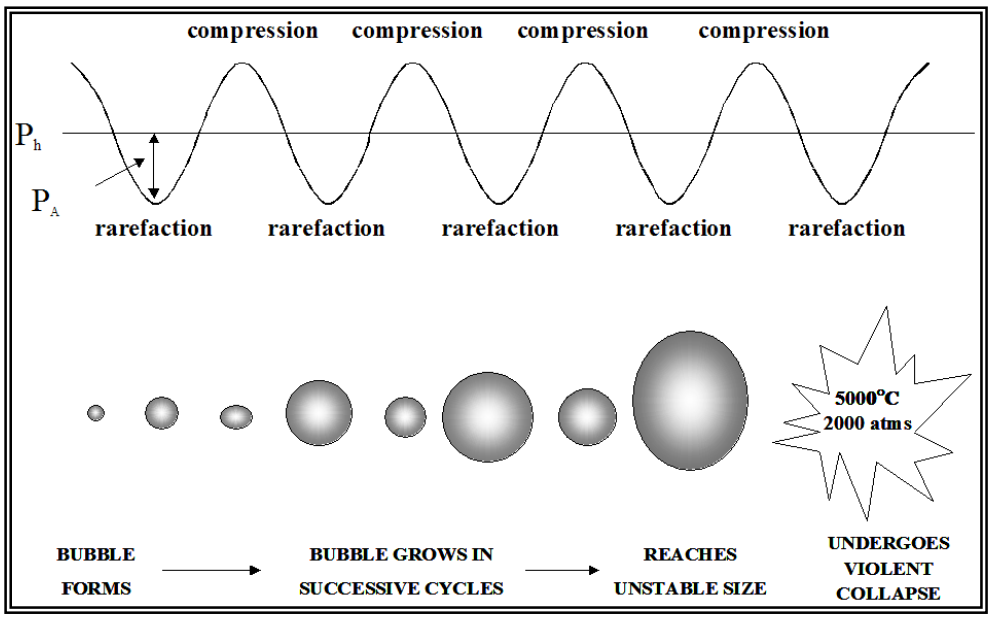


Figure 2-4: Formation, growth and collapsing of an acoustical bubble during cavitation [41].

The lifetime of these microbubbles are of the order of microseconds and their sudden collapse leads to localized, transient high temperatures and pressures that may reach up to and above 5000 K and 2000 atm, respectively. This is known as the "hot spot" theory. These rather extreme conditions are very short-lived but have shown to result in the generation of highly reactive species including hydroxyl ($OH^{\cdot}$), hydrogen ($H^{\cdot}$) and hydroperoxyl ($HO_2^{\cdot}$) radicals, and hydrogen peroxide [9, 10].

2.2.4 Sonolysis of Water

The formation of $H^{\cdot}$ and $OH^{\cdot}$ is attributed to the thermal dissociation of water vapor present in the cavities during the compression phase (R1). Sonolysis of water also produces H_2O_2 and H_2(g), via hydroxyl radicals and hydrogen atoms (R5, R8-R11). The chemistry during this process is described in Table 2-4.

Table 2-4: Chemistry of Sonolysis in water (Adewuyi 2003) [10]

Sonolysis of water	
$H_2O +))) \longrightarrow H^{\cdot} + {\cdot}OH$	(R1)
${\cdot}OH + {\cdot}OH \longrightarrow H_2O + O^{\cdot}$	(R2)
${\cdot}OH + H_2O \longrightarrow H_2O_2 + O^{\cdot}$	(R3)
$H^{\cdot} + {\cdot}OH \longrightarrow H_2O$	(R4)
$H^{\cdot} + H^{\cdot} \longrightarrow H_2$	(R5)
$O^{\cdot} + O^{\cdot} \longrightarrow O_2$	(R6)
${\cdot}OH + {\cdot}OH \longrightarrow H_2 + O_2$	(R7)

$\cdot OH(aq) + \cdot OH(aq) \longrightarrow H_2O_2(aq)$	(R8)
$H\cdot + O_2 \longrightarrow HO_2\cdot$	(R9)
$HO_2\cdot + H\cdot \longrightarrow H_2O_2$	(R10)
$HO_2\cdot + HO_2\cdot \longrightarrow H_2O_2 + O_2$	(R11)
$O_2 \longrightarrow 2O\cdot$	(R12)
$O_2 + O\cdot \longrightarrow O_3$	(R13)

The presence of oxygen improves sonochemical activities, but it is not essential for water sonolysis, and sonochemical oxidation can go on in the presence of any gas.

There are several publications reporting degradation of aqueous organic and inorganic pollutants by ultrasound irradiation or combined ultrasound with other AOPs. Berlan et al. [11] achieved total degradation of 100 ppm phenol, aniline, and 2-chlorophenol after 100 minutes with 1 W/cm^2 intensity at 541 kHz, 27 $\pm$ 2 ºC, pH = 6 and under air, O_2, and Ar dissolved gasses. In their work, hydroquinone, cathecol, p-benzoquinone, oxalic, maleic, formic and propanoic acids, and CO_2 were among the reaction intermediate/products and neither of them was obtained at 20 kHz 27 W/cm^2 because the concentrations of the starting reagents remained unchanged.

Cost et al. [12] used 20 kHz 50 W ultrasound at 10 ºC, pH =5.5 and irradiating air and proved that the degradation of 2 x 10^{-5} M p-nitrophenol to 4-nitrocatechol was not affected by chemicals of natural water.

In other studies, Gonze et al. employed ultrasound irradiation as a preoxidation step before biological treatment of wastewater. They utilized 0.1mM sodium pentachlorophenate

(NaPCP) as a model compound in a sequential ultrasonic/biological treatment reactor with an electrical generator of 500 kHz and at 20 $\pm$ 2 ºC, 6.8-7.5 pH, and the operating wattage was 55-65 W. No degradation products were reported and the toxicity of NaPCP to microorganisms was immensely decreased [13].

Another pollutant degraded with ultrasound was parathion (O,O-diethy O-p-nitrophenyl thiophosphate), a major pesticide that is used worldwide [14]. Initially parathion was degraded in almost two hours into p-nitrophenol, SO_4^{2-}, PO_4^{2-}, $C_2O_4^{2-}$, NO_2^- and NO_3^- using ultrasound waves of 20 kHz (75 W/cm^2) at a temperature of 30ºC. One interesting fact of their results was that the pH of the solution decreased from 6.0 to 3.7 after two hours of sonication indicating a possible role and/or influence of pH in the reaction.

Based on the previous discussion, sonolytic degradation of organic compounds is widely known for its success in removing many organic compounds, most of them well-known environmental pollutants. Most PPCPS have some similarities in chemical structures or functional groups, which should be the determining factor for the achievability of hydroxyl attack to pursue an effective degradation of PPCPs using sonolysis.

2.2.4.1 Hydroxyl Radicals Reaction Mechanism

Hydroxyl radicals are not only generated by means of sonolysis of water. In fact, the literature describing the reaction mechanisms at which several organic compounds are decomposed, degraded, and/or broke down by these reagents is very broad and diverse. The

works done by Lesko et al. [48] and Kyu Kim et al. [53] on phenol and benzothiophene, respectively, describes different reaction pathways and byproducts as a result of continuous $OH^{\cdot}$ attacks on the mentioned compounds.

Kyu Kim et al. suggested that the radicals could either directly react with the organic species at the bubble-water interface or diffuse to the solution and then react with the organic species in the solution phase. These routs leaded to the formation of hydroxylated products such as 3- hydroxybenzothiophene, which were mineralized to end products such as CO_2 and inorganic sulfur species, according to their results. Figures 2-5 to 2-7 depict how the thiophene ring seems to be more attractive to the hydroxyl radicals than the benzene ring in a proposed reaction pathway involving these chemicals.

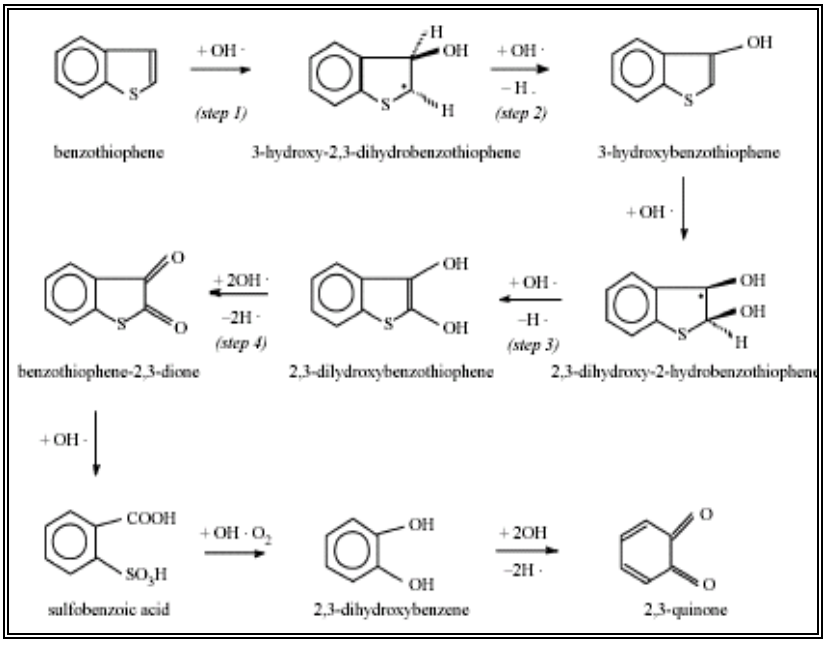


Figure 2-5: Proposed reaction pathways for the photocatalytic oxidation of benzothiophene: step 2 [57].

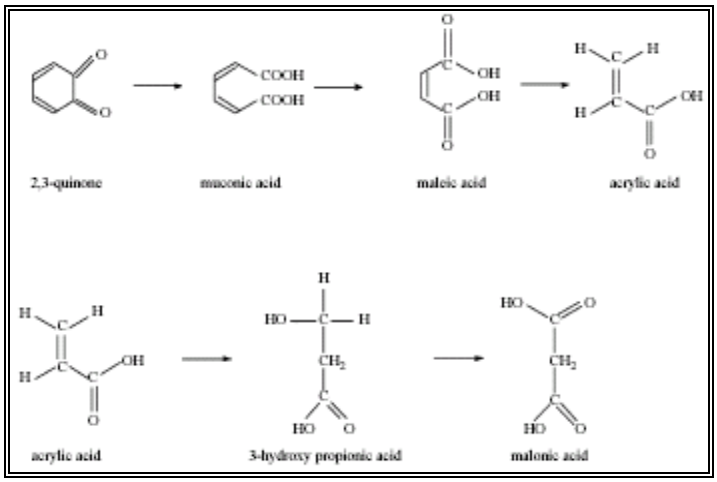


Figure 2-6: Proposed reaction pathways for the photocatalytic oxidation of benzothiophene: step 3 [57].

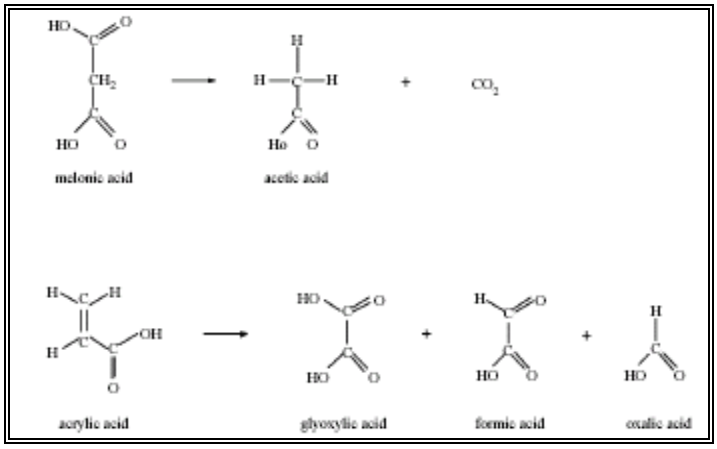


Figure 2-7: Proposed reaction pathways for the photocatalytic oxidation of benzothiophene: step 4 [57].

In other studies, Lesko et al. proposed a reaction mechanism for the sonochemical decomposition of phenol. While the works done on benzothiophene, described above, clearly shows more affinity between the radicals and the thiophene ring, the reaction pathway for phenol demonstrates that indeed $OH^{\cdot}$ radical can also attack and start the oxidation of the

molecule through the benzene ring. The reactivity of the hydroxyl radicals with the benzene ring of phenol is illustrated in Figure 2-8.

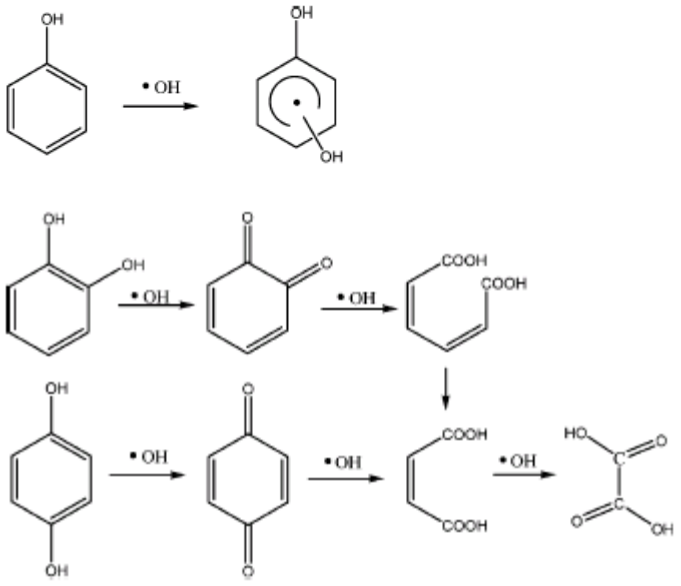


Figure 2-8: Reaction mechanism for the sonochemical decomposition of phenol [48].

As shown in the previous figure, the first reaction of phenol with hydroxyl radicals generates dihydroxyl cyclohexadienyl radicals that yield hydroquinone and cathecol in the presence of oxygen. Further OH· reactions produce ring cleavage products that oxidizes to yield unsatured carboxylic acids (i.e. muconic and maleic acids), which continue to react with the production of oxalic acid. Carbon dioxide is formed after oxalic acid (HO_2CCO_2H) reacts with OH· [48].

Another reaction mechanism, the ozonolysis of phenol, which produces similar byproducts as the ones discussed above for the sonolysis of phenol, is included in the Appendix.

2.2.5 Sonoluminescence of Water

H. Frenzel and H. Schultes at the University of Cologne as an indirect result of wartime research first observed sonoluminescence in an ultrasonic water bath in 1934 in a marine acoustic radar. This early work involved very strong ultrasonic fields and yielded clouds of unpredictable and non-synchronous flashing bubbles, now termed "multi-bubble sonoluminescence". Such a chaotic phenomenon did not lend itself to detailed scientific investigation. Then, in 1990, the first observation of sonoluminescence from a single air bubble levitating in water energized at its acoustic resonance termed single-bubble sonoluminescence (SBSL). Once per acoustic cycle, coincident with a sharp decrease in bubble size, bluey-white light is emitted in a brief flash shorter than 100 ps in duration, with incredible regularity [30]

The origin of sonoluminescence is still elusive, and there is some uncertainty regarding the true mechanism at which it occurs. It is generally agreed that the adiabatic compression of the bubble leads to very high interior temperatures, but beyond that, shocks, plasmas, ionization and photo-recombination, and even fusion are all fiercely debated possible explanations [50].

In the literature there are lots of books and articles about sonoluminescence whose explanations of this phenomenon extend from simple to very complex in areas such as its

emission spectrum, effects and mechanisms. Nevertheless, some of the most relevant and useful findings were about the relation between the acoustic pressure and the intensity of cavitation before and after the bubble collapse. Gaitan et al [51] measured the radious-time behavior of the bubble, which pulsated at the frequency of insonation and with amplitudes up to R_{max}/R_o of about 7. Also, they compared time resolved measurements of the sonoluminescence, which was bright enough to be seen in the dark room by unaided eye, and which microscope observations showed to originate from the geometric center of the bubble, with radius-time measurements of the nonlinear pulsation, made a few seconds later. From that measurements and comparisons, it was found that the sonoluminescence flashes were shown to be simultaneous with the bubble collapse, which is strongly dependent of the acoustic pressure. Figure 2-9 shows simultaneous plots of the sound field, the bubble radius and sonoluminescence for a driving pressure of 1.2 atm and a frequency of 22.3 kHz.

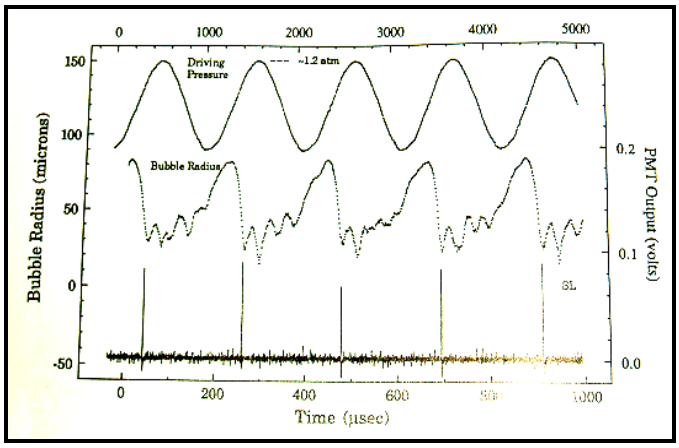


Figure 2-9: Acoustic field (top), bubble radius (middle) and photomultiplier output (bottom) as a function of time during an acoustic field of 22.3 kHz and a driving pressure of 1.2 atm (Taken from Gaitan et al. [51].

