CHARACTERIZING ULTRASONIC SYSTEMS FOR IMPROVED REMEDIATION OF CONTAMINATED SEDIMENTS

DISSERTATION

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By

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ABSTRACT

Ultrasound (US) was studied as an alternative method to remediate contaminated sediments. Different ultrasonic systems were designed and characterized to fundamentally understand ultrasonic effects in porous sediment and to strategically improve the ultrasonic remediation process. These include a flow-through packed-media column coupled with US, the combination of US and persulfate (PS), and a scaled-up design of a multi-stepped horn.

First, 20 kHz US waves propagating in a flow-through column packed with porous media were characterized. Sound penetration and location of cavitation were measured by a hydrophone; enhanced pore flow velocity and faster bromide tracer breakthroughs were observed. In particular, US pressure decreased exponentially with distance from the US source due to wave absorption and scattering by porous media resulting in localized cavitation close to the horn tip. A Darcy model incorporating ultrasonic effects (i.e., acoustic pressure and cavitation heating) revealed that acoustic pressure increased flow velocity at the beginning of sonication while reduced water viscosity due to cavitation heating was accounted for the enhanced pore flow in long-time sonication. Bromide breakthrough tests verified the US accelerated solute transport, as well as the dispersion of tracer in the porous media. Findings of this column study
suggest that US may improve remediation through enhancing fluid flow and mass transfer in porous sediments.

To improve contaminant degradation in sediments, sonication combined with PS was examined. PS is an *in-situ* chemical oxidation (ISCO) method. An ultrasonic reactor coupled with an electron paramagnetic resonance (EPR) spectrometer through a flow-cell was used to gain insight into the mechanisms of ultrasonic activation of PS. The high hydroxyl radical (·OH) yield in the US-PS system was attributed to the rapid reaction between sulfate radical anion (SO₄⁻) and water molecules at the bubble-water interface. Likewise, the high dissociation rate of PS, estimated from steady-state approximation, was expected at the high temperature interface. Modeling of temperature and reactivity distribution surrounding a single cavitation bubble indicated a much larger interfacial region as compared to previous results. Addition of tert-Butyl alcohol and nitrobenzene to the US-PS system verified the location of PS dissociation at the interface and elucidated the ·OH activation of PS to SO₄⁻. The mechanisms unveiled provide mechanistic support to implement US-PS system for sediment remediation.

In addition, a novel ultrasonic horn with a multi-stepped configuration and a cone-shaped tip was designed to enable scaled-up testing of sonication. Hydrophone and sonochemiluminescence experiments showed and verified multiple cavitation zones around the horn neck and tip. Calorimetry and dosimetry results demonstrated higher energy efficiency (31.3%) and faster hydroxyl radical formation rate (0.36 μM min⁻¹) for the new horn, which led to faster degradation of aqueous phenanthrene, a model contaminant. Characterization of the designed horn using COMSOL modeling and
acoustic pressure maps in a large water tank exhibited a much improved treatment capacity (~ 5 L) as compared to typical horn systems. The scale-up efforts allows a potential of large-scale performance with the designed horn for remediation of contaminated sediments.
Dedicated to my son, Fanyi
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# TABLE OF CONTENTS

ABSTRACT ................................................................................................................................. ii  
DEDICATION ................................................................................................................................. v  
ACKNOWLEDGMENTS .................................................................................................................. vi  
VITA ............................................................................................................................................... ix  
LIST OF TABLES .......................................................................................................................... xvi  
LIST OF FIGURES ......................................................................................................................... xvii  

CHAPTER 1 INTRODUCTION AND MOTIVATION ................................................................. 1  

CHAPTER 2 USE OF ULTRASOUND FOR REMEDIATION OF CONTAMINATED  
SOILS AND SEDIMENTS: A REVIEW .................................................................................. 5  
  2.1 Abstract .................................................................................................................................. 6  
  2.2 Introduction ............................................................................................................................. 10  
  2.3 Treatment of Slurries ............................................................................................................. 12  
     2.3.1 Ultrasound Fundamentals in Slurries ............................................................................ 12  
     2.3.2 Laboratory-Scale Batch Studies of Slurries ................................................................. 16  
     2.3.3 Scale-up Consideration for Ultrasonic Treatment of Slurries .................................... 24  
  2.4 Treatment in Porous Media .................................................................................................. 26
2.4.1 Ultrasound Fundamentals in Porous Media ............................................. 26
2.4.2 Laboratory-Scale Column Studies in Porous Media ............................. 33
2.4.3 Field Application of Ultrasound in Porous Media ............................... 35
2.4.4 Design Criteria for Large-Scale Application ....................................... 36
2.6 Future Work ......................................................................................... 37
2.7 Acknowledgments ................................................................................ 38

CHAPTER 3  CHARACTERING ULTRASONIC CAVITATION AND
HYDRODYNAMICS IN DIFFERENT SIZED POROUS MEDIA ....................... 58

3.1 Abstract .............................................................................................. 59
3.2 Introduction .......................................................................................... 63
3.3 Materials and Methods ......................................................................... 66
  3.3.1 Materials .......................................................................................... 66
  3.3.2 Experimental Setup .......................................................................... 66
  3.3.3 Experimental Procedure .................................................................... 67
  3.3.4 Theory .............................................................................................. 69
3.4 Results and Discussion .......................................................................... 73
  3.4.1 Ultrasound Propagation in Porous Media ......................................... 73
  3.4.2 Cavitation in Porous Media .............................................................. 75
  3.4.3 Ultrasound Enhanced Pore Flow ...................................................... 77
3.4.4 Ultrasound Enhanced Solute Transport ........................................ 80
3.5 Conclusion .................................................................................... 82
3.6 Acknowledgments ........................................................................ 83