Gaitan et al. compared their experimental results with theoretical models. They suggested that the minimum temperature required for observable luminescence was between 2,000 and 3,000 K. In fact, those models predicted temperatures up to 10,000 K for their experimental conditions.

In another set of studies, Steer et al. [50] determined that the acoustic resonant frequency decreased with temperature. They found two resonances, at 25.5kHz and at 25.1kHz - the former was stronger at room temperature, and the latter much better below 16°C. According to them, the two resonances were specific to their flask causing sonoluminescence bubble to cycles its size between about 50 and 0.5µm with each acoustic wave. In the Appendix, their pictures evidencing the emission of light through sonoluminescence are depicted.

3 Experimental Methods and Equipment

Materials and Method

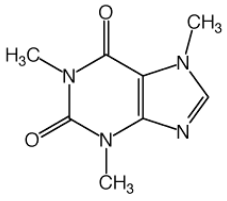
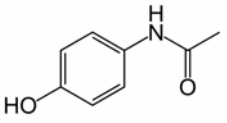
To study the viability of using power ultrasound as a tertiary wastewater treatment, two model compounds were selected from the PPCPs list based on consumer demand, chemical activity and structure, and more importantly by analysis feasibility. These two chemicals were subjected to ultrasound waves in an aqueous environment in a reactor at different temperatures. Liquid Chromatography, UV-VIS spectrometry, and titration methods were used to perform quantitative and qualitative analysis of the model chemicals and reaction byproducts. Another set of experiments, sonoluminescence, was used to study and understand better the cavitation phenomena behind sonolysis. These equipments and methods used in this project will be discussed in this chapter.

3.1 Analytical Reagents

Caffeine and acetaminophen reagents were used for the sonolysis experiments. Methanol (HPLC Grade), Glacial Acetic Acid, and deionized water were used for the preparation of the calibration curves. A 30% Hydrogen Peroxide stock solution was used for the preparation of a calibration curve to monitor the emergence of this oxidant during the sonolysis of water (see section 3.5.2.1 and 3.5.2.2), and for its coupling with ultrasound as an AOP. All chemicals, except caffeine and acetaminophen, were purchased and used as shipped from Fischer-Scientific. Caffeine and acetaminophen reagents were obtained from

Sigma-Aldrich Co. Table 3-1 contains some general information and properties for these two PPCPs model compounds.

Table 3-1: General information and properties for caffeine and acetaminophen

Reagent	Molecular Mass (g/mol)	Chemical Structure	Boiling Point (ºC)	Melting Point (ºC)	Solubility in Water at 25ºC
Caffeine	194.19		N/A	238	22 mg/mL
Acetaminophen	151.17		> 500	170	11 mg/mL

3.2 Equipments for the Ultrasound Experiments

3.2.1 Ultrasonic Reactor

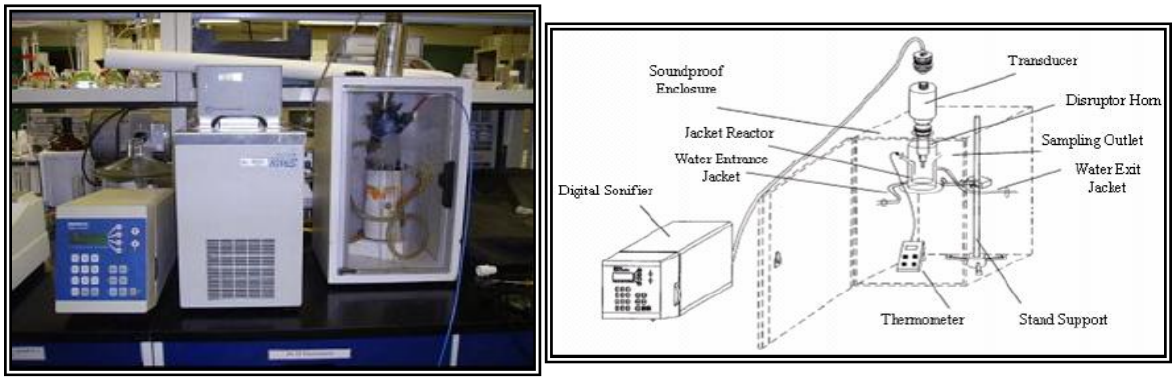


Figure 3-1: Picture (a) and (b) Schematic of the Ultrasonic Reactor (Scheme taken from Borrero 2002).

The Branson® Digital Sonifier Model 250 probe system used in these studies operates at a frequency of 20 kHz. It has a digital wattmeter to measure the power applied to the transducer to maintain the amplitude for any given output control setting. The converter vibrates in a longitudinal direction and transmits this motion to the horn tip immersed in the solution, which causes cavitation. In addition, a Fisher Scientific® ISOTEMP 1016S Temperature Controller is used to maintain a constant temperature during the reactor. This controller was used to set the reaction temperatures from 20 to 35°C.

3.2.2 Teach Spin® Sonoluminescence SL100 B

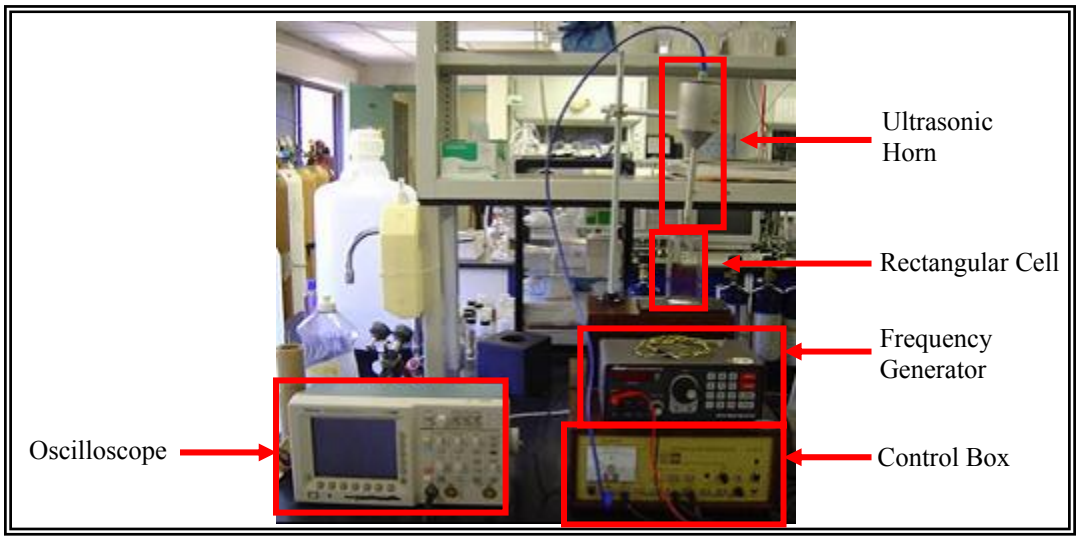


Figure 3-2: Picture of the Teach Spin® Sonoluminescence SL100 B Equipment

The Sonoluminescence Equipment consists of a Ramsey SG-550 Frequency Synthesizer Signal Generator, a controller for a horn with an output of 30 VAC, DC-100kHz, 3A max, a function generator with an input of 1 VAC into 10 kΩ. The ultrasonic horn has an acoustic power of 50 W and a maximum input of 1500 V and the Oscilloscope is a Tektronix® TDS 3032 Two Channel Color Digital Phosphor. The sample is placed in a plastic rectangular cell.

The cell is a plastic container onto which is epoxied a small ceramic transducer that serves as a microphone. Since this transducer is not compressed small fluctuations in its diameter produce a measurable signal. By attaching this transducer to the bottom of the rectangular cell one can easily detect when the pressure in the cell is in resonance mode. The cell also contains a small NiCr filament wire that connects to the front panel of the control box. A bubble is seeded when a current is passed through this filament momentarily causing many vapor bubbles to be formed, which then coalesce into a single bubble which is trapped at the closest pressure anti node.

The transducer picks up the signal produced by the standing waves in the water as well as the acoustic signature of a trapped bubble. When a bubble is trapped both signals are superimposed. The signal input to the control box is sent to a buffer that filters off any 60 Hz line noise that may be present on the signal and then passes it to an output. The signal is also sent to a peak detector where its peak value is amplified by a factor of 4 and sent to the analog display on the front of the control box. This allows one to adjust the frequency and simply look at the value on the display to determine when one has passed through a resonance mode of the cell.

3.3 Analytical Equipments

3.3.1 Reverse Phase High Performance Liquid Chromatography

Figure 3-3: Picture of the Hewlett Packard Series 1100 High Performance Liquid Chromatographer

The High Performance Liquid Chromatographer (HPLC) used to quantitatively analyze the analytical reagents and monitor their degradation during ultrasonic irradiation is a Hewlett Packard Series 1100 with a Diode Array Detector (DAD). The stationary phase column is a Princeton SPHERE C18 60A 5µm column from Princeton Chromatography Inc., with a length of 150 mm and ID of 4.6 mm. The mobile phase used consisted of two different volume ratios of H_2O, CH_3OH (HPLC Grade) and Glacial Acetic Acid for caffeine and acetaminophen. Table 3-2 summarizes the analysis set points of the equipment used for our model compounds.

Table 3-2: Summary of the HPLC parameters for each chemical

Compound	Retention Time (min)	Mobile Phase (%V)			DAD Settings (nm)			
		H_2O	CH_3OH	CH_3COOH	λ_{max}	BW	λ_{ref}	BW
Caffeine	3.7	60	40	1.5	272	24	360	100
Acetaminophen	3.2	70	30	1.5	245	24	360	100

The column temperature was held at 35°C and the mobile phase flow rate was set to 1.0 mL/min. Approximately, 50 μL of sample were injected manually in an injector loop of 20 μL. Data Analysis was made using the Chemstation® 10.2.1 software.

3.3.2 UV-VIS Scanning Spectrophotometer

Figure 3-4: Picture of the Cecil® 3000 Series Scanning Spectrophotometer

The Cecil® 3000 Series Scanning Spectrophotometer to be used in the quantitative and qualitative analysis of our analytical reagents is a high performance equipment that works in

the wavelength range of 190-1000 nm with an accuracy better than $\pm$ 1 nm, optical bandwidth of 1.8 nm, stray light of less than 0.01%, wavelength precision of 0.1 nm and baseline stability of + 0.001% A/h. This equipment contains tungsten (W) and deuterium (D_2) lamps along with a silicon photodiode detector.

3.4 Weighing and volumetric equipment

Calibrated analytical scales were used to weight the analytical reagents. Volumetric determinations and manipulation of liquid reagents and/or solutions were made using beakers, pipettes, burettes, flasks, and calibrated syringes ranging from 1μL to 300 mL.

3.5 Experimental Methodologies

3.5.1 Sonolysis and Sonoluminescence of PPCPs

For the sonolysis experiments, solutions of caffeine and acetaminophen were prepared with an initial concentration of 10 ppm. An initial volume of 160 mL of the corresponding chemical solution was added to the reactor with its temperature and amplitude already set. Before and during the reaction, samples of the reaction were taken manually from the sampling port at different time intervals. These samples were then injected to the HPLC to monitor the degradation of our model compounds.

Sonoluminescence experiments were carried out using partially degassed pure water and solutions of 100-1000 ppm of caffeine and acetaminophen to study the light emission

and the effects of increasing frequencies on the mentioned solutions. The frequency generator of the instrument, allowed the variation of the frequency of irradiation from 1-60 kHz. The corresponding signal from the transducer were graphed and compared for each solution. These experiments were performed at room temperature. Tables 3-3 summarize these parameters used for both studies.

Table 3-3: Summary of the experimental parameters used for the sonolysis and sonoluminescence of PPCPs experiments

Parameter	Range
Reaction Temperature in the Ultrasonic Reactor	20, 25, 30, 35 and 40°C
Ultrasonic Reactor Frequency	20 kHz
Ultrasonic Reactor Power Output Amplitude	40%
Ultrasound irradiation frequency (kHz) in the sonoluminescence equipment	1 to 60 kHz
PPCPs model compounds concentration:	
Sonochemical Degradation	C_0 = 10 ppm
Sonoluminescence Studies	0 to 1000 ppm
Ultrasound treatment time	0 to 4 hr
Fenton type catalyst loading during ultrasonic treatment of PPCPs	$[Fe^{2+}]$ = 60 mM
	$[H_2O_2]$ = 60 mM

3.5.2 Hydrogen Peroxide Determination

3.5.2.1 Iodometric Titration Method

The concentration of H_2O_2 in our purchased stock solution was determined by iodometry. This method is widely used, taught and described in many analytical chemistry

textbooks as a fundamental skill for students and professionals in chemistry. Specifically, the general procedure used in our studies, with some minor modifications, was given by a technical data sheet from Solvay Chemicals, Inc. This method is capable of determine hydrogen peroxide concentrations from 0.1% to 5%.

In the presence of an ammonium molybdate [$(NH_4)_6$ Mo_7O_{24}] catalyst, triiodide ions are produced after the H_2O_2 present in the sample reacts with excess potassium iodide (KI). These ions are then titrated with a previously standardized, using potassium iodate (KIO_3) primary standard, thiosulfate ($Na_2S_2O_3$) solution with starch as an indicator. The amount of H_2O_2 was calculated by equation 3-1 as follows:

$$\%\frac{wt}{v} = \frac{(A-B)(N)(1.7007)}{Sample\ Volume} \qquad \textbf{Equation 3-1}$$

where: A = titration volume for sample
B = titration volume for blank
N = normality of $Na_2S_2O_3$

3.5.2.2 DMP Method

Two colorimetric methods were used to study the generation of hydrogen peroxide through sonolysis. The first one the iodometric method was used to study the generation of hydrogen peroxide during sonolysis, but there were some experimental limitations and interferences that prevented to continue using this method.

The first method reagents were similar to the ones used in iodometric titration, one of these the starch, started fouling the rectangular cell sample holder walls with its typical blue color. This interference along with the time consumption of the analysis (20 minutes for color generation per sample) forced the literature search for an alternative more convenient and reliable method. After an extensive search, this method resulted to be the DMP method [22].

The 2,9-dimethyl-1,10-phenanthroline (DMP) method has been proven as one suitable method for the determination of H_2O_2 in AOPs. This method was selected due to its simplicity, lack of interference from decomposition byproducts of high molecular weight organic compounds on AOPs (i.e. aldehydes, carbonate ions), reasonable sensitivity and also because the concentration range that can be detected suggests its applicability to AOPs. The priniciple of the analysis is the reduction of copper (II) with H_2O_2 and its stoichiometry is given by the reaction:

$$2Cu^{2+} + 4DMP + H_2O_2 \longrightarrow 2Cu(DMP)_2^{+} + O_2 + 2H^{+}$$

As shown, this reaction produces a complex, $2Cu(DMP)_2^{+}$, which generates a bright yellow color whose maximum absorbance is measured at 454 nm. When H_2O_2 is not present, the blank solution generates a color different from the one mentioned. Hence, the differences between the absorbance of the sample and the blank solutions are approximately proportional to H_2O_2 concentration, and can correct for any negative and positive effects during the measurement.

The procedure as described by Baga et al. [27] and later revised by Kosaka et al. [26] was used with minor modifications. Aliquots of one milliliter each of certain solutions of DMP, copper (II) sulfate, and phosphate buffer (pH = 7.0) was added and mixed in 10 mL amber volumetric flasks. After addition of a quantifiable volume of sample and filling of the remaining volume with ultra pure water, the difference in absorbance between each sample and the blank is measured at 454 nm. Solutions of known concentration from a previously standardized H_2O_2 stock solution were used for the preparation of a calibration curve in a concentration range typical of our AOP under study. This allowed the determination of unknown H_2O_2 solutions using the following equation:

$$\Delta A_{454} = \varepsilon[H_2O_2] \times \frac{V}{10} \qquad \textbf{(Equation 3-2)}$$

where: ΔA_{454} is the difference in absorbance between sample and blank solutions at 454 nm

ε is the slope of the calibration curve [(% wt/v)$^{-1}$ cm^{-1}]

$[H_2O_2]$ is the concentration of H_2O_2 (% wt/v)

V is the sample volume (mL) (typically 1-5 mL)

The breakdown of ·OH radicals during sonolysis of ultra pure water was assessed by measuring the amount of H_2O_2 present in samples manually taken from the reactor, using a syringe, at different reactions times during the course of the experiment.

4 Results and Discussion

The cavitation phenomena have been investigated in two different but related areas. The first involved a general kinetic study for the sonolytic degradation of selected PPCPs (caffeine and acetaminophen) at different reaction temperatures with a fixed initial concentration for both substances. The other area explored the, feasibility of using sonoluminescence as both an analytical tool for toxic waste identification and monitoring, as well as a novel approach to have a better understanding about the formation, growth, and violent collapse of bubbles that result in sonolysis.

4.1 Sonolysis of PPCPs

Standard solutions of caffeine and acetaminophen were prepared at different known concentrations and the corresponding signals of the analytical instruments were correlated. These relations were used to monitor the degradation of our model compounds as well as determine the pseudo first order rate constant. The concentration range of the calibration curve was from 40.64 to 1.626 ppm. Figure 4-1 shows the linear relationship of the HPLC response signal with caffeine and acetaminophen concentrations.

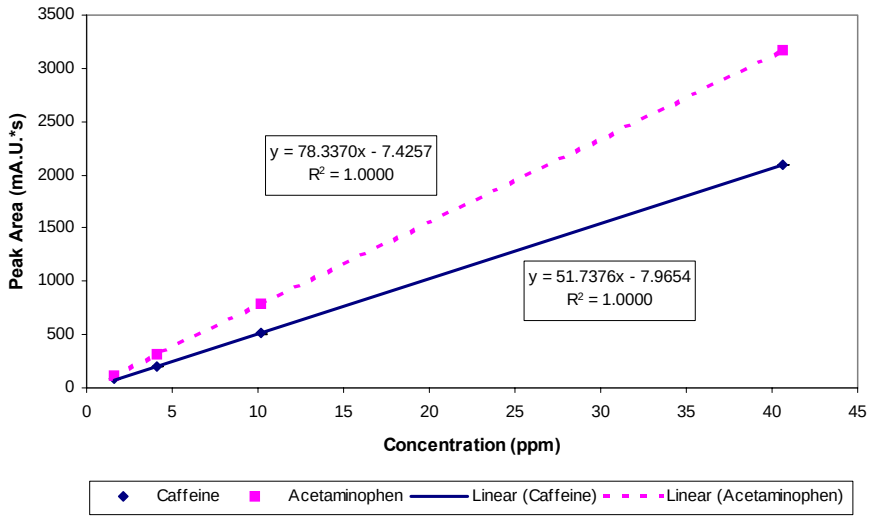


Figure 4-1: Caffeine and Acetaminophen Calibration Curves

A concentrated hydrogen peroxide stock solution was standardized with an iodometric titration method in order to know its exact concentration. This allowed the preparation of other calibration curves with more diluted concentrations of the mentioned reagent. Table 4-1 presents the results from which the exact concentration of the stock solution was determined.

Table 4-1: Iodometric Determination of the Concentration of Hydrogen Peroxide

I. Standardization of Sodium Thiosulfate ($Na_2S_2O_3$)				
Trial	Initial Volume (mL)	Final Volume (mL)	Mean Titration Volume (mL)	$[Na_2S_2O_3]$ (N)
1	0.00	20.50	20.55	0.0974
2	21.00	41.50		
3	0.00	20.50		
II. Determination of Hydrogen Peroxide in the Stock Solution				
Trial	Initial Volume (mL)	Final Volume (mL)	Mean Titration Volume (mL)	$[H_2O_2]$ (%w/v)
1	0.00	46.10	41.94	2.31
2	0.00	43.65		
3	0.00	38.15		
4	0.00	39.85		

In order to quantify for the generation of hydrogen peroxide during sonolysis of water, a calibration curve was prepared in a concentration range from 5.43 x 10^{-6} to 2.72 x 10^{-5} M. The DMP method was effective and interference free throughout the analysis as expected. The following graph, depicted in Figure 4-2, contains the response of the UV-VIS Spectrophotometer at 454nm for different solutions prepared in the mentioned concentration range.

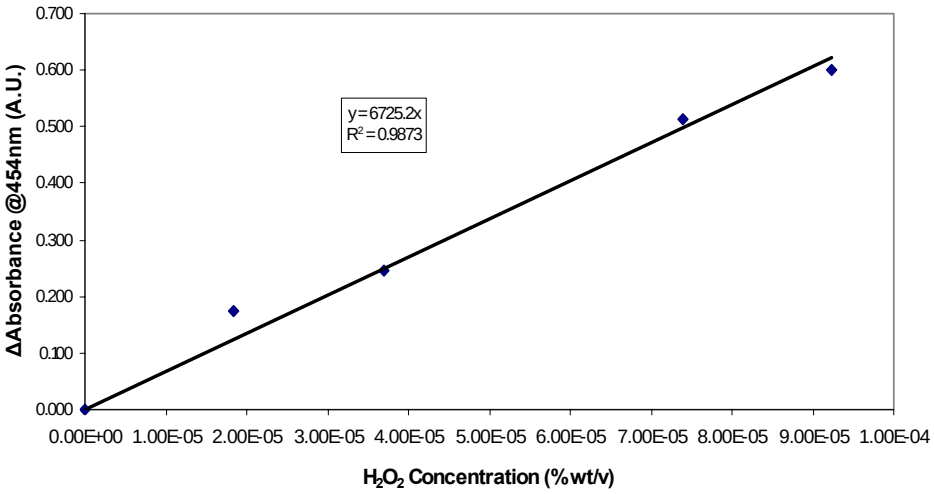


Figure 4-2: Hydrogen Peroxide Calibration Curve using the DMP Method

As shown in Figure 4-2, there is a linear relationship between the yellow color generation of the $Cu(DMP)_2^+$ complex as H_2O_2 concentration increases. Hydrogen peroxide is frequently used as a hydroxyl radical (HO·) agent in AOPs. It also acts as a hydroxyl radical scavenger and its concentration during the process is related to treatment efficiency,

since it is generated as a reaction product of hydroxyl radicals as previously shown in Table 2-4.

The measurement of H_2O_2 concentration is important and helpful in the evaluation and analysis of AOPs. This is possible since H_2O_2 is the only stable activating oxygen in the process and its time dependence concentration gives relevant information on the radical reactions in the process. In these studies, the generation of OH· proved to be the main mechanism for the degradation of PPCPs. Hence the DMP method was used to quantify the formation of H_2O_2 in our reactive system as illustrated in Figure 4-3.

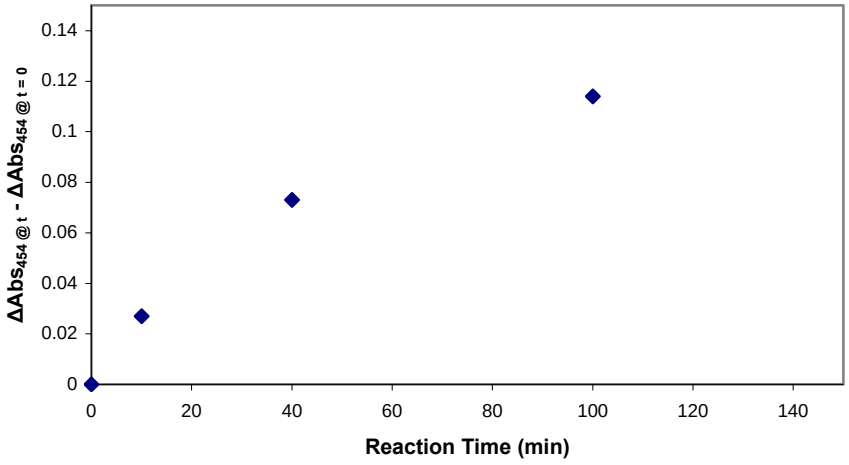


Figure 4-3: Determination of H_2O_2 during Sonolysis of Water at 35ºC under 20 kHz Ultrasound Waves Irradiation ($[Acetaminophen]_0$ = 10 ppm): DMP Method.

As we saw in the previous figure, even with the presence of the solute acetaminophen, there is still H_2O_2 formation during the process given the fact that part of the peroxide originates from reaction R11, which cannot be inhibited by the contaminant.

$$HO_2\cdot + HO_2\cdot \longrightarrow H_2O_2 + O_2 \qquad \text{(R11)}$$

However, H_2O_2 yield should decrease in the presence of solute as witnessed by Pétrier et al in the sonochemical degradation of Phenol [52]. Using the calibration curve, the concentration of H_2O_2 after 100 minutes of irradiation was determined to be 2.34 x 10^{-5} M. In previous works, they encountered that the amount of H_2O_2 increased linearly and its concentration, after the same reaction time, was higher ranging from 6.8-7.5 x 10^{-5} M [17, 52]. These values were measured with both the iodometric and DMP methods in ultra pure water (without solute) during its treatment with 20 kHz ultrasound waves at 20ºC with an acoustic power density of 0.143 W/mL. In our experiments, the amount of H_2O_2 was measured at a higher temperature (35ºC), in the presence of solute, and with 0.2 W/mL.

With all this in mind, sonolysis of aqueous solutions of caffeine and acetaminophen was achieved in different temperatures and oxidative environments. For caffeine, with the 20 kHz ultrasonic reactor, nearly 46% of caffeine was degraded after 4 hours or irradiation. The kinetic model that best fit and described the sonolytic degradation of caffeine was a Pseudo first order rate law. This approach was used by Neppolian et al. [18] to obtain rate constants for methyl tert-butyl ether, and resulted to be a good fit to our data for caffeine and acetaminophen. Following their approach, for caffeine, it can be seen that:

$$-\frac{dC_i}{dt} = \left(k_{pyr} + k_{i,OH\cdot}[OH\cdot]\right)C_i \qquad \textbf{Equation 4-1}$$

Assuming that $k_{i,OH\cdot}[OH\cdot] >> k_{pyr}$

$$-\frac{dC_i}{dt} = k_1 C_i$$

Equation 4-2

where: k_{pyr} is the pseudo first order rate constant for the thermolytic cleavage of component i

$k_{i,OH\cdot}$ is the second order rate constant for the degradation of component i by OH· radical

k_1 represents the overall pseudo-first-order rate constant

Pétrier et al. previously stated this presumption with phenol. They believed that the pyrolysis of the mentioned organic compound in the interfacial area had only a minor contribution, because acetylene and methane, which are products of sonochemical destruction of VOCs, were not detected in their studies [52]. This finding was later confirmed by Lesko et al [48] who added that phenol is not expected to be found at significant levels in the vapor phase of the cavitation bubbles due to its moderate solubility, and relatively low vapor pressure (4.6 x 10^{-4} atm) and Henry's law constant (4.0 x 10^{-4} L·atm·M^{-1}).

As with phenol, this approximation should be a good assumption for caffeine and acetaminophen because both chemicals have moderate solubility in water (see Table 3-1), with the latter been in dilute concentrations, and negligible vapor pressures and Henry's law constants. Thus, the sonochemical reactions of our model compounds should primarily occur within the bulk solution, through a free-radical (i.e. OH·) mechanism, rather than in the superheated regions of the interfacial zone surrounding the cavitation bubble.

Even though caffeine and acetaminophen solutions are not considered volatile, different temperatures were studied in order to analyze the Arrhenius type kinetic

dependence. Theoretically, the transient temperature produced in the ultrasonic reactor during the degradation process is up to 5,000ºC. In our experiments for both caffeine and acetaminophen solutions, the bulk solution increased its temperature from 26ºC to 63ºC after just 60 minutes of irradiation with ultrasonic waves.

In order to perform any comprehensive kinetic study, continuous cooling of the reactor was necessary to maintain a constant temperature. The Arrhenius plots will be seen and discussed later on in this chapter.

Given the temperature effect during cavitation, and to create a control experiment to asses the oxidative effect of ultrasound waves in the degradation of micro pollutants, solutions of both compounds with initial concentrations of ~10ppm were loaded in the reactor in silent mode (no ultrasonic irradiation) at 35ºC for 4 hours under constant stirring. The purpose of these two non-complex experiments was to prove that the indeed the degradation is caused by the ultrasound waves alone and not by the reactor system and experimental conditions. Figures of both experiments, demonstrating that the concentrations of both model compounds remained constant in the absence of these waves, are shown in Figures 4-4 and 4-5.

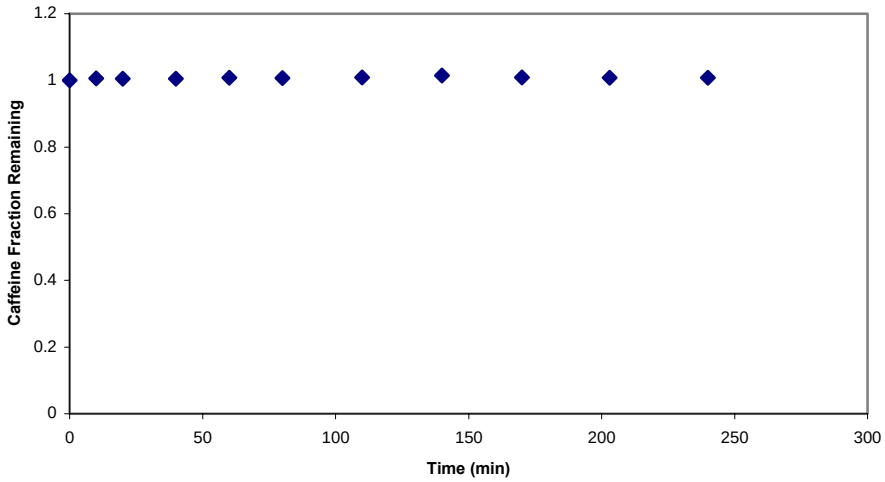


Figure 4-4: Control Experiment (silent mode) for the Sonolysis of Caffeine at 35ºC.

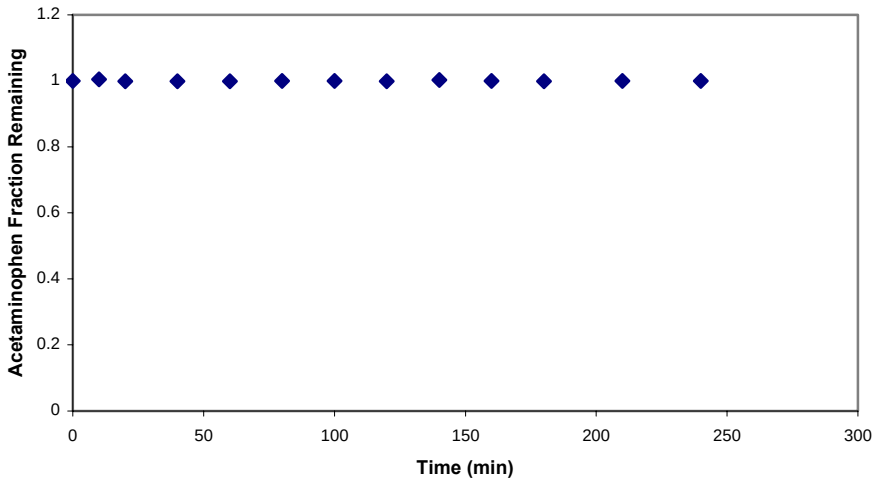


Figure 4-5: Control Experiment (silent mode) for the Sonolysis of Acetaminophen at 35ºC.

The temperature effect on the sonolysis of our PPCPs model compounds was studied in these experiments. Some researchers had agreed that the cavitational bubble collapse decreases in intensity at higher temperatures probably due to the subsequent increase of the vapor pressure of the solution and/or its constituent. But, as expected with many chemical reactions, an increase in temperature resulted in higher degradation rates, as evidenced by the decrease in the amount of caffeine remaining during the reaction. This is shown in Figure 4-6.

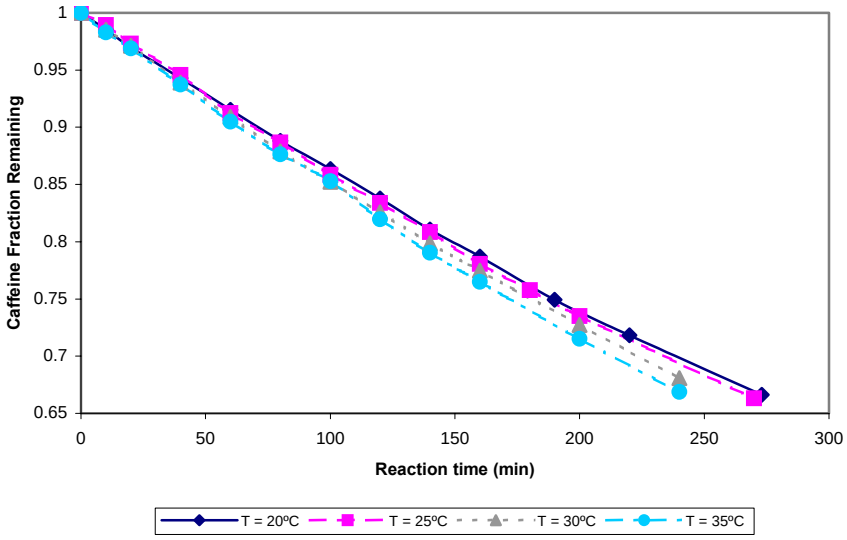


Figure 4-6: Sonolysis of caffeine at different temperatures

Visually, the preceding figure gave a glance of the role of reaction temperature in caffeine sonolysis. Other researchers have reported the same behavior [18], but with other organic compounds. Here, after four hours of reaction, we have achieved reduction percents of 30, 31, 32 and 34% in the amount of caffeine concentration at 20, 25, 30, and 35ºC respectively.

Using chemical reaction engineering's integral method and the data obtained during sonolysis, the pseudo first order reaction rate model (Equation 4-2) can be rearranged into:

$$\ln \frac{[Caff]_t}{[Caff]_0} = -k_1 t \qquad \textbf{Equation 4-3}$$

A plot of the natural logarithm of the existing fraction of caffeine versus time yields a linear equation from which the negative slope k_1, the pseudo first order degradation rate constant, and an arbitrary constant a_o can be obtained at different temperatures. With this in mind, data for caffeine sonolysis was rearranged mathematically and the mentioned plots and parameter were obtained as depicted in Figure 4-7 to 4-10.