CHAPTER 4  KINETICS AND MECHANISM OF ULTRASONIC ACTIVATION OF PERSULFATE: AN IN-SITU EPR SPIN TRAPPING STUDY ......................... 95

4.1 Abstract ....................................................................................... 96
4.2 Introduction .................................................................................. 97
4.3 Materials and Methods .................................................................. 99
  4.3.1 Materials ................................................................................ 99
  4.3.2 Experimental Setup .................................................................. 100
  4.3.3 Sonication and EPR Experiments ............................................ 100
4.4 Results and discussion ................................................................. 102
  4.4.1 Radical Production in US-PS System ......................................... 102
  4.4.2 Spin Adduct Decay ................................................................. 104
  4.4.3 Thermal Activation at the Bubble-Water Interface .................. 104
  4.4.4 Role of Free Radicals in Activation ......................................... 108
  4.4.5 Modeling Reactivity at the Bubble-Water Interface ................. 110
4.5 Environmental Application .......................................................... 117
4.6 Acknowledgements ...................................................................... 118
CHAPTER 5 DESIGNING AND CHARACTERIZING A MULTI-STEPPED ULTRASONIC HORN FOR ENHANCED SONOCHEMICAL PERFORMANCE .... 130

5.1 Abstract ................................................................................................................. 131

5.2 Introduction ............................................................................................................. 134

5.3 Ultrasonic Horn Design .......................................................................................... 135

  5.3.1 Design Principles ............................................................................................... 135

  5.3.2 Horn Configuration Design .................................................................................. 137

5.4 Materials and Methods .......................................................................................... 140

  5.4.1 Materials ............................................................................................................ 140

  5.4.2 Ultrasonic System .............................................................................................. 141

  5.4.3 Horn Characterization ....................................................................................... 142

5.5 Results and Discussion .......................................................................................... 145

  5.5.1 Hydrophone and Sonochemiluminescence (SCL) Measurements ................. 145

  5.5.2 Calorimetry ....................................................................................................... 146

  5.5.3 Dosimetry .......................................................................................................... 148

  5.5.4 Naphthalene Sonolysis ..................................................................................... 149

5.6 Conclusions ........................................................................................................... 151

5.7 Acknowledgments .................................................................................................. 151
CHAPTER 6 COMBINING COMSOL MODELING WITH ACOUSTIC PRESSURE MAPS TO DESIGN SONO-REACTORS

6.1 Abstract .................................................................................................................. 162

6.2 Introduction ............................................................................................................. 166

6.3 Methodology .......................................................................................................... 168

6.3.1 COMSOL Simulation .......................................................................................... 168

6.3.2 Experimental Verification .................................................................................... 171

6.3.3 Acoustic Emission ............................................................................................... 172

6.4 Results and Discussion ........................................................................................... 173

6.4.1 Acoustic Field Modeling ...................................................................................... 173

6.4.2 Acoustic Field Mapping ...................................................................................... 174

6.4.3 Cavitation Threshold and Reactive Region ......................................................... 176

6.5 Summary and Future Work ...................................................................................... 180

6.6 Acknowledgments ................................................................................................... 180

CHAPTER 7 CONCLUSIONS ......................................................................................... 189

APPENDIX A: SUPPORTING INFORMATION ................................................................ 193

BIBLIOGRAPHY ............................................................................................................ 216
LIST OF TABLES

Table 2. 1 Ultrasonic treatment of heavy metal in soils, sediments and solid wastes ...... 39
Table 2. 2 Ultrasonic treatment of organic contaminants in soils, sediments, and solid wastes.................................................................................................................................................................................. 42
Table 2. 3 Ultrasonic treatment of oil in soils, sands, and solid wastes......................... 46
Table 2. 4 Summary of laboratory studies on sonic/ultrasonic treatment of porous media .................................................................................................................................................................................. 48
Table 2. 5 Summary of field studies on sonic/ultrasonic treatment.................................. 52
Table 3. 1 Characteristics, attenuation abilities, and hydrodynamics of pore flow for tested particles.................................................................................................................................................................................. 84
Table 4. 1 Principal reactions in US-PS system ............................................................... 119
Table 4. 2 Observed and fitted reaction rate constants in aqueous solution.................... 120
Table 5. 1 Characteristics of designed and typical horns................................................... 152
Table A. 1 Bubble number and distribution at different oscillating frequencies (PD = 1.5 W mL$^{-1}$).................................................................................................................................................................................. 207
Table A. 2 Initial inputs for three domains in COMSOL simulation .............................. 212
LIST OF FIGURES

Figure 2. 1 Acoustic vibration and wave propagation (a — molecule oscillation; b — harmonic wave; c — attenuated wave)................................................................. 54

Figure 2. 2 Acoustic cavitation and its effects (a — cavitation bubble; b — particle).... 55

Figure 2. 3 Acoustic effects on porous media (gray — particle; brown — NAPL; black — colloid; ))) — sound waves; arrow — flow)................................................................. 56

Figure 2. 4 Conceptual design for acoustically enhanced soil remediation............. 57

Figure 3. 1 Schematic of experimental setup............................................................ 85

Figure 3. 2 Propagation of ultrasound from source in column with large sand (mean diameter of 0.760 ± 0.005 mm; color key in kPa; numbers indicate power intensity in W cm²)........................................................................................................... 86

Figure 3. 3 Ultrasound waveforms (a and c) and frequency spectrum (b and d) observed from water at different power intensities......................................................... 87

Figure 3. 4 Frequency spectrum at different locations for large sand (mean diameter of 0.760 ± 0.005 mm; power intensity of 6.26 W cm²)........................................... 88