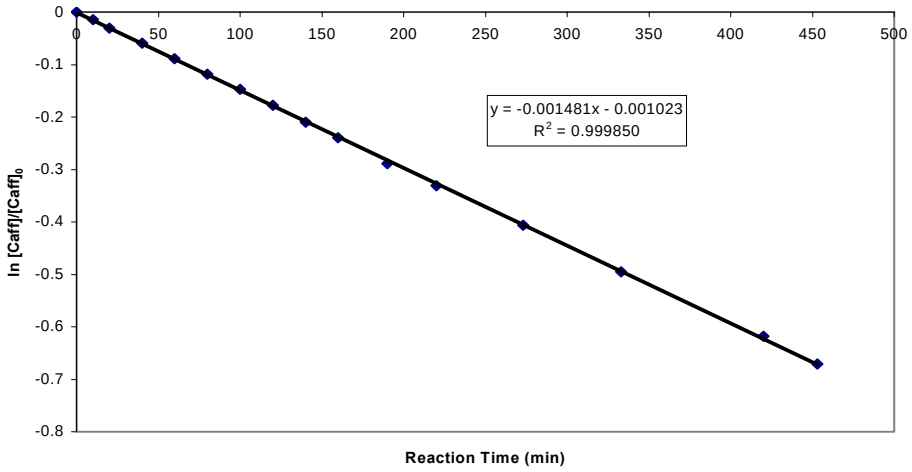


Figure 4-7: Sonolytic Degradation of Caffeine at 20°C: Pseudo first order degradation rate constant determination

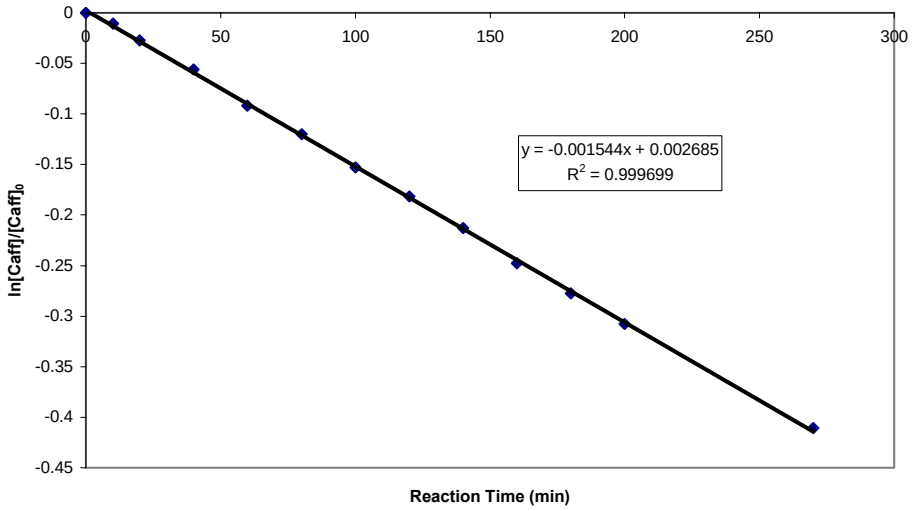


Figure 4-8: Sonolytic Degradation of Caffeine at 25°C: Pseudo first order degradation rate constant determination

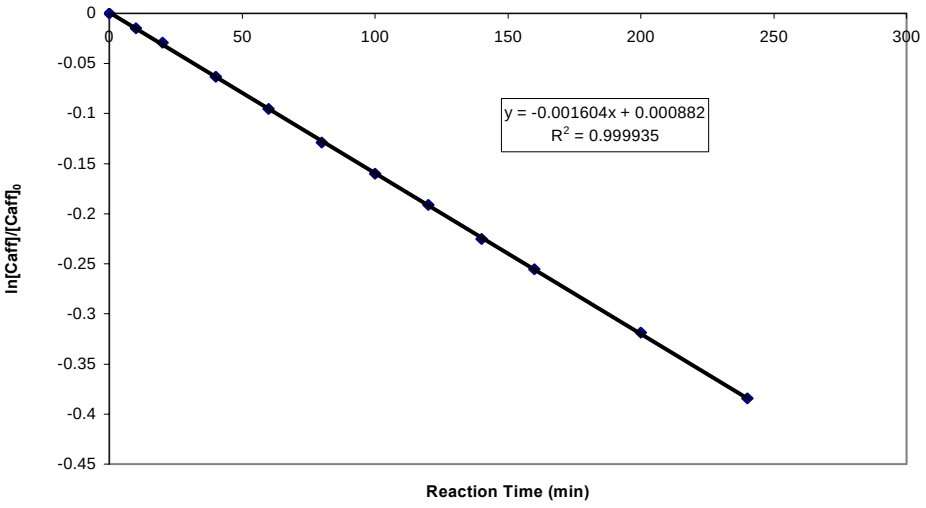


Figure 4-9: Sonolytic Degradation of Caffeine at 30°C: Pseudo first order degradation rate constant determination

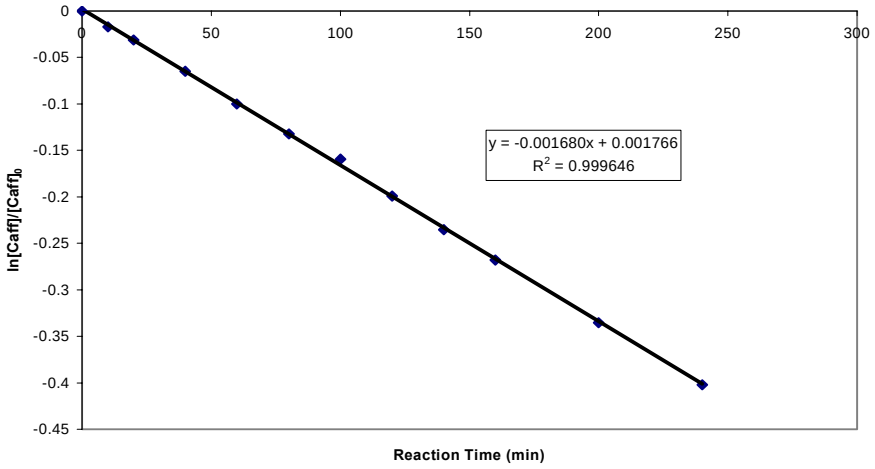


Figure 4-10: Sonolytic Degradation of Caffeine at 35°C: Pseudo first order degradation rate constant determination

All the experimental plots for the determination of the degradation rates were added in the same graph to compare their difference in magnitude as shown in Figure 4-11.

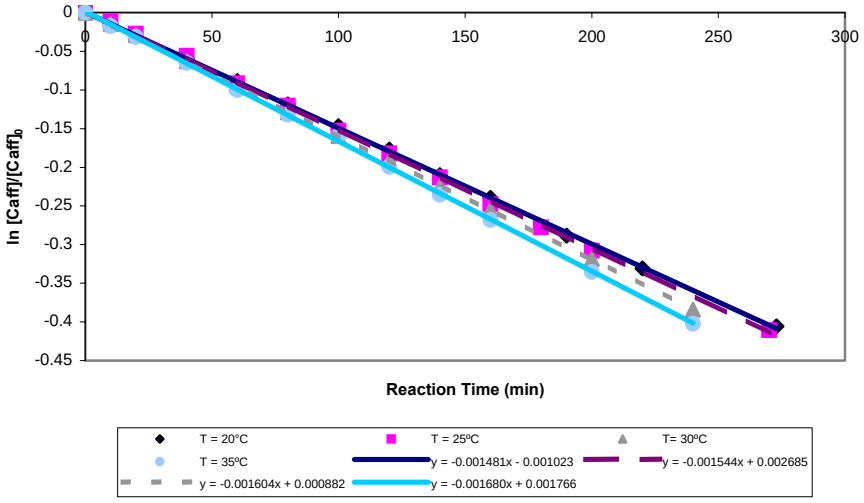


Figure 4-11: Graphical Comparisons for the Sonolysis of Caffeine: Degradation Rate Constant Determination at Different Temperatures

Using Equation 4-3, the pseudo first order degradation rate constants at 20, 25, 30 and 35ºC were 1.48, 1.54, 1.60, and 1.68 x 10^{-3} min^{-1} respectively. These constants increased with reaction temperature.

The reaction rate constant is not truly a constant but is merely independent of the concentrations. For most laboratory experiments, as ours, and industrial reactions the reaction rate constant is assumed to depend only on temperature. In liquid systems it can also be a function of total pressure, and also can be dependent of other parameters, such as ionic strength and choice of solvent. Since, all these parameters except temperature were kept controlled for every experiment, the Arrhenius plot proved to be a great fit to our data as expressed by Equation 4-4:

$$k(T) = Ae^{-E_A/RT} \qquad \textbf{Equation 4-4}$$

where A: preexponential factor or frequency factor

E_A: activation energy, KJ/mol

R: gas constant = 8.314 J/K·mol

T: absolute temperature, K

This relation was rearranged mathematically in the form of a linear equation and it was possible to obtain the activation energy for the sonolysis of caffeine as illustrated in Figure 4-12.

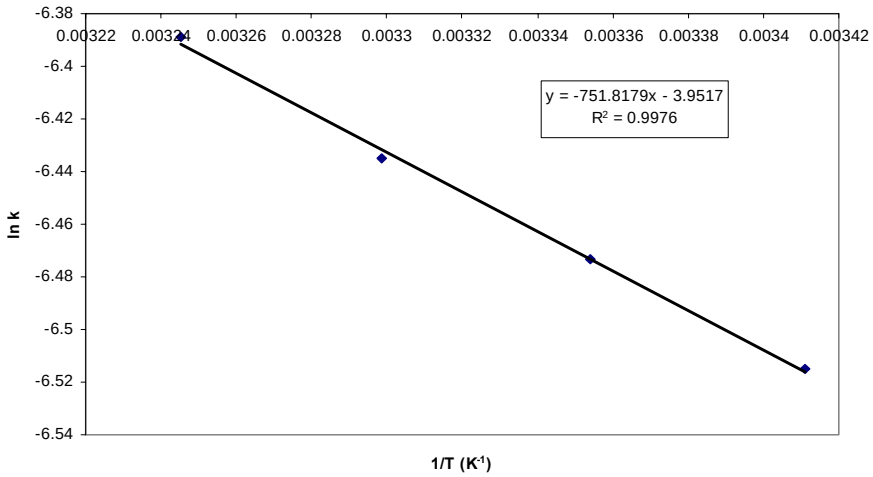


Figure 4-12: Arrhenius Plot for the Sonolytic Degradation of Caffeine

All the results describing the temperature dependence for the sonolytic degradation of caffeine and the energy of activation for the process itself are summarized in Table 4-2. The magnitude and implications of these values in comparison with other hydroxyl radical reactions will be analyzed later on in this chapter.

Table 4-2: Summary of the results for Caffeine.

Results for the Sonolysis of Caffeine				
Chemical	Temperature (K)	Degradation (%)[1]	k (min^{-1})	E_A (kJ/mol)
Caffeine	293.15	30	1.48E-03	6.25
	298.15	31	1.54E-03	
	303.15	32	1.60E-03	
	308.15	34	1.68E-03	

[1] Degradation percent after 4 hours of reaction

It is no coincidence that the same principles and equations that were used for caffeine are applicable for acetaminophen. Both chemicals (see Table 3-1) have some functional

groups in common (i.e. carbonyl C=O, alkenes C=C, amine R-N) that may have some affinity toward hydroxyl radical attack. Several peer-reviewed articles, specially [48], have reported the reaction pathways for the sonochemical oxidation of phenol, which is through the benzene ring. A more detailed discussion on the $OH^{\cdot}$ attack to the C=C double bond of the cyclic rings of both chemicals will be discussed later on in this chapter.

The procedure discussed above was used with our second model compound acetaminophen. This chemical was also subjected to ultrasonic waves at 20 kHz in the same temperatures and conditions as with caffeine. The characteristic plots that were obtained with acetaminophen showed the same behavior but were not as smooth as caffeine's. However, reliable and good representative results were obtained for the sonolysis of acetaminophen. Figure 4-13 shows all the results at different temperatures in which we can see the behavior of the acetaminophen fraction remaining through out the reaction time.

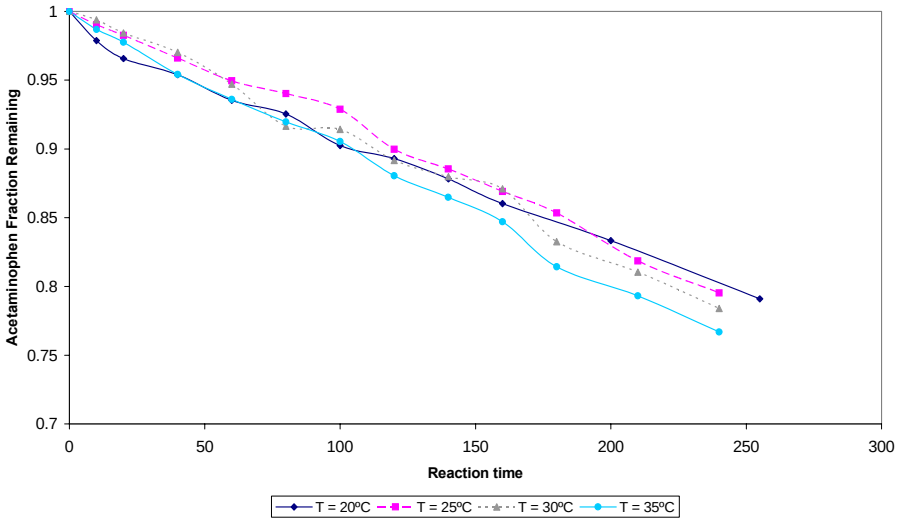


Figure 4-13: Sonolysis of Acetaminophen at different temperatures.

As we can see, there is a clear reduction in acetaminophen concentration with time. After 150 minutes of reaction time the expected pattern of higher degradation rates at higher temperatures was more evident. After 240 minutes, the resulting degradation percents for acetaminophen were 20, 21, 22, and 23% at 20, 25, 30, 35º C respectively. The pseudo first order kinetic model also had an acceptable fit for acetaminophen. From Equation 4-1 the following equation was obtained:

$$\ln \frac{[Acet]_t}{[Acet]_0} = -k_1 t \qquad \textbf{Equation 4-5}$$

Experimental data for acetaminophen were substituted in Equation 4-5. Acetaminophen was not as susceptible as caffeine when treated with ultrasound waves. The slopes of each graphs at the different temperatures studied were smaller in magnitude when compared with caffeine's. In other words, acetaminophen had a slower degradation rate than caffeine. Nevertheless, once again ultrasound waves proved to be valid for the degradation of our model compound. Figures 4-14 to 4-17 gives a picture of the sonolytic degradation rates for acetaminophen at the established experimental conditions.

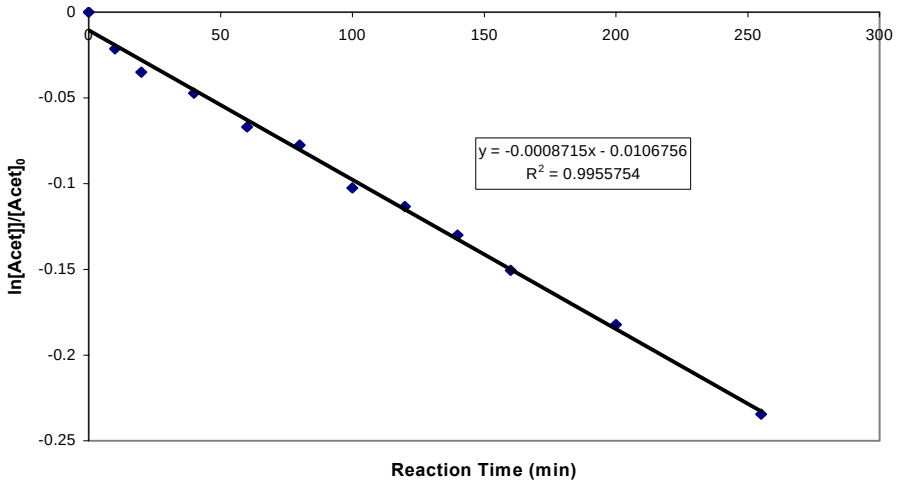


Figure 4-14: Sonolytic Degradation of Acetaminophen at 20°C: Pseudo First Order Reaction Rate Constant Determination

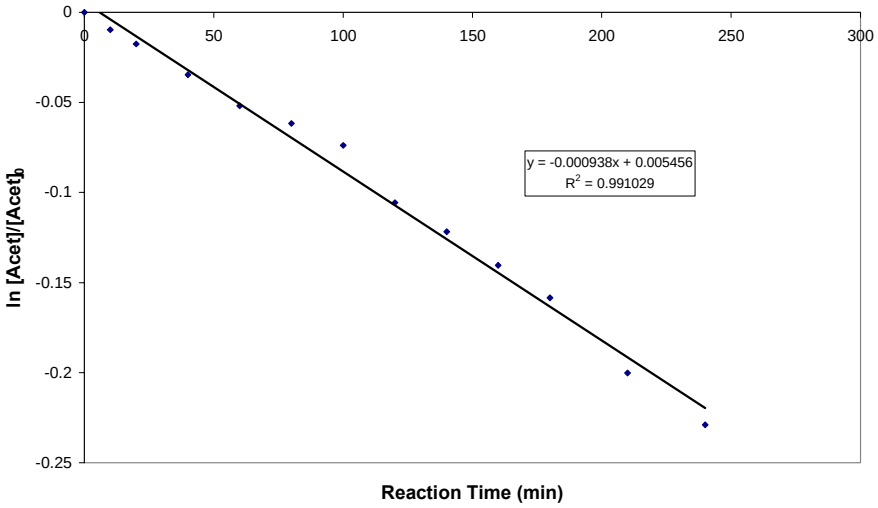


Figure 4-15: Sonolytic Degradation of Acetaminophen at 25°C: Pseudo First Order Reaction Rate Constant Determination

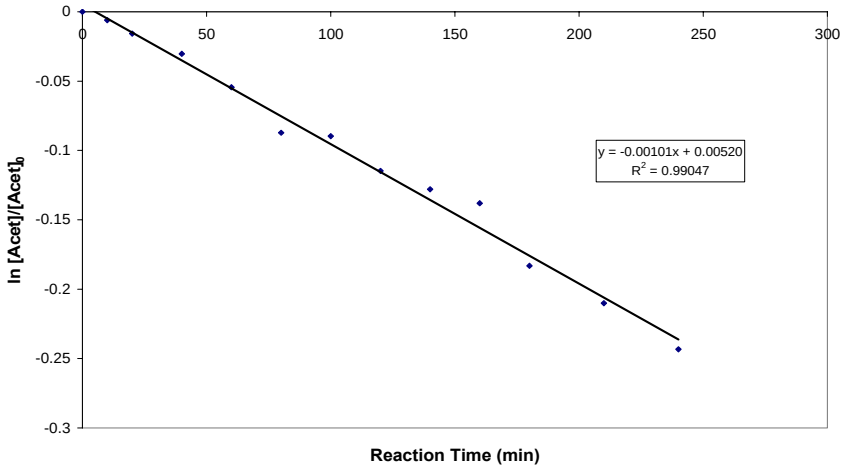


Figure 4-16: Sonolytic Degradation of Acetaminophen at 30°C: Pseudo First Order Reaction Rate Constant Determination

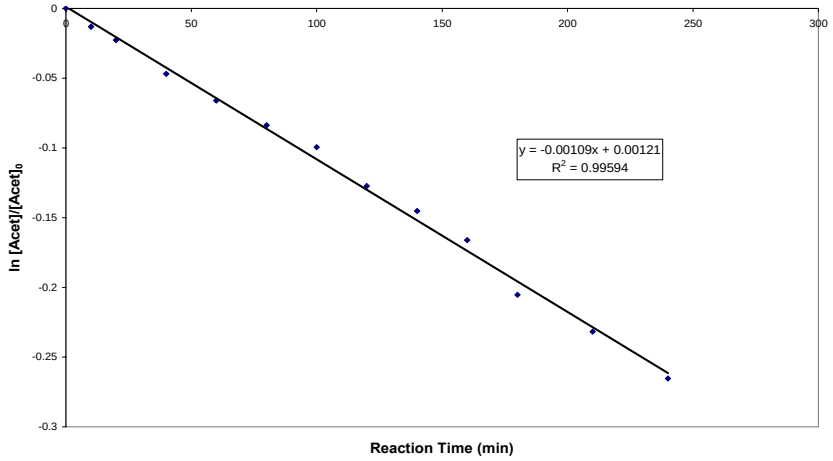


Figure 4-17: Sonolytic Degradation of Acetaminophen at 35°C: Pseudo First Order Reaction Rate Constant Determination

A summary of all the results for acetaminophen was also prepared so that a magnitude in the temperature effect on sonolysis can be seen. It could be seen that the chemical structure plays a role on the efficiency of sonolysis since acetaminophen rate of

degradation was a little slower than caffeine's. Figure 4-18 shows the increase in the degradation rate as a result of increasing temperature.

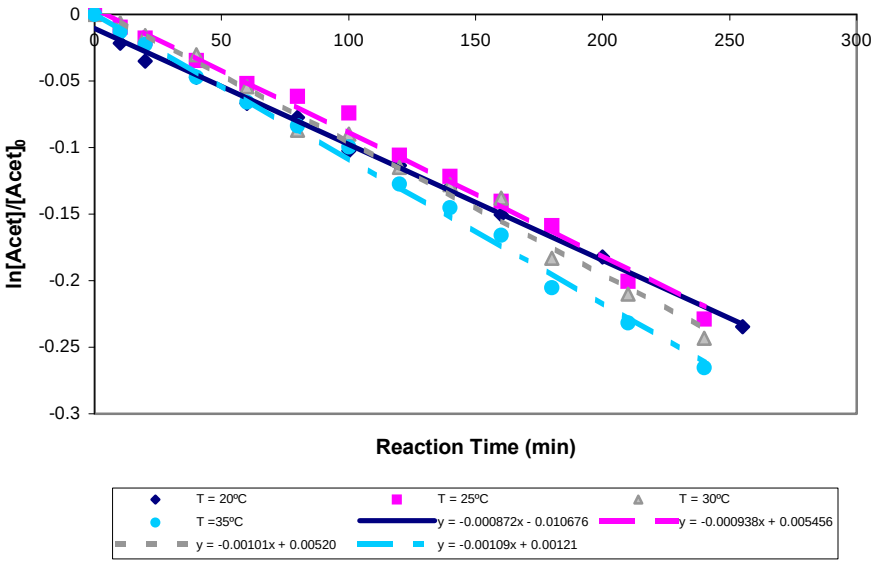


Figure 4-18: Graphical comparisons for the Sonolysis of Acetaminophen: Degradation Rate Constant Determination at Different Temperatures

The extend of all slopes obtained from the previous figures, from which the degradation rate constants were determined and compared in magnitude to assess the temperature effect in a different compound as acetaminophen (see Table 4-3).

As with caffeine, all the natural logarithm for the degradation constants and the inverse of their respective temperatures were graphed following Equation 4-3 and the activation energy for the sonolysis of acetaminophen was obtained. The results are shown in figure 4-19. It could be interesting to see in a future how the either the activation energy or

degradation rate for the process could be lowered and increased, respectively, using more powerful frequencies, those above 20 kHz.

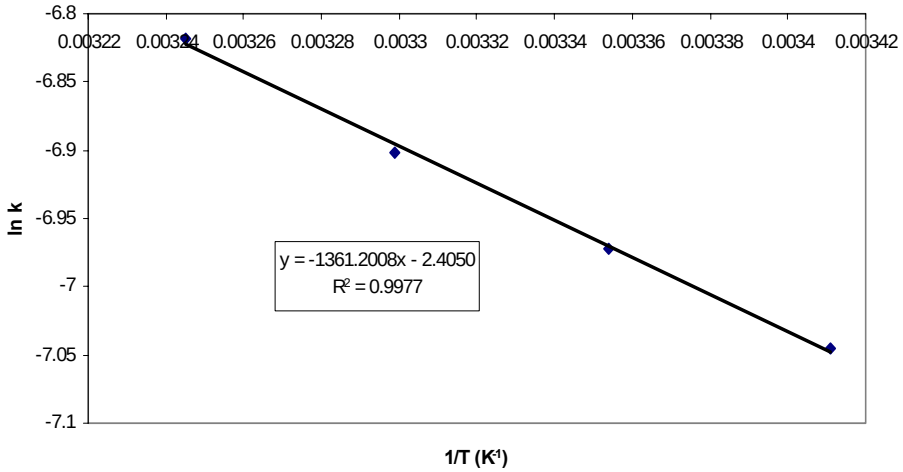


Figure 4-19: Arrhenius Plot for the Sonolytic Degradation of Acetaminophen

The extend of all slopes obtained from the previous figures, from which the degradation rate constants were determined, are compared in magnitude to assess the temperature effect in a different molecule as acetaminophen. Table 4-3 gathers up all the information obtained for acetaminophen from the previous plots

Table 4-3: Summary of the results for Acetaminophen

Results for the Sonolysis of Acetaminophen				
Chemical	Temperature (K)	Degradation (%)[1]	k (min^{-1})	E_A (kJ/mol)
Acetaminophen	293.15	20	8.715E-04	11.3
	298.15	21	9.379E-04	
	303.15	22	1.006E-03	
	308.15	23	1.094E-03	

[1] Degradation percent after 4 hours of reaction

Using the slopes of Figure 4-14 through 17, the pseudo first order degradation rate constants at 20, 25, 30 and 35ºC were 0.872, 0.938, 1.01 and 1.09 x 10^{-3} min^{-1} respectively. Like caffeine, acetaminophen's degradation rate constants had an increase in magnitude as a result of higher temperatures.

The activation energy parameter provides another mean to kinetically compare caffeine and acetaminophen with each other as well as with other pollutants studied under the same or different reactive conditions (i.e. frequency, temperature, oxidants added). Table 4-4 summarizes this comparison between our model compounds with other chemicals undergoing hydroxyl radical reactions, and gaseous decomposition.

Table 4-4: Kinetic comparison of hydroxyl radical reactions with other common reactions

I. Sonolysis (OH· radical) in 20 kHz Ultrasonic Reactor				
Chemical	**E_A kJ/mol**	**E_A kcal/mol**	**Temp range (ºC)**	**k @ 20ºC (min^{-1})**
Caffeine[1]	6.25	1.49	20 to 35	1.48E-03
Acetaminophen[1]	11.3	2.70	20 to 35	8.72E-04
MTBE [18]	12.6	3.02	20 to 30	2.69E-03
Phenol [17]	_	_	_	3.00E-04
Benzothiophene [53]	20.57	4.91	20 to 50	1.09E-02
II. Fenton Reaction Fe(II) + H_2O_2 → Fe(III) + OH· + OH^-				
Chemical	**E_A kJ/mol**	**E_A kcal/mol**	**Temp range (ºC)**	**k @ 25ºC (min^{-1})**
Nitrobenzene [56]	59.7	14.26	5 to 45	9.24E-02
III. Laser photolysis of HNO_3 to produce OH· radical (gas phase reaction)				
Chemical	**E_A kJ/mol**	**E_A kcal/mol**	**Temp range (ºC)**	**k @ 25ºC (10^{-13} $molecule^{-1}cm^3s^{-1}$)**
ethane [54]	_	_	25	2.74
propane [54]	_	_	25	1.4
cyclopropane [54]	9.2	2.2	25 to 217	1.10
cyclobutane [54]	_	_	25	17.5
cyclopentane [54]	_	_	25	50.6

cyclohexane [54]	_	_	25	72

IV. Typical Values of Arrhenius Parameters for 1st order gaseous decomposition				
Chemical	**E_A kJ/mol**	**E_A kcal/mol**	**Temp range (ºC)**	**Frequency factor (min^{-1})**
Nitrogen tetroxide [55]	58.2	13.9	_	4.80E+16
Ethyl chlorocarbonate [55]	131.9	31.5	_	5.52E+10
1-Butene [55]	263.7	63.0	_	3.00E+14
p-Xylene [55]	319.0	76.2	_	3.00E+15
Toluene [55]	324.4	77.5	_	1.20E+15

[1]Results from this work

In order to discuss any difference between the compounds of interest included in the previous table, and therefore relate any of their properties with their respective kinetics for OH· reactivity, Table A-1 (see Appendix) contains some of this essential information for comparison purposes (for caffeine and acetaminophen, see Table 3-2).

In our studies, caffeine was more readily degraded than acetaminophen and it was quantitatively confirmed by the experimental results. The degradation rates were the highest for caffeine and its temperature dependence resulted in smaller activation energy 6.25 kJ/mol, while that for acetaminophen was 11.3 kJ/mol. These findings were made using the same reactive conditions of 20 kHz ultrasound waves with a power density of 0.2 W/mL. Even though caffeine sonochemical degradation is more kinetically favored than acetaminophen, the latter one showed to be more sensitive to increase its degradation rate constant by increasing its reaction temperature (Arrhenius effect). Common sense and chemical intuition suggest that the higher the temperature, the faster the chemical reaction will proceed. However, since sonolysis of aqueous solutions has a limiting temperature (T_{max}), the temperature at which cavitation reaches a maximum threshold before its sudden decrease

with higher temperatures (see Chapter 2), further increase on this intensive property will not necessarily increase the degradation rate.

As we know, the activation energy (E_A) has been equated with a minimum energy that must be possessed by reacting molecules before the reaction can occur. Judging by the results for caffeine and acetaminophen, one could have assumed that the compound with the lowest activation energy for sonochemical degradation will react with $OH^{\cdot}$ radical more readily. But, if we take a look at Table 4-5, it can be seen that despite benzothiophene has a higher activation energy its pseudo first order degradation rate (1.09×10^{-2} min^{-1}) is higher than the ones obtained for caffeine and acetaminophen.

These differences in reactivity can be attributed to some properties of parameters that had already been discussed in the literature for organic compounds undergoing hydroxyl radical reactions. For example, in [54] they found that the reactivity of cycloalkanes in the reactions with these radicals decreases with ring size and that the strained cycloalkanes, cyclopropane, and cyclobutane react significantly slower than do their open chain counterparts (see Table 4-4). In the same way, caffeine degradation rate could be higher than acetaminophen due to the bigger ring size of the first when compared to the other.

Other factors and properties that can be considered as possible causes of the higher degradation rate of caffeine in these studies, is its higher solubility in water than acetaminophen. Also, as described in Chapter 2, benzothiophene composes of two bonded rings (benzene and thiophene), but the ring that showed more affinity toward hydroxyl radical attack was the latter one. Similarly, caffeine reaction with $OH^{\cdot}$ could be proceeding

more favorably at the C8 position (alkene double bond at the right side of the smaller ring) than acetaminophen's strained benzene ring.

In fact, it has been reported that OH· radicals attack purines, xanthine, isocaffeine, guanine and adenine at C8-position [59-62]. The product of oxidation of caffeine by OH· radicals has been reported to be 1,3,7-trimethyluric acid formed via C8-OH adduct radicals. In addition, oxidation of caffeine by $PO_4^{\cdot -}$ has been reported to follow a similar mechanism [58]. This reaction pathway is depicted in Figure 4-20.

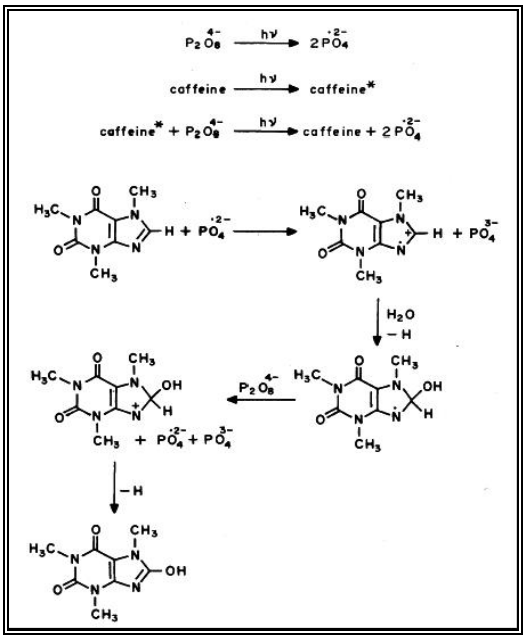


Figure 4-20: Reaction mechanism for the photooxidation of caffeine in the presence of peroxydiphosphate in aqueous solution [58].

The caffeine oxidation byproduct, 1,3,7-trimethyluric acid, illustrated in the previous figure could also be the derivative of caffeine obtained in these studies. However, a more specific analytical analysis (i.e. GCMS) should be performed to confirm this finding.

Meanwhile, from the information summarized in Tables 4-2 and 4-3, it is evident that the oxidative environment in the 20 kHz ultrasonic reactor and it effects on caffeine and acetaminophen were not enough, taking into consideration that the general scope of this particular or any other remedial process aims for the complete removal of these kind of pollutants at least bellow the actual detection limits. However, given the effectiveness that previous researchers had with the coupling of different AOP by completely eliminating other organic pollutants from aqueous solutions (See Chapter 2), the oxidative setting of our reactive system was increased in these studies. The addition of the oxidant H_2O_2 had a synergistic effect with ultrasound by increasing the decomposition of caffeine and acetaminophen as we can see in Figures 4-21 and 4-22.

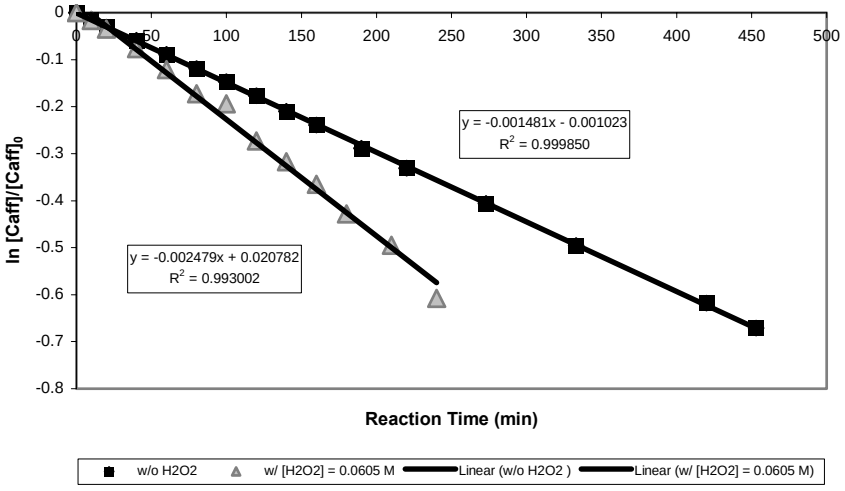


Figure 4-21: Coupling of ultrasound with hydrogen peroxide addition for the sonolytic degradation of caffeine at 20°C under 20 kHz ultrasound waves.