Figure 3. 5 Frequency spectrum observed from different porous media (—1cm; —2.5cm; power intensity of 6.26 W cm²)............................................................................. 89

Figure 3. 6 Temperature (□) and flow velocity (■) changes at column outlet for large sand (mean diameter of 0.760 ± 0.005 mm; power intensity of 6.26 W cm²)............. 90
Figure 3. 7 Flow velocities in tested media under different power intensities ............... 91

Figure 3. 8 Enhancement of pore flow (□) and decrease in viscosity (■) at different initial temperatures for large sand (mean diameter of 0.760 ± 0.005 mm; power intensity of 6.26 W cm⁻²) ................................................................................................................................. 92

Figure 3. 9 Bromide breakthrough curves for different media in the presence and absence of 20 kHz ultrasound waves (□— no sonication; ■— sonication at power intensity of 6.26 W cm⁻²) ................................................................. 93

Figure 3.10 Kinetic and viscous contribution to enhanced dispersion coefficients in different media in the presence of ultrasound (power intensity of 6.26 W cm⁻²) .......... 94

Figure 4. 1 Experimental setup for in-situ EPR measurements of sonicated solution.... 121

Figure 4. 2 EPR spectrum of sonicated persulfate (PS = 100 mM; DMPO = 40 mM; PD = 1.5 W mL⁻¹; □— DMPO•−OH, a_N = 15.01, a_β-H = 14.72; ■— DMPO•−SO_4^−, a_N = 13.67, a_β-H = 10.24, a_γ-H_1 = 1.52, a_γ-H_2 = 0.79) ......................................................................................................................... 122

Figure 4. 3 Adduction formation at different DMPO concentrations (PS = 1 mM; PD = 1.5 W mL⁻¹) ........................................................................................................................................................................... 123

Figure 4. 4 DMPO adduct formation with sonication time (□— DMPO•−OH at 100 mM persulfate; ■— DMPO•−SO_4^− at 100 mM persulfate; △— DMPO•−OH at 1 mM persulfate; ▲— DMPO•−SO_4^− at 1 mM persulfate; ○— DMPO•−OH under sonication only; DMPO = 40 mM; PD = 1.5 W mL⁻¹) ............................................................................................................. 124

Figure 4. 5 Hydrolysis of DMPO adducts with time (□— DMPO•−OH; ■— DMPO•−SO_4^−; PS = 100 mM; DMPO = 5 mM; PD = 1.5 W mL⁻¹) ............................................................................................................. 125
Figure 4. 6 Linear relationship between initial zero-order formation rate constants and persulfate concentrations for DMPO$^+$−SO$_4^−$ (a) and DMPO$^+$−OH (b; DMPO = 40 mM; PD = 1.5 W mL$^{-1}$) ................................................................. 126

Figure 4. 7 Adduct formation in the absence and presence of nitrobenzene (DMPO = 1Mm; PS = 1 mM; PD = 1.5 W mL$^{-1}$; P-value < 0.05 for DMPO$^+$−OH suggests significant difference and P-value = 0.36 for DMPO$^+$−SO$_4^−$ suggests no significant difference) .................................................................................................................. 127

Figure 4. 8 Predicting spatial temperature distribution and corresponding dissociation rate of persulfate at the bubble-water interface ($R_0$ = 2.0 μm in argon purged solution; bubble temperature = 5000 K and $T_{min}$ = 303 K; small graph depicts temperature change in outer layer) ........................................................................................................................................ 128

Figure 4. 9 Schematic of double layer model for interfacial region ........................................... 129

Figure 5. 1 Configurations of a typical horn (a) and the designed horn (b; I — the transitional section; II — the reactive section; all measurement numbers in mm). 153

Figure 5. 2 Schematic diagram of longitudinal vibration of a single-step horn (a) and its equivalent circuit (b). ................................................................................................................................. 154

Figure 5. 3 Measured frequency spectrum of the designed horn (1/8f and 1/2f are subharmonic frequencies, f is resonant frequency, and 2f and 3f are ultraharmonic frequencies). ......................................................................................................................... 155

Figure 5. 4 Acoustic field distribution around designed horn (a) and typical horn (b) as determined from hydrophone measurements (color key in volts, initial temperature = 20 ºC). ........................................................................................................................................ 156
Figure 5. 5 Sonochemiluminescence imaging of designed horn (a) and typical horn (b) in the reactor (initial luminol concentration = $10^{-3}$ M, pH = 11.3, and initial temperature = 20 ºC).

Figure 5. 6 The influence of initial temperature on calorimetrically determined acoustic power input into solution at different electrical power inputs (■ — 500 W; ● — 600 W; ▲ — 700 W; ▼ — 800 W; ◆ — 900 W; ★ — 1000 W as electric input power levels by dial setting using Branson BCA 900 series power supplier).

Figure 5. 7 The influences of calorimetrically determined acoustic power (a; initial temperature = 20 ºC, pH = 7.4) and initial temperature (b; calorimetric acoustic power = 147 W, pH = 7.4) on the zero-order rate constant for HTA formation.

Figure 5. 8 The first-order sonolytic degradation rate constants of naphthalene by designed horn (grey; power density = 252 W L$^{-1}$, pH = 7.4) and typical horn (white; power density = 430 W L$^{-1}$ pH = 7.4; value normalized to the rate constant of designed horn using Eq. 5.12).

Figure 6. 1 Schematic diagram of experimental setup for hydrophone measurements in the plexiglass box (Dimension is 61 cm × 61 cm × 45 cm and volume is 167.5 L; the depth tangential to horn tip is defines Z = 0; 1 — Branson 902R Model transducer; 2 — serial stepped ultrasonic horn; 3 — Reson T4013 hydrophone; 4 — water; 5 — plexiglass box).