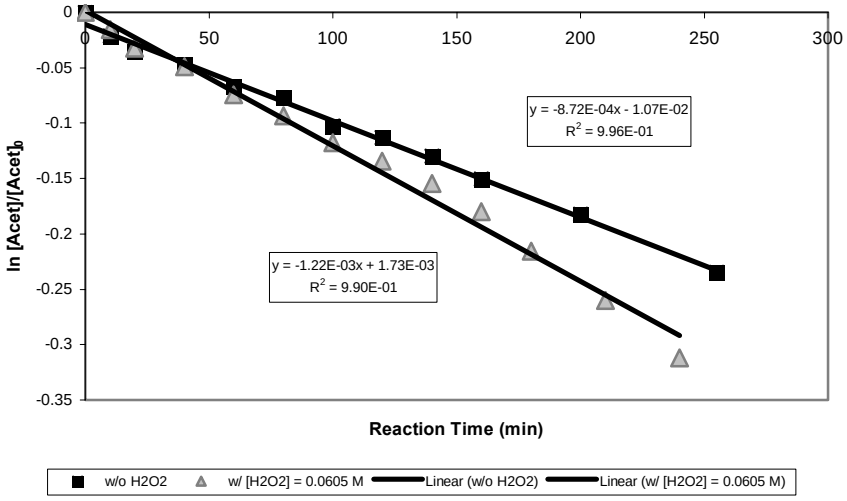


Figure 4-22: Coupling of ultrasound with hydrogen peroxide addition for the sonolytic degradation of acetaminophen at 20ºC under 20 kHz ultrasound waves

Using Equations 4-3 and 4-5 as Entezari et al. [17] did with phenol for the coupling of 20 kHz ultrasound waves with H_2O_2 addition, the following results, which are summarized in Table 4-5, were obtained.

Table 4-5: Summary of the Results for the Coupling of Ultrasound with H_2O_2 addition

Results for the Coupling of Ultrasound with H_2O_2 addition				
Chemical	Temperatute (K)	H_2O_2 Presence	Degradation (%)[1]	k (min^{-1})
Caffeine	293.15	No	30	1.48E-03
		Yes	46	2.48E-03
Acetaminophen	293.15	No	20	8.72E-04
		Yes	27	1.22E-03

[1] Degradation percent after 4 hours of reaction

Accordingly, it has been demonstrated that the addition of an oxidant to the reaction process, indeed increases the effectiveness of sonolysis. In the previous figures, it is also clear that the degradation rates of the model compounds increased from 1.48 x 10^{-3} to 2.48 x 10^{-3} min^{-1} for caffeine, and from 8.72 x 10^{-4} to 1.22 x 10^{-3} for acetaminophen at 20ºC with 20 kHz ultrasound waves in the presence of 0.0605 M H_2O_2. As a result, the degradation percents for the coupled process increased from 30 (without H_2O_2) to 46% for caffeine, and from 20 (without H_2O_2) to 27% for acetaminophen.

From Equation 4-1 and 4-2, it is evident that both $k_{i,OH\cdot}$ and [OH·] increased with the addition of H_2O_2. This was due to the introduction of hydrogen peroxide into the cavity and its cleavage into OH· during the collapse of the cavitation bubble. Additional hydroxyl radicals contributed to the higher decomposition of our model compounds. Chemically, this is explained by the mechanism of sonolysis of water in the presence of O_2 and H_2O_2 obtained from [63] and presented in Table 4-6.

Table 4-6: Chemistry of Sonolysis of Water in the Presence of O_2 and H_2O_2 (Adewuyi 2005)

Sonolysis of water in the presence of O_2 and H_2O_2	
$O_2 +))) \longrightarrow 2O\cdot$	(R14)
$O\cdot + HO_2\cdot \longrightarrow OH\cdot + O_2$	(R15)
$O_2 + O\cdot \longrightarrow O_3$	(R16)
$H_2O_2 +))) \longrightarrow 2OH\cdot$	(R17)

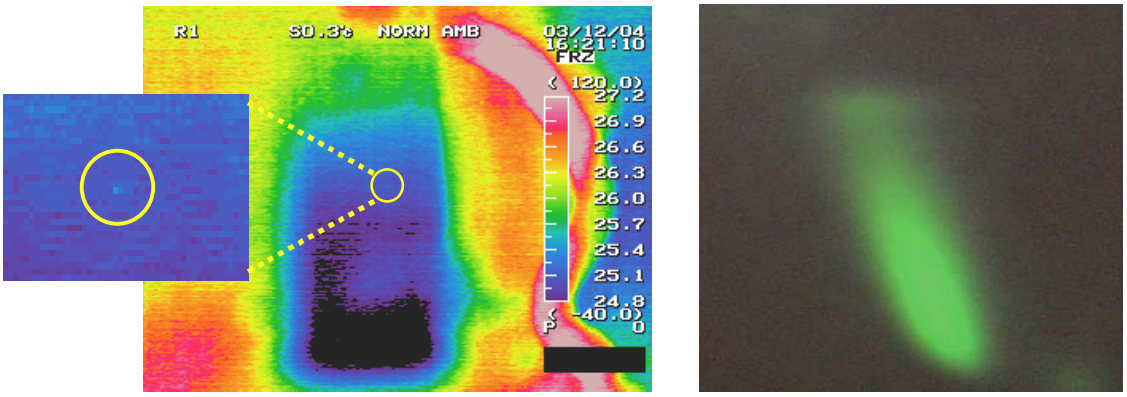
These results, suggest for more comprehensive research on AOP to eliminate this kind of pollutants. It is a fact that 20 kHz is just the beginning of the power ultrasound range, which leads toward the idea that a higher frequency could be just enough to destroy this kind of unwanted chemicals compounds from waste, ground and surface waters more efficiently. Furthermore, there is this huge potential to dramatically improve the oxidative capability and cost effectiveness of these processes by coupling them. Ozonation, Fenton reagent and UV radiation, were the most popular among the literature and there is no doubt about their applicability in the treatment of PPCPs and other emerging pollutants. In this research, only H_2O_2 was added and it was clear that the presence of the peroxide enhanced the remedial treatment. Interestingly, it has been observed in other studies that higher frequencies and its coupling with other more powerful AOPs are able to modify the generation of $OH\cdot$ in a significant way. Thus, there is enough room for the optimization and combination of these alternatives.

4.2 Sonoluminescence

4.2.1 Water

In order to better understand the observed enhanced degradation rates, another set of experiments were made with the sonoluminescence equipment. Since this instrument was primarily designed to measure and/or see the light emission that results from cavitation of pure water, this was our primary task. Following the procedure described in chapter 3, but purging with Argon, and after several trials, the phenomenon was captured with two different cameras: an IR camera and a Pentax® with a Fujifilm® ISO 800. Figure 4-23 displays both

the infrared picture (left) and a zoomed image (right) of the picture taken by the other camera, whose lent aperture time was controlled in order to maximize the amount of captured light for the picture.



a. b.

Figure 4-23: Light emission from the sonoluminescence of water: captured by (a) Infrared Camera and (b) a Pentax® with a Fujifilm® ISO 800, after purging Argon for 5 minutes. [Special thanks to S. Figueroa, E. Huertas, A. Flores, R. Defendini, and E. Caro for their collaboration with these pictures]

The resonance frequencies, at which the bubbles were controlled, thus resulting in a tiny visible emission, were in the region between 26.1 and 27.9 kHz. At these frequencies the captured resonant micro bubble was still, but there was a slow but rhythmical oscillation in the intensity of the light emitted. Before every experiment, our pupils needed to get used to dark for several minutes in order to be able to see the sonoluminescence of water from our instrument and experimental conditions. All experiments were carried out in a dark room.

The noble gas argon increased light intensity making it able to be witnessed and evidenced more easily with both bared eyes and with the cameras.

Even though the infrared camera had the capability of estimating the bulk temperature of the surroundings captured in its images based on IR radiation, and since sonoluminescence theoretical temperatures are localized inside these micro bubbles, the camera was able to capture what is believed to be the light emitting bubble. Coincidentally, the image displays the bubble in exactly the same place where it was witnessed bare eyed. However, the temperature readings made by the camera were not even near the huge theoretical amount as expected, since these calculated temperatures are believed to be much localized inside the imploding microbubbles making it even more difficult to measure it.

4.2.2 Water with traces of PPCPS model compounds

This instrument was also able to measure the pressure amplitude with two devices, one built inside and already included in the instrument control box, and the other was externally connected to the same controller. The first one uses an analog voltage amplitude meter while the other is digital. The magnitude of the voltage readings is proportional to the acoustical pressure amplitudes. As explained in Chapter 3, it is believed that during cavitation the collapsing bubble pushes against one of the probe tips, causing a change in capacitance between the differential probe tips of the transducer. If the tips move closer it results in pressure spikes that decreases as the tips are separated. In addition, using the oscilloscope, we were able to follow the ultrasound wave's resonance and its effects on the captured

bubble. In the case of pure water sonoluminescence, lots of data points from the measurements of the maximum pressure amplitudes as a function of frequency were collected and graphed. This led to a spectrum illustrated in Figure 4-24.

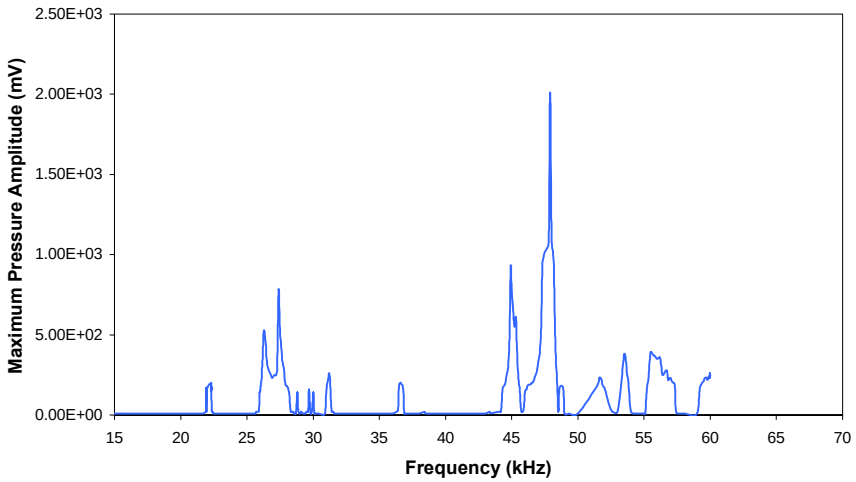


Figure 4-24: Sonoluminescence of water measured with the oscilloscope.

Another objective of these experiments was to investigate the effects of ultrasound waves at different acoustic frequencies as a possible mean to optimize this technique as an AOP for the complete degradation of PPCPs. After pure water was measured and analyzed, there was this idea that maybe the presence of small traces of the chemicals under study could, in some way, attenuate the amplitude of the acoustic pressures and enable the application of this technique as an analytical mean for chemical detection of organic compounds. Solutions of caffeine and acetaminophen in concentrations of different orders of magnitudes, but in the range of parts per million (ppm), were prepared and analyzed in the sonoluminescence equipment.

To our surprise, there was this effect of attenuations and also increases in the signal captured by the cell transducer in some particular frequencies. However, even though there was the appearance of different resonant frequencies that were not present in the water (blank) experiment as we saw in the previous figure, there were these higher peaks that appeared in nearly the same resonant frequency regions for all cases (pure water and its solutions of PPCPs). The pressure peaks were in the resonant frequencies of ~27, ~45 and ~48 kHz.

In the case of different traces amount of caffeine present in the solution, the maximum pressure amplitudes in the frequency of ~48 kHz were reduced when compared to pure water. This could be one of the reasons why as the concentration increases the more difficult is to decompose these kind compounds as reported in the literature [18, 53]. For example, Kim et al. encountered that benzothiophene first-order rate constant decreased from 4.9×10^{-2} to 1.4×10^{-2} min^{-1} with the initial concentrations of 0.01 mM and 0.21 mM, respectively [53].

In the following graphs, sonoluminescence experiment results for caffeine and acetaminophen in the concentrations of 100, 500 and 1000 ppm are each outlined in a single graph so that its differences and effects of different traces of the chemicals can be compared more clearly with the data points obtained for pure water.

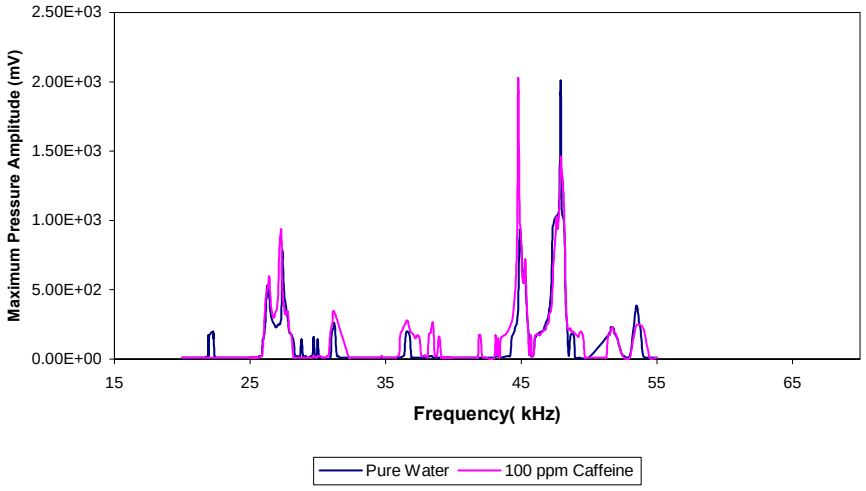


Figure 4-25: Sonoluminescece for water with 100ppm caffeine solution measured with the oscilloscope voltage meter and its comparison with pure water.

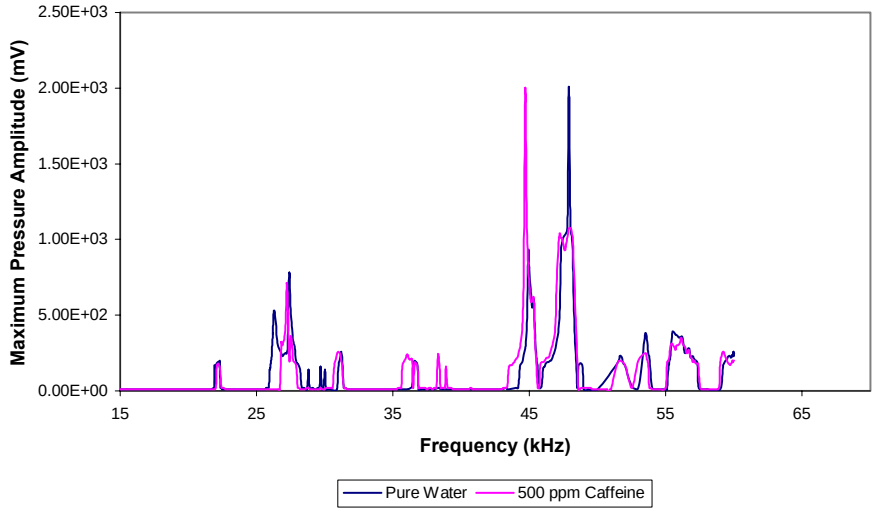


Figure 4-26: Sonoluminescece for water with 500ppm caffeine solution measured with the oscilloscope voltage meter and its comparison with pure water.

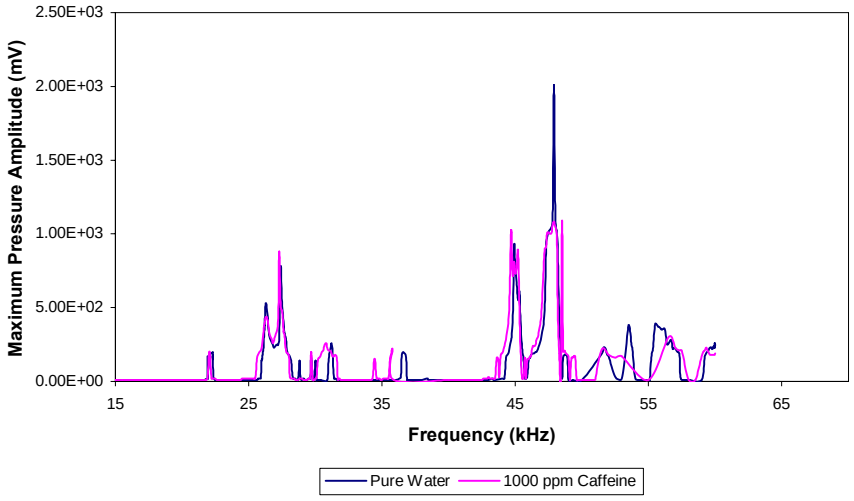


Figure 4-27: Sonoluminescece for water with 1000ppm caffeine solution measured with the oscilloscope voltage meter and its comparison with pure water.

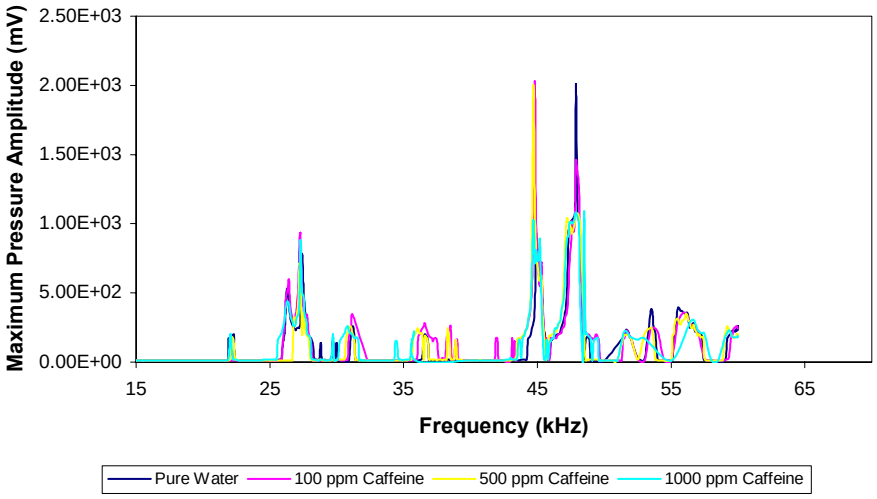


Figure 4-28: Comparison of the sonoluminescece for water with different amounts of caffeine measured with the oscilloscope.

Similar results were obtained for acetaminophen but the effect of increasing the concentration of the chemical lead to different patterns of increasing and decreasing pressure peaks. As we can see in the following figures, the sonoluminescence of acetaminophen at 100 and 1000 ppm had a different effect specifically and more vigorously in the frequencies of ~45 and ~48 kHz. Still, the true nature and extends of these results are not to well understood. Figures 4-29 through 4-31 show these results.

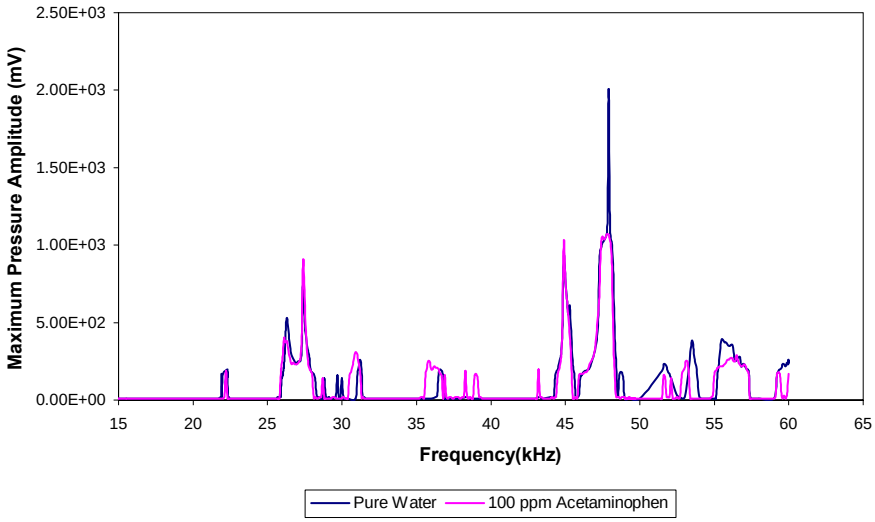


Figure 4-29: Sonoluminescece for water with 100ppm acetaminophen solution measured with the oscilloscope voltage meter and its comparison with pure water.

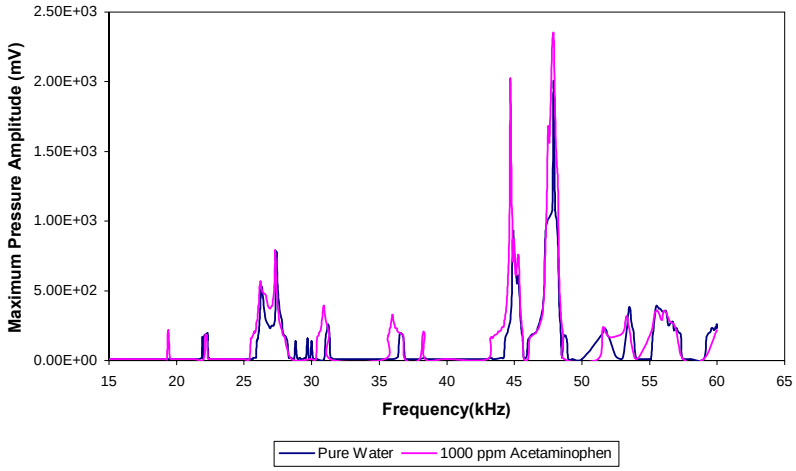


Figure 4-30: Sonoluminescece for water with 1000ppm acetaminophen solution measured with the oscilloscope voltage meter and its comparison with pure water.

As with caffeine, all results were combined in the same graph so that the effect of increasing acetaminophen concentrations could be compared. Figure 4-31 combines all the results for acetaminophen in water.

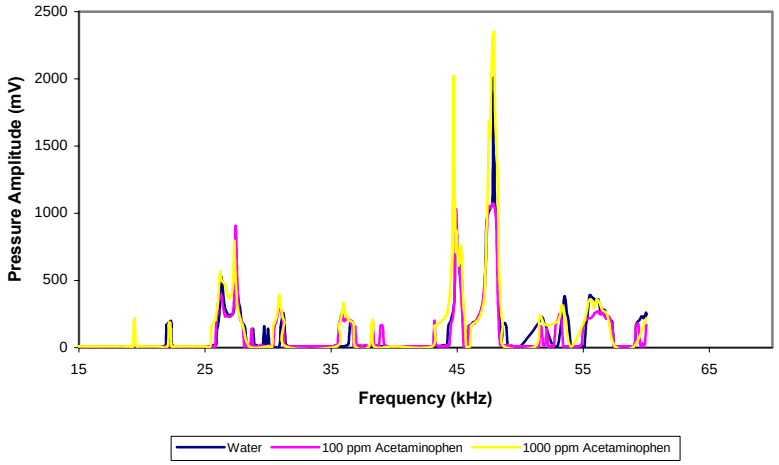


Figure 4-31: Comparison of the sonoluminescece for water with different amounts of acetaminophen measured with the oscilloscope voltage meter.

5 Conclusions and Recommendations

5.1 Conclusions

The existence, origins, effects and subsequent concern due to the already existing and emerging PPCPs as environmental pollutants were investigated. Ultrasound waves of 20 kHz proved to be a feasible mean for the decomposition of our PPCPs model compounds. Based on an extensive literature review, 1,3,7-trimethyluric acid, a possible bypoduct or intermediate for the sonochemical decomposition of caffeine was identified. However, its presence and fate before an after the continuous attack of hydroxyl radicals should be analytically determined and/or confirmed.

Using the DMP Method, the formation of H_2O_2 as a scavenger of hydroxyl radical formation was quantified in order to prove and determine the oxidative effectiveness of this process. After 100 minutes of reaction the concentration of hydrogen peroxide was estimated to be 2.34×10^{-5} M. When compared to the literature values ($6.8\text{-}7.5 \times 10^{-5}$ M), it seems that the difference in concentration was due to the presence of acetaminophen (C_0 = 10 ppm) evidencing the interaction between the solute and the hydroxyl radicals.

Increasing the reaction temperature led to higher pseudo first order degradation rates for both caffeine and acetaminophen. Results indicate that caffeine's alkene double bond located at the C8 position, appears to be more suitable (have more affinity) for the hydroxyl radical oxidative attack than acetaminophen's double substituted (strained) phenyl group.

It has been demonstrated that the addition of an oxidant to the reaction process, indeed increases the effectiveness of sonolysis. The presence of hydrogen peroxide in the sonolysis of water also increased the degradation rates for both model compounds. Our results clealy shows, that this remedial technique can be further optimized in several ways.

In other studies, sonoluminescence tests showed higher and increasing acoustical pressures for the frequencies of ~27, ~45, and ~48 kHz, which could led to an increase in cavitation. These frequencies could be used to perform more effective sonolytical degradation of PPCPs and/or other current or emerging pollutants. Nevertheless, the sudden increase and decrease of the acoustical pressure in the presence of different traces of caffeine and acetaminophen is a matter that should be further investigated.

5.2 Recommendations

In order to consider this technique or a coupling of this technique for a larger scale implementation in a future, its applicability to treat other emerging PPCPs (i.e. clofibric acid, estradiol, etc.), should be investigated. These studies should include an optimization study for the sonolysis of PPCPs. Some of the suggested experimental parameters to optimize are the frequency, reaction temperature, coupling with other AOP (i.e. ozone, photolysis) and the reactor design (i.e. cylindrical geometry). Then, the real efficiency of this remediation process can be assessed with other analytical techniques such as a Total Organic Carbon analysis.

It is also important to determine the reaction mechanisms and byproducts for the sonolysis of caffeine and acetaminophen using different analytical techniques such as GC-MS and other experimental conditions for the HPLC system to identify potential byproduct such as 1,3,7-trimethyluric acid (caffeine oxidation byproduct)

Even though, our sampling procedure was optimized and carefully carried on in these studies in order to avoid errors on precision, an automation of this methodology can minimize the duration of the experiment as well as increase its accuracy.

A Appendix

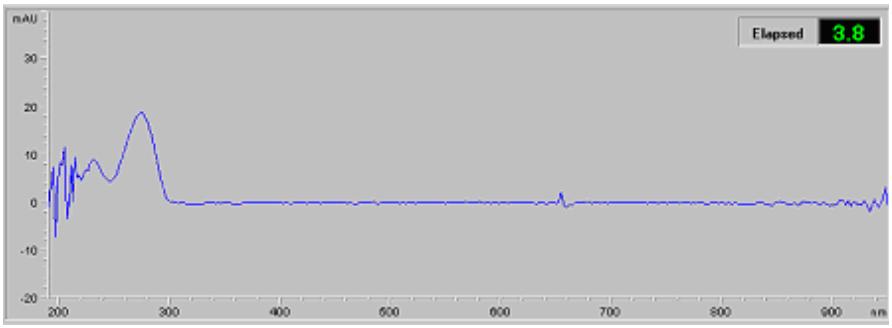


Figure A-1: UV-VIS Online Spectra in the HPLC System for caffeine before treatment with 20 kHz ultrasound waves at 20ºC. C_0 = 10 ppm, Retention time = 3.7 minutes.

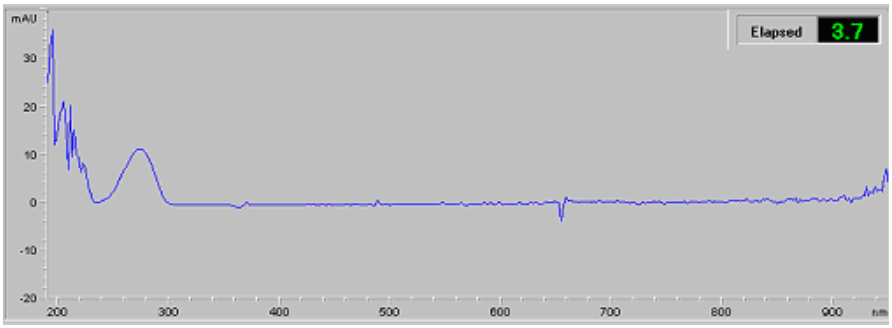


Figure A-2: UV-VIS Online Spectra in the HPLC System for caffeine after 240 minutes treatment with 20 kHz ultrasound waves at 20ºC. Retention time = 3.7 minutes.

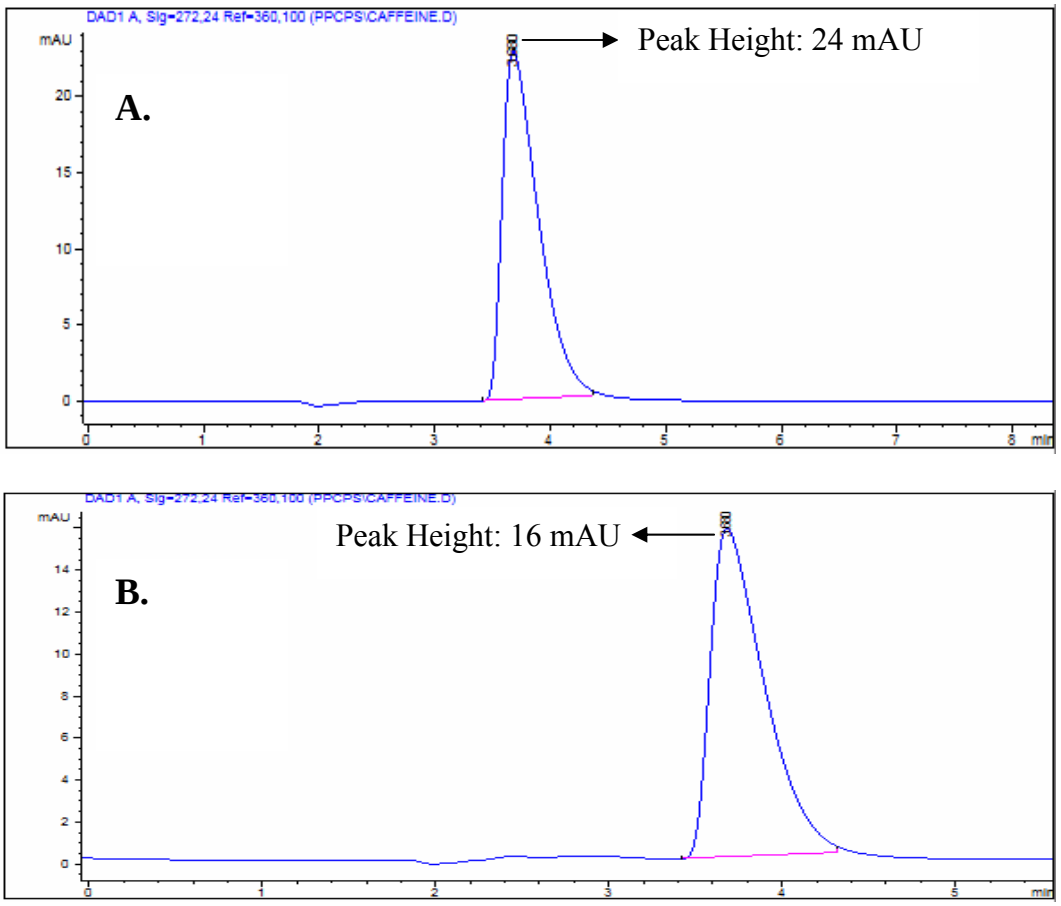


Figure A-3: Typical HPLC chromatograms showing the decrease in peak area for caffeine after treatment with 20 kHz ultrasound waves at 30°C during (A) 0 minutes, and (B) 240 minutes.

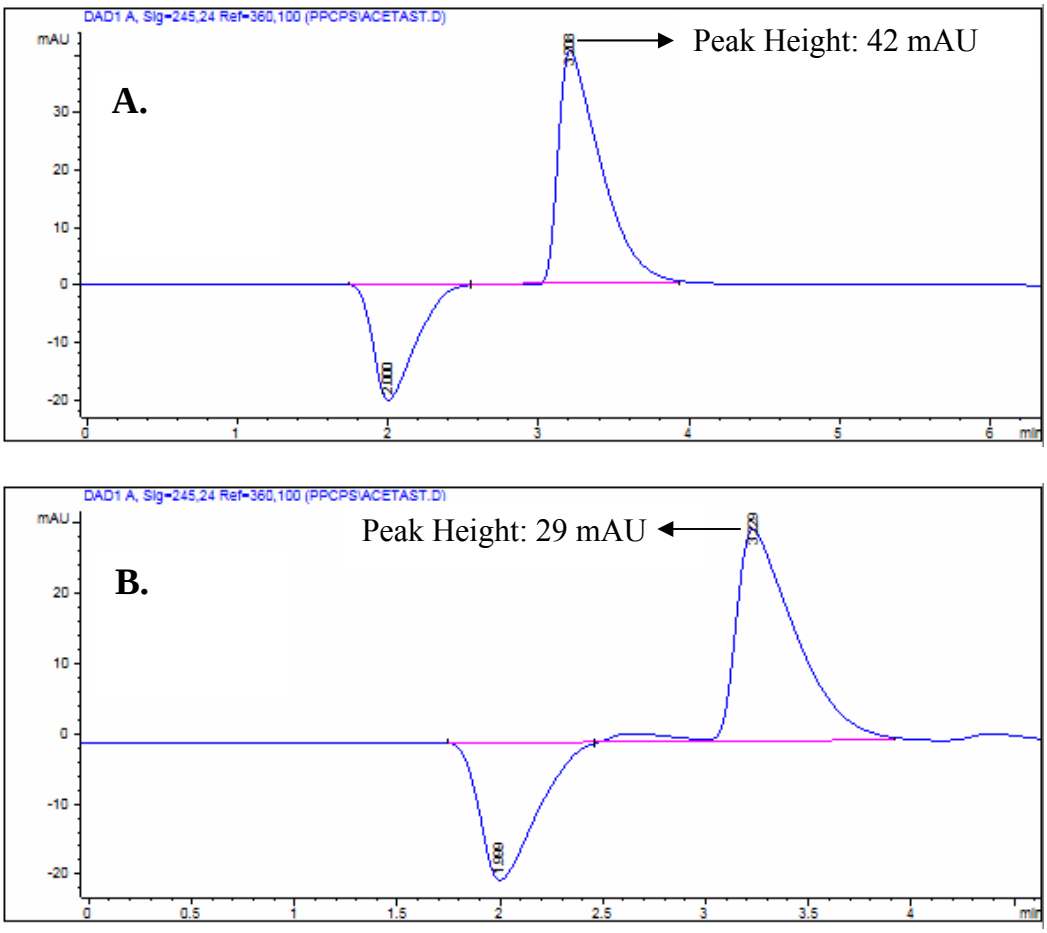


Figure A-4: Typical HPLC chromatograms showing the decrease in peak area for acetaminophen after treatment with 20 kHz ultrasound waves at 30°C during (A) 0 minutes, and (B) 240 minutes.