Figure 6. 2 Simulation of acoustic pressure distribution in a X-Z plane (Units for color label and number are Pa and mm, respectively).
Figure 6. 3 Simulation of acoustic pressure distribution in X-Y planes at different depths (1 — X-Y plane near water surface; 2 — X-Y plane in the middle of horn neck; 3 — X-Y at Z = 0 cm; 4-6 — X-Y planes at Z < 0 cm; units for color label and number are Pa and mm, respectively) ......................................................................................................................... 183

Figure 6. 4 Acoustic pressure distribution in Z-direction at different distances (2cm, 5cm and 10cm) and power levels (50%, 75% and 100%; red dotted line is the cavitation threshold value of 0.63 V) .......................................................................................................................... 184

Figure 6. 5 3D (left) and contour (right) mapping of hydrophone measurements in plexiglass tank (This scan was carried out at room temperature with 50% power input from power supplier to transducer; a — X–Y plane at Z = +4 cm; b — X–Y plane at Z = 0 cm; c — X–Y plane at Z = −4 cm; red dotted line is the cavitation threshold value of 0.63 V) .................................................................................................................................. 185

Figure 6. 6 Ultrasonic waveforms and frequency spectrum observed in water at different power intensities (Convex feature in the waveform results from the sum of waveforms in different frequencies to the original waveform) .............................................................................. 186

Figure 6. 7 Percentage of cavitation zones in different X-Y planes (% of cavitation zones = Measurements not less than 0.63 V in a X-Y plane / Total measurements in the X-Y plane × 100%; 0.63 V is measured cavitation threshold using acoustic emission method) .................................................................................................................................. 187

Figure 6. 8 Simulation of acoustic pressure propagation in proposed reactor (red — up to + 1.59 × 10^5 Pa; blue color — down to − 1.59 × 10^5 Pa) ......................................................................................................................... 188
Figure A. 1 Schematic diagram of longitudinal vibration in porous media packed column (a) and mechanical energy for the experimental setup (b; P — acoustic pressure; $V_0$ — micro-volume of media packed in the column; $h$ — piezometric head = 63 cm; $z$ — elevation head; $p$ — pressure head; $k$ — media permeability; datum plane is defined at $h = 0$ cm) ……………………………………………………………………………………………………………………………. 194

Figure A. 2 Propagation of ultrasound from source in column with small sand (mean diameter of $0.316 \pm 0.011$ mm; color key in kPa; numbers indicate power intensity in W cm$^{-2}$) ………………………………………………………………………………………………………………………………………………………………………………………………………………… 195

Figure A. 3 Propagation of ultrasound from source in column with medium sand (mean diameter of $0.547 \pm 0.012$ mm; color key in kPa; numbers indicate power intensity in W cm$^{-2}$) ………………………………………………………………………………………………………………………………………………………………………………………………………………………… 196

Figure A. 4 Propagation of ultrasound from source in column with small glass beads (mean diameter of $0.500$ mm; color key in kPa; numbers indicate power intensity in W cm$^{-2}$) ………………………………………………………………………………………………………………………………………………………………………………………………………………………… 197

Figure A. 5 Propagation of ultrasound from source in column with media glass beads (mean diameter of $1.000$ mm; color key in kPa; numbers indicate power intensity in W cm$^{-2}$) ………………………………………………………………………………………………………………………………………………………………………………………………………………………… 198

Figure A. 6 Propagation of ultrasound from source in column with large glass beads (mean diameter of $2.000$ mm; color key in kPa; numbers indicate power intensity in W cm$^{-2}$) ………………………………………………………………………………………………………………………………………………………………………………………………………………………… 199

Figure A. 7 Flow velocity under long sonication time for large sand (mean diameter of $0.760 \pm 0.005$ mm; power intensity of $6.26$ W cm$^{-2}$) ……………………………………………………………… 200
Figure A. 8 Ultrasound propagation in water and in large sand (mean diameter of 0.760 ± 0.005 mm; power intensity of 6.26 W cm⁻²) ................................................................. 201

Figure A. 9 Temperature change in the column packed with tested particles (measurement locations at 1.0, 4.0, 7.0, and 10.0 cm; power intensity of 6.26 W cm⁻²) 202

Figure A. 10 Breakthrough as a function of pore volume in different media (□ — no sonication; ■ — sonication at power intensity of 6.26 W cm⁻²) ......................................... 203

Figure A. 11 DMPO•−SO₄⁻ adduct formation in the absence and presence of TBA (100 mM; PS = 1 mM; DMPO = 40 mM; PD = 1.5 W mL⁻¹; P-value = 0.50 suggests no significant difference) ........................................................................................................ 205

Figure A. 12 Geometry of multi-stepped horn and sonicated water region in 2-D axisymmetric dimension in COMSOL setup (1 — transducer; 2 — multi-stepped horn; 3 — water) .............................................................................................................................. 211
CHAPTER 1

INTRODUCTION AND MOTIVATION
Sediment contamination by toxic and persistent organic compounds and heavy metals is a worldwide concern and locally in the Great Lakes region [1, 2]. These contaminants (e.g., polycyclic aromatic hydrocarbons, PAHs) released from sediments accumulate in biota and are passed up the food chain, posing a long term risk to the aquatic ecosystem [3], thus endangering both fish-eating wildlife and humans. Traditional technologies of capping sediment in place and dredging sediment with transfer to a waste landfill are energy-intensive, expensive, and destructive to the environment [4]. Thus, alternative technologies to treat contaminated sediment are sought.