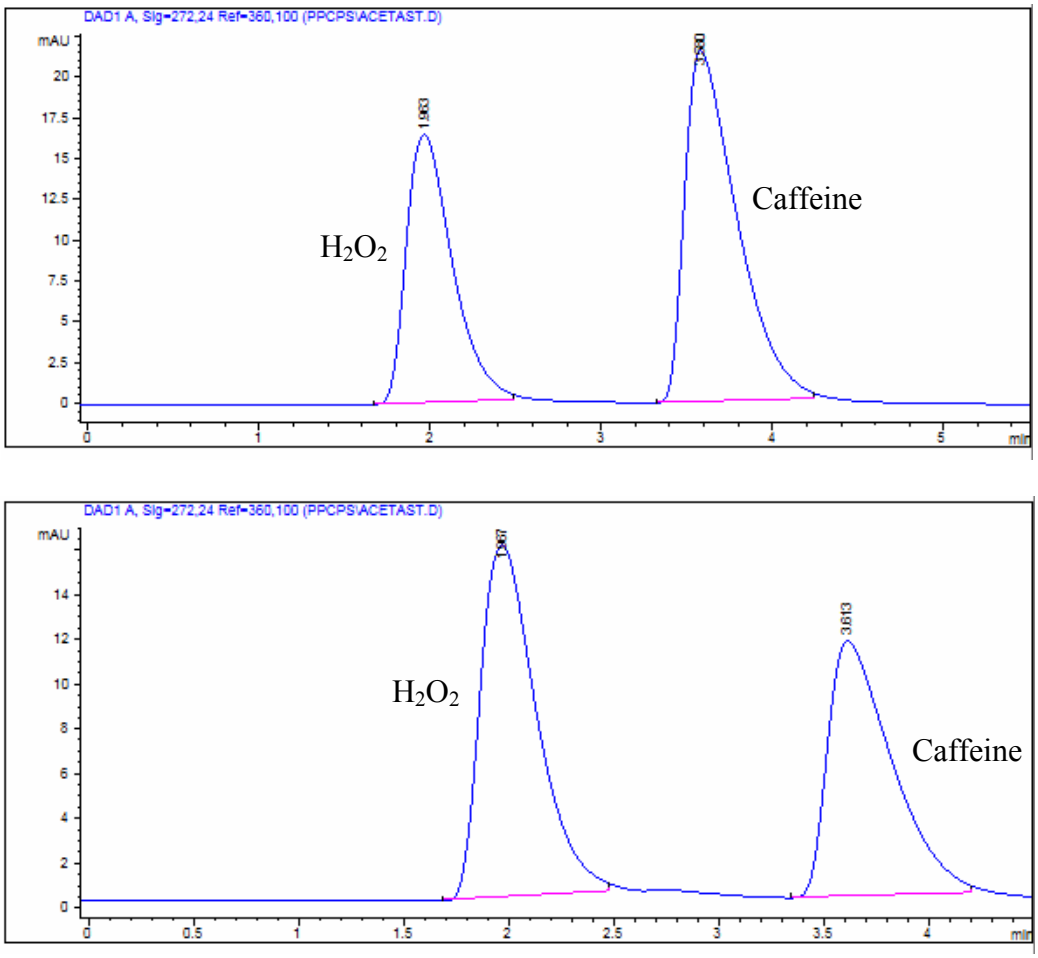


Figure A-5: Typical HPLC chromatograms showing the decrease in peak area for caffeine after treatment with the coupled 20 kHz ultrasound waves and H_2O_2 ($[H_2O_2]$ = 0.06 M) at 20°C during (A) 0 minutes, and (B) 240 minutes.

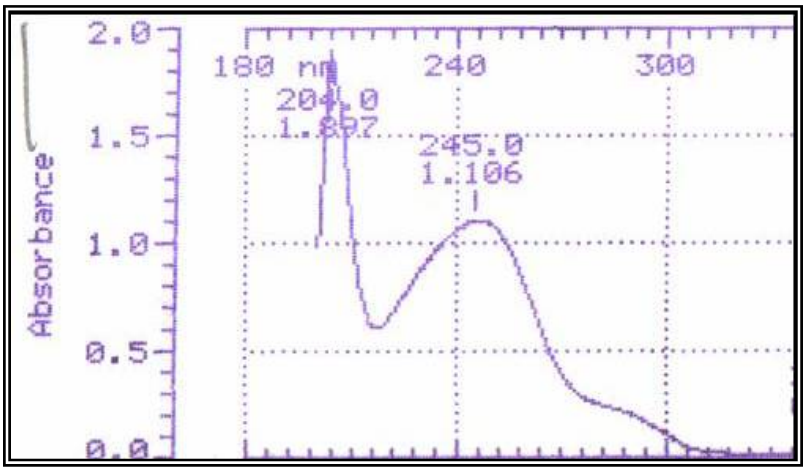


Figure A-6: UV-VS Spectra printout from the UV-VIS Spectrophotometer for acetaminophen.

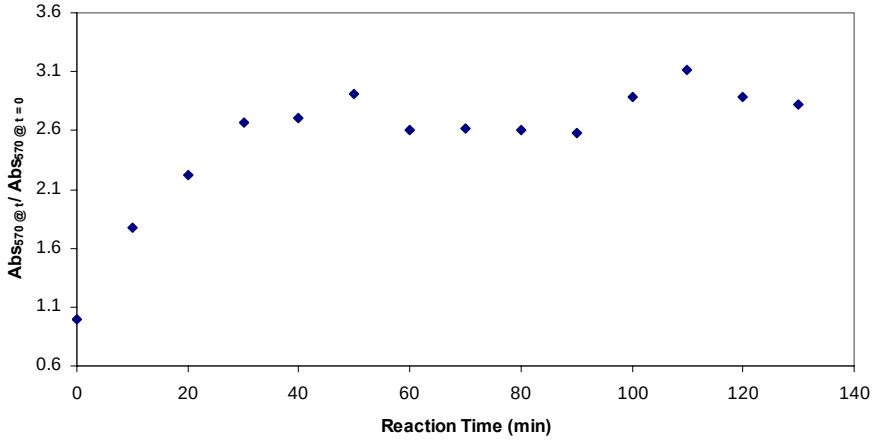


Figure A-7: Determination of H_2O_2 during Sonolysis of Water at 35ºC under 20 kHz Ultrasound Waves Irradiation ($[Caffeine]_0$ = 10 ppm): Iodometric Method.

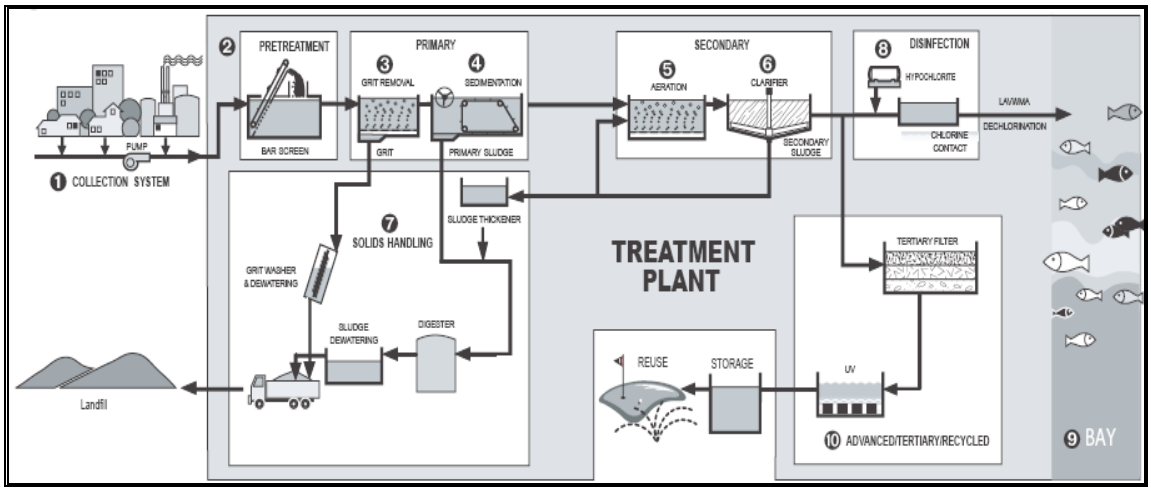


Figure A-8: Schematic of a Wastewater Treatment Plant with a Tertiary Treatment Capability.

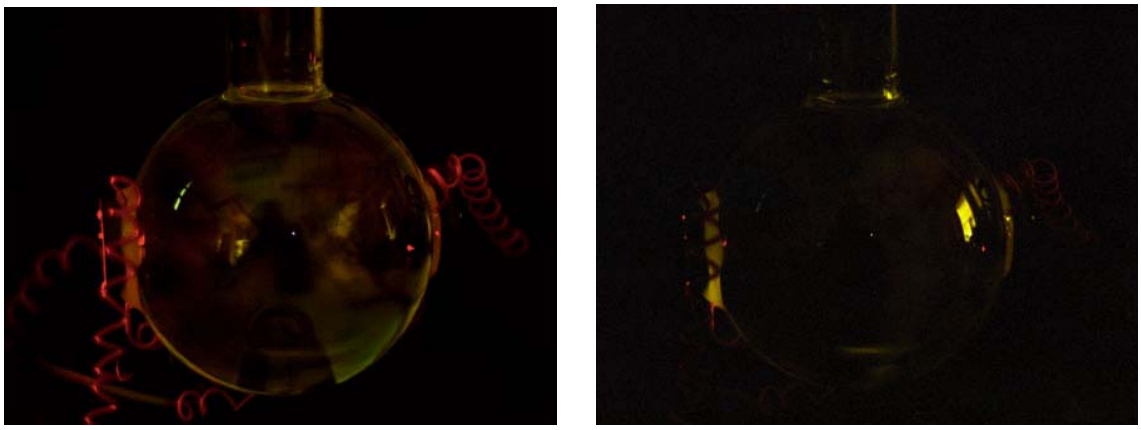


Figure A-9: Sonoluminescence of water (tiny blue bubble) captured by W. Steer (2005).

The frequencies at which the amplitude has a maximum response can be described by the wave equation:

$$\nabla^2 P = \frac{1}{c^2}\frac{\partial^2 P}{\partial t^2} \qquad \textbf{Equation A-1}$$

which in rectilinear systems has a solution in the form of:

$$P = X(x)Y(y)Z(z)\exp^{i\omega t} \qquad \textbf{Equation A-2}$$

where X, Y and Z are given by:

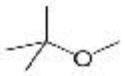
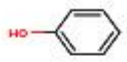
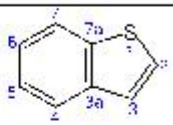
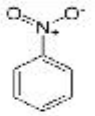
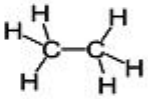
$$X = \begin{Bmatrix}\cos(k_x x)\\ \sin(k_x x)\end{Bmatrix}$$
$$Y = \begin{Bmatrix}\cos(k_y y)\\ \sin(k_y y)\end{Bmatrix}$$
$$Z = \begin{Bmatrix}\cos(k_z z)\\ \sin(k_z z)\end{Bmatrix}$$

The sin is chosen when the boundary is a pressure release and the cos is selected when the boundary is rigid and the velocity is zero. The eigen frequencies are given by:

$$f = \frac{c}{2\pi}\left[\left(\frac{n_x \pi}{L_x}\right)^2 + \left(\frac{n_y \pi}{L_y}\right)^2 + \left(\frac{n_z \pi}{L_z}\right)^2\right]^{\frac{1}{2}} \qquad \textbf{Equation A-3}$$

Solving the previous equations for the dimensions of the rectangular cell and quantity of sample used in our studies, the first significant resonant frequency result should be in the region of 27-28 kHz as witnessed previously by our results.

Table A-1: General information and properties for other compounds of interest

Reagent	MWt (g/mol)	Chemical structure	Boiling Point (°C)	Melting Point (°C)	Solubility in water
MTBE	88.15		55.2	-102	4.5 - 5.5 g/L 4.8 g/100g
Phenol	94.11		181.7	40.5	8.4 g/100 ml
Benzothiophene	134.2		221	32	29 mg/L
Nitrobenzene	123.06		210.9	5.85	0.2 g/100 ml
Ethane	30.07		-88.6	-182.76	4.7 g/100 ml
Propane	44.096		-42.09	-187.6	0.1 g/cm3
Cyclopropane	42.08		-33	-128	slight
Cyclobutane	56.107		12.5	-91	_
Cyclopentane	70.1		49	-94	_
Cyclohexane	84.16		80.74	6.55	inmiscible

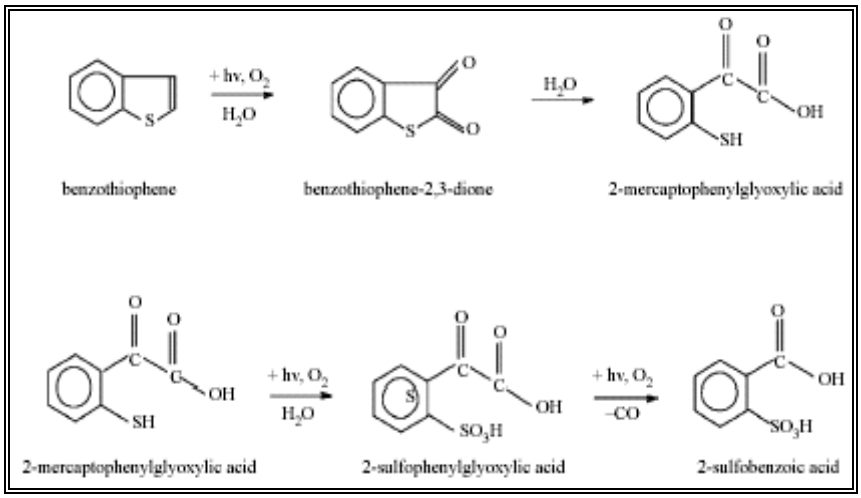


Figure A-10: Reaction pathways for the photocatalytic oxidation of benzothiophene proposed by Andersson and Bobinger (1992): step 1

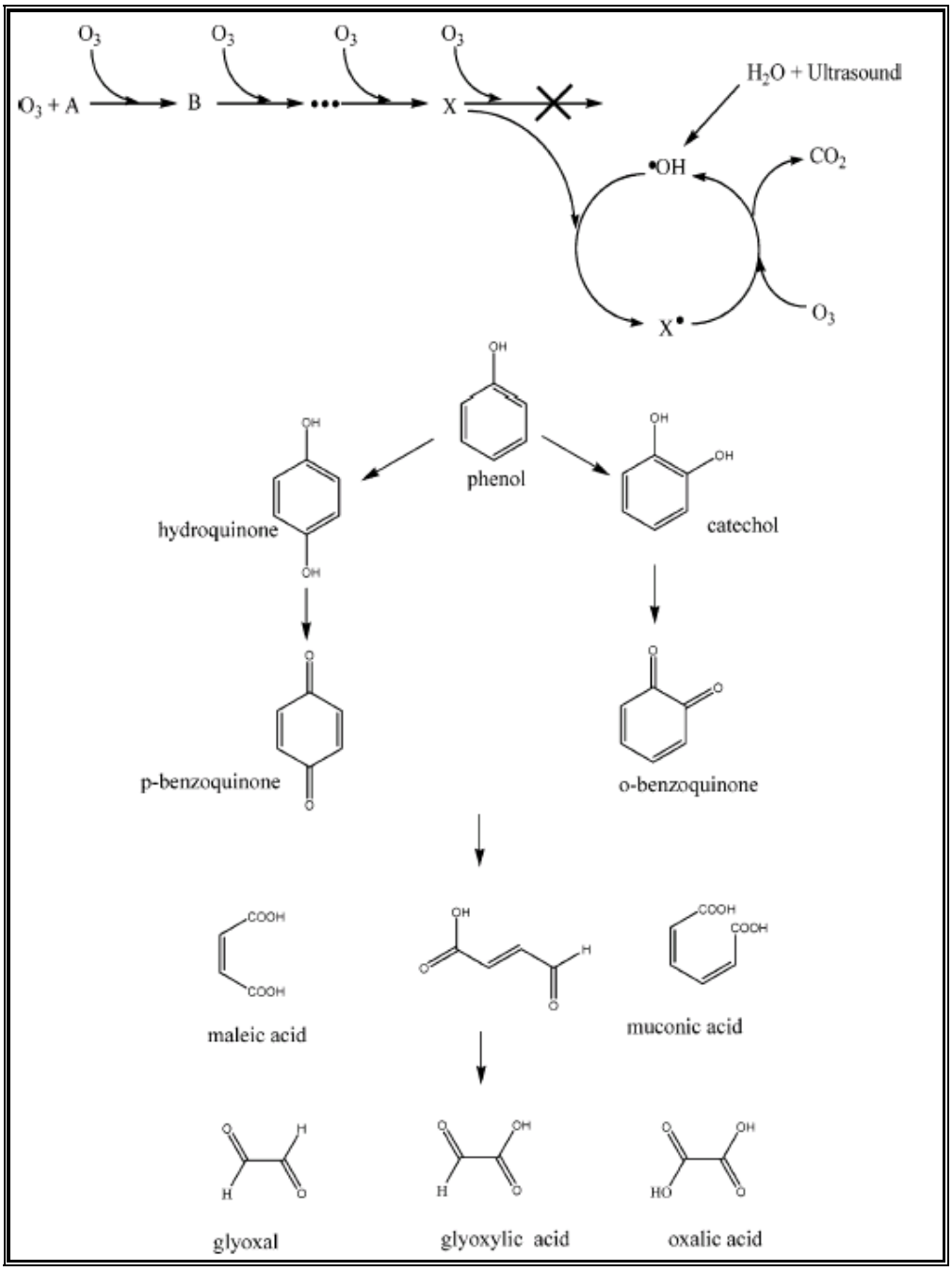


Figure A-11: Proposed reaction mechanism for the oxidation of phenol with ultrasonic irradiation combined with ozonolysis resulting in the total elimination of TOC [48].

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