Ultrasound (i.e., sound waves with frequency higher than 20 kHz [5, 6]) as an alternative remediation technology has gained use due to the physical and chemical effects achieved from sonication [7-11]. These unique effects result in contaminant degradation through radical oxidation and thermolysis [12-14], increased availability of solid-associated contaminants [15, 16], and enhanced contaminant transport in the porous media [17, 18]. Thus, sonication process is applied when slow reaction and limited mass transfer occur in traditional treatments [9].

Most investigations of ultrasonic treatment are in bench-scale slurry systems [19-28]. Few studies have investigated ultrasonic treatment in porous media. Ultrasonic effects including ultrasound penetration and hydrodynamics in porous sediments are not well-understood, necessitating an exploration of ultrasound behavior and its impacts on the porous media. In addition, sonication is usually energy-intensive and long treatment times are needed for contaminant degradation in the presence of organic and inorganic matrices at contamination sites [29]. While the success of previous work with in-situ
oxidation of contaminated sites has shown promise [30], the combination of ultrasound with persulfate oxidation [31] can potentially enhance radical formation and thus effectively reduce the health hazards of sediments. Furthermore, the extension of ultrasound technology to engineering-scale applications requires proper scale-up strategies for improved remediation [32, 33]. A redesign of the ultrasonic horn configuration can overcome the disadvantages of typical ultrasonic horns which generate localized cavitation below the horn tip [7, 34, 35].

The overall objective of this research is to improve ultrasonic remediation of contaminated sediments through designing and characterizing different ultrasonic systems. Literature regarding ultrasonic remediation of contaminated sediments and soils in both laboratory and field scales are critically reviewed in Chapter 2. In Chapter 3, a typical column study coupled with a horn type ultrasonic system was designed to elucidate the ultrasonic properties in relation to porous media. To gain mechanistic insight into the enhancement of radical formation with a chemical oxidant, persulfate, reaction kinetics and pathways were investigated using a flow-cell allowing for in-situ electron paramagnetic resonance (EPR) measurements. Modeling of temperature and reactivity distribution surrounding a cavitation bubble provided more in-depth conclusions on the ultrasonic activation of persulfate as explained in Chapter 4. Chapters 5 and 6 explore a conceptual design of ultrasonic horn for improved sonochemical performance. A multi-stepped configuration and a cone-shaped tip were introduced into the design. Physical and chemical characterizations were conducted to evaluate the performance of the designed horn for a large-scale remediation process. In Chapter 7,
findings in each chapter are highlighted and compared to previous studies. Suggestions on future studies are also given.
CHAPTER 2

USE OF ULTRASOUND FOR REMEDIATION OF
CONTAMINATED SOILS AND SEDIMENTS: A REVIEW
2.1 Abstract

Ultrasound is emerging as an alternative to remediate contaminated soils and sediments, providing a cross-disciplinary link between physics, chemistry, and engineering in the practice of environmental remediation. Unique physical and chemical effects introduced by ultrasound alter pore space between solids, increase accessibility of solid-associated contaminants, and enhance pore flow and mass transfer in soils and sediments. Most studies that have investigated ultrasonic remediation are at laboratory and pilot scales, where both inorganic and organic contaminants are successfully removed from soils or sediments. However, full-scale application of ultrasound in remediation is limited. First, exploring mechanistic insights into ultrasonic properties in relation to porous media is necessary before ultrasound will see widespread application. Low energy efficiency of current ultrasonic devices is a significant problem for ultrasonic treatments. It is particularly important to design novel ultrasonic systems that aim to improve the energy efficiency and economic feasibility of this technology. Likewise, harnessing synergistic effects through technology combinations, such as ultrasound and chemical oxidation, seems to be an effective and economically viable option for in-situ remediation. The objective of this review is to provide a straightforward summary of the ultrasonic remediation literature and to ignite future research using ultrasonic treatment of contaminated soils and sediments in a sustainable manner.

Keywords: ultrasound, remediation, synergistic effect, scale-up, economic
Nomenclature

a  interfacial area of solid particles (m²)
A  unit area (m²)
c  speed of the sound wave (m s⁻¹)
C  elastic coefficients related to porosity
C_A  aqueous concentration of solid species (M)
C_A*  saturation concentration of solid species (M)
C_m  aqueous concentration of compound (M)
d  distance from sound source (m)
da  spherical diameter of grains (m)
D  hydrodynamic dispersion coefficient (m² s⁻¹)
D*  dispersion coefficient in the presence of ultrasound (m² s⁻¹)
D_us  enhanced dispersion coefficient due to sonication (m² s⁻¹)
e  dilation of bulk material
E  acoustic energy (J)
E_k  kinetic energy (J)
E_p  potential energy (J)
f  acoustic frequency (Hz)
Δh  head difference (Pa)
H  elastic coefficients related to bulk modulus of bulk material
I  acoustic intensity (W m⁻²)
I₀  acoustic intensity at sound source (W m⁻²)
\( k_{sl} \) dissolution rate constant
\( K_b \) bulk modulus of porous frame
\( K_f \) bulk modulus of bulk material
\( L \) longitudinal distance (m)
\( M \) elastic coefficients related to shear and bulk moduli of porous frame
\( M_1 \) parametric constant
\( M_2 \) parametric constant
\( P \) acoustic pressure (Pa)
\( Q \) pore flow rate (mL min\(^{-1}\))
\( t \) time (s)
\( u \) particle vibration velocity (m s\(^{-1}\))
\( v \) seepage flow velocity (m s\(^{-1}\))
\( v^* \) seepage velocity in the presence of ultrasound (m\(^2\) s\(^{-1}\))
\( v_{us} \) enhanced seepage velocity due to sonication (m s\(^{-1}\))
\( V \) micro-volume of element (m\(^3\))
\( V_0 \) initial micro-volume of element (m\(^3\))
\( V_m \) volume of porous media after ultrasonication (m\(^3\))
\( V_{m,0} \) volume of porous media before ultrasonication (m\(^3\))
\( W \) power of acoustic waves (J s\(^{-1}\))
\( Z \) acoustic impedance (Pa·s m\(^{-1}\))
Greek letters

\( \alpha \) attenuation coefficient
\( \beta \) porosity of media
\( \varepsilon \) energy density (J m\(^{-3}\))
\( \eta \) fluid viscosity (Pa s)
\( \mu_b \) shear stress (Pa)
\( \rho \) media density (kg m\(^{-3}\))
\( \rho_f \) fluid density (kg m\(^{-3}\))
\( \rho_s \) solid density (kg m\(^{-3}\))
\( \xi \) dilation of bulk material and the relative dilation of fluid
\( \omega \) angular frequency of waves (rad s\(^{-1}\))
2.2 Introduction

Among many remediation methods, ultrasound (> 20 kHz [36, 37]) is finding its niche as a clean technology featuring a smaller environmental footprint and minimal pollution [38]. Application on-site and potential lack of added chemicals are advantages of this technology [7, 39-41]. These two advantages mirror the broad definition of green chemistry, which is “the design of chemical products and processes that reduce or eliminate the use and generation of hazardous substances and seek to reduce and prevent pollution at the source” [42]. In addition to fostering “green” remediation of soils and sediments, ultrasound is now a feasible option to promote digestion of activated sludge in wastewater treatment plants and solid waste in landfills [43, 44]. To improve contaminant removal and economic viability of ultrasound as a technology, synergistic combinations of ultrasound with electrokinetics, thermolysis, or biodegradation has been investigated [22, 28, 45]. Thus, ultrasound is emerging as an alternative option for environmental remediation, particularly for the treatment and processing of contaminated soils, sediments, and solid wastes.

Given the emerging status for ultrasonic remediation, the full-scale treatment of contaminated soil and sediment is hindered by technical and mechanistic challenges. The technical challenges associated with scale-up of ultrasonic systems include low energy efficiency of ultrasonic devices (< 30%) [46, 47] and limited horn configuration designs capable of large-scale treatments [47, 48]. In addition to these technical challenges, it is difficult to elucidate the mechanisms of ultrasonically enhanced remediation of soils or sediments due to: 1) the heterogeneity in grain size and composition of porous media; 2)
the complexity of several competing mechanisms occurring simultaneously; and 3) the lack of reliable techniques to characterize physical and chemical effects of ultrasonic waves (e.g., cavitation) on contaminant fate and transport in porous media. These challenges entail continuous efforts that necessitate both careful engineering designs and mechanistic investigations for full-scale ultrasonic applications.

In this review, we systematically summarize previous and current literature with an emphasis on ultrasonic remediation of soils and sediments. Instead of an exhaustive critical review, we attempt to categorize available publications and present their results for researchers who want to find previous and recent research advances in ultrasonic remediation. Ultrasound first attracted attention for soil/sediment remediation in the 1990s. Most remediation studies are conducted in slurry systems; studies related to porous media are mostly on enhanced oil recovery. Mechanisms determined from these fundamental studies at the laboratory-scale provide insight to design large-scale ultrasonic remediation systems [8, 33, 42]. We also include fundamental principles of ultrasound properties in slurry and porous media to elucidate the enhancement for remediation due to ultrasound. This theoretical and experimental review provides a basis to advance our understanding and guide future research on ultrasound as a clean remediation technology.
2.3 Treatment of Slurries

This section is devoted to the application of ultrasound in slurry treatments. While most studies have been conducted at ultrasonic frequencies, some studies using lower frequencies (< 20 kHz) are also included in this work. In this review, the term sound (sonic or sonication) refers to lower frequency waves, while ultrasound (ultrasonic or ultrasonication) refers to sound waves with a frequency higher than 20 kHz. We also included studies investigating sonic/ultrasonic treatment of activated sludge and solid waste due to their similar characteristics to soil or sediment slurry.

2.3.1 Ultrasound Fundamentals in Slurries

Highly energetic ultrasonic waves produce alternating compression and rarefaction zones in irradiated solutions [49-51] (Figure 2.1). A cavity is formed when the rarefaction wave pressure exceeds the tensile strength of the liquid [12]. In pure water, forming the “cavity” requires a pressure as high as 1500 atm [52]. In practice, however, the pressure threshold necessary to produce cavitation in water is only several atm due to the presence of weak spots in the water, such as gas nuclei and fine particles [8, 53]. The occurrence of cavitation produces heat, forms free radicals, promotes mass transfer, and fractures particles. These physical and chemical effects due to ultrasound are expected in soil or sediment slurries.
2.3.1.1 Chemical and thermal effects

The “hot spot” theory has been widely accepted to interpret the violent implosion of cavitation bubbles [13, 14]. In the hot spot theory (Figure 2.2a), three reactive regions are postulated: 1) the gas phase with extremely high temperature (> 15000 K for a single bubble collapse [54, 55] and ~ 5000 K for multi-bubble clouds [55, 56]) and pressure (500 – 1000 atm [12]); 2) interfacial region with steep temperature and radical concentration gradients; and 3) bulk solution at ambient temperature. In this extremely hot gaseous region, water molecules are thermally dissociated into ‘OH and ‘H:

\[
\text{H}_2\text{O} \rightarrow \cdot\text{OH} + \cdot\text{H}
\]

Thus, thermolysis and oxidation by free radicals (e.g., ‘OH) are the two degradation pathways for contaminants in the aqueous phase [9]. Extensive studies have been conducted to investigate the sonochemical degradation of contaminants in water as an advanced oxidation process (AOP) [9-11, 41, 57], allowing in-depth mechanistic insights into chemical effects of cavitation and related applications.

2.3.1.2 Physical effects

In addition to chemical and thermal effects, ultrasound induces a variety of physical effects including acoustic streaming, microstreaming, microjets and shock waves. Water flow in the direction of sound propagation is called acoustic streaming [52], which can disperse fine particles in a reactor generating a slurry [33]. Microscopically, micro-streaming, micro-jets, and shock waves are associated with bubble dynamics and collapse. When a stable cavitation bubble oscillates in an acoustic field, the fluid
surrounding it also moves after absorbing the kinetic energy from bubble vibration. Such micro-fluid flow is termed micro-streaming [58]. The other two phenomena: micro-jets and shock waves, occur near liquid-solid and gas-liquid interfaces (Figure 2.2b). Spherical shock waves are induced by bubble collapse [58-60]. At the localized spot of bubble collapse, the pressure from shock waves can be as high as 10000 atm [61]. However, the presence of other bubbles, particles, and external forces (e.g., gravity) may deform the cavitation bubbles at collapse [11, 62]. For example, when a bubble is close to a solid surface several times larger than the bubble, the unbalanced external forces (i.e., acoustic and hydrostatic pressures acting on bubble surface) result in rapid collapse of the liquid-side bubble wall, which impinges into the solid-side bubble wall fragmenting the bubble [8]. The impinging liquid forms a micro-jet perpendicular to the solid surface with an estimated velocity of 100 – 1000 m s⁻¹ [13, 63]. The micro-jets and possible shock waves are the cleaning mechanisms in an ultrasonic bath [9].

In applying ultrasound for soil and sediment washing in a slurry, the physical effects mobilize particles in the reactor and modify the physical surface of particles. In particular, acoustic streaming agitates particles causing collision and abrasion. Shock waves with high pressure result in local acceleration of particle movement and collision which contribute to the size reduction. The micro-jets formed near solid surfaces bombard the surface and fracture particles (Figure 2.2b), promoting contaminant detachment from surfaces [64] and reducing grain size [65].
2.3.1.3 Mass transfer and dissolution

Acoustic streaming, microstreaming and shock waves/micro-jets formed from cavitation significantly accelerate mass transfer in the slurry and diffusivity at the liquid-solid interface [11]. Mathematical models describing mass transfer in liquid-solid systems are reaction dependent and empirical equations to predict mass transfer coefficients do not agree well with modeling values [11]. It seems specific models coupling mass transfer and sonochemical reactions in a slurry system are necessary.

Enhanced diffusion at the liquid-solid interface, together with surface pitting from transient cavitation, leads to dissolution of species from the particle surface [11]. The following equation describes the rate of dissolution in the presence of ultrasound waves:

\[
- \frac{dC_A}{dt} = k_{sl}a(C_A^* - C_A)
\]  

(2.2)

where \(C_A\) and \(C_A^*\) are aqueous concentration and saturation concentration of solid species (M), respectively, \(k_{sl}\) is the dissolution rate constant or solid-liquid mass-transfer coefficient, and \(a\) is the interfacial area of solid particles (m²). Since ultrasonication improves mass transfer coefficients at the liquid-solid interface and increases external surface areas of particles through reducing grain size, the dissolution rate in Eq. (2.2) is significantly increased in the presence of ultrasound.

Overall, ultrasonication improves remediation of contaminated solids in two steps: 1) release of heavy metals/organic compounds from particle surface to aqueous solution; and 2) chemical reactions that chelate or oxidize the released metal ions/organic contaminants. Compound release due to desorption and dissolution is usually the rate
limiting step in the remediation process since chelation or oxidation occurs rapidly in aqueous solution [66].

2.3.2 Laboratory-Scale Batch Studies of Slurries

With these unique physical and chemical effects, ultrasound is an interesting option to increase the accessibility of solid-bound contaminants [42], decrease or eliminate the need for chemicals [67, 68] and reduce the high operational cost of the soil/sediment washing process (e.g., mechanical screening and acid extraction). We review applications of ultrasound in batch slurry studies to remove heavy metals (Table 2.1), organic contaminants (Table 2.2), and oils (Table 2.3) from solid phases, which are listed chronologically and for convenient information retrieval.

2.3.2.1 Ultrasonic extraction

Ultrasound assisted extraction (UAE) is a commonly used extraction method for laboratory analysis [69]. Heavy metals (e.g., Cu, Hg, Mn, Ni, Pb, and Zn) can be universally extracted by UAE in acid reagents, with greatly varied recovery rates for soil, sediment, and solid waste samples [69]. Organic solvents (e.g., acetone) are usually used to extract organic compounds such as polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) [19, 70]. For a hydrophilic compound with polarized structure (e.g., endocrine disruptors), more water content in the organic solvent is beneficial to the extraction [69, 70]. Ultrasonic bath and horn type system in the low frequency ranges (< 50 kHz) are common laboratory tools for UAE. UAE achieves faster
extraction rate and reduces volume of solvent as compared to traditional extraction methods [69]. However, one significant problem associated with UAE is the potential sonochemical degradation of target compounds. Appropriate selection of organic solvents and ultrasonic conditions (e.g., short extraction time) can reduce the sonochemical degradation [71].

The application of UAE is extended to leach and collect heavy metals from solids. Newman et al. (1997) reports that 20 kHz ultrasonication greatly improves copper leaching (40%) from copper oxide than conventional shaking (6%) [64]. Satisfactory leaching results by 50 – 60 kHz ultrasonication are observed as compared to acid bomb and conventional digestion methods [21]. The recovery rates of heavy metals reach 90% in the ultrasonic extraction [72]. Mason et al. (2004) introduced a vibrating tray device that originally developed for coal or metal ores processing [33]. The ultrasonic agitation induced by the transducer welded below the tray removes unwanted clay coated on the surface of raw ore and then to accelerate mineral leaching through ultrasonic surface pitting [64]. This ultrasonic device enables a potential engineering-scale metal leaching process.

Ultrasound is considered as a complementary technique to extract viscous oil from contaminated soils and tar sands (Table 2.3). Feng and Aldrich (2000) report that 30 kHz ultrasonication is more effective in diesel extraction than high-speed mechanical agitation, with a 98.5% diesel removal after six stages of treatment [73]. Ye et al. (2008) utilize 10 kHz sonication to pretreat crude oil and obtained 92.6% dewatering and 87.9% desalting [74]. In general, increasing sonication power increased oil extraction until
cavitation depressed the mass transfer process [75]. Xu et al. (2009) observe increased de-oiling from sludge and soil at a higher temperature of 40 °C [76], which is confirmed by a later study performed by Ji and Guo (2010) [77]. Wulandari (2010) reports decreased oil recovery with decreased particle size and pore water flow rate [78], yet Sui and Ji (2010) find that the smaller molecule fraction in the oil more readily elutes in the presence of 28 kHz ultrasound [79]. To further improve ultrasonic oil extraction, sodium silicate and surfactants such as Triton X-100 are used [79, 80].

2.3.2.2 Ultrasonic remediation

Ultrasonic remediation utilizes extraction mechanisms, but also targets reduction or removal of contaminants from soils, sediments, and solid wastes. Optimization of ultrasonication is of importance to the clean-up of contaminated solids.

**Type of solid matrix**

Most studies in Tables 2.1 – 2.2 utilize soil or sediment samples to investigate ultrasonic enhancement for release and degradation of contaminants. In addition to field samples, minerals such as aluminum oxide, sand, or kaolin are used as model soil and sediment samples. For example, He et al. (2005 and 2007) observe accelerated mercury release by ultrasonication for aluminum oxide [15, 81]; Pham et al. (2010) use kaolin to verify ultrasonically enhanced release and destruction of PAH and hexachlorobenzene (HCB) [82]. Lignite coal and cinnabar (HgS) are used as model particles of fly ash to explore sulfur and mercury removal, where the observed release mechanism was through
oxidizing sulfur into sulfur oxidation products (e.g., \( \text{S}_2\text{O}_3^{2-} \), \( \text{SO}_3^{2-} \) and \( \text{SO}_4^{2-} \)) instead of physical detaching [83].

**Particle size**

The grain size of soil or sediment particles is an important factor for ultrasound propagation and cavitation in a reactor. Meegoda and Perera (2001) observe chromium leaching rates as high as 83% from silty sediment; however, the clayey fraction is resistant to ultrasonication at 20 kHz [24]. Similarly, Meegoda and Veerawa (2002) report that ultrasound shows higher removal and separation efficiencies for coarse solids than fine ones [25]. It seems that smaller particles exhibit high acoustic attenuation for ultrasound waves, thereby reducing cavitation effects that are responsible for release and degradation of contaminants. Meanwhile, the intensive treatment from the ultrasonic horn also causes size reduction of contaminated solids as well as change of surface morphology through shock waves and micro-jets [84].

**Frequency and power**

Horn type and standing wave type apparatus are common ultrasound transmitters [7, 85-87]. A horn type device driven at relatively low frequencies is commonly used for solid phase treatment (i.e., soils and sediments) since it delivers a higher power output and better mixing effectiveness as compared with a standing wave device [15, 24, 27, 88, 89]. Therefore, power ultrasound at kHz levels (20 – 60) is usually used for release of heavy metal or organic contaminants from soils and sediments (Tables 2.1 – 2.3). Very few studies have utilized MHz ultrasound for removal of organic contaminants such as 1,1,1-trichloro-2,2-bis(p-chlorophenyl) ethane (DDT) [90]. Likewise, a higher ultrasound
intensity applied to the system corresponds to a higher release from the solid surface and more intensive sonochemical degradation [81]. However, a long ultrasonication time may not be favored for release due to re-precipitation of released compounds (e.g., mercury) onto sediment particles [81].

**Surfactant and chelant**

Use of ultrasonication alone may have limited enhancement in release due to the re-precipitation or re-association of hydrophobic contaminants with solids. The addition of chelating agents or surfactants into ultrasonic systems is shown to improve the release of heavy metals or hydrophobic organic compounds (HOCs) from soils or sediments [66]. For example, presence of chloride and organic matter as chelating reagents kept metal ions (e.g., Hg\(^{2+}\)) in solution [81]. Surfactants have been added to sono-reactors to enhance the mass transfer and aqueous solubility of HOCs [25, 91]. However, Lu and Weavers (2002) studied ultrasonic release and degradation of 4-chlorobiphenyl (4-CB) from synthetic sediments (i.e., silica and alumina particles) and observed that degradation process is not favored in the presence of humic acid [16, 81]. The sonochemically formed 
\(^{'}\text{OH}\) is scavenged by humic acid resulting in reduced oxidation of 4-CB.

**pH of slurry**

Achieving efficient release from solids necessitates appropriate adjustment of pH in slurries. In general, the release process is favored at acidic pH when metal ions remained dissolved in aqueous solution. Since pH determines the form of polarized organic compounds present in the aqueous phase, a pH value that keeps the compound in
in solution is beneficial to the release and degradation. For non-polar HOCs, pH effect is negligible during ultrasonication.

2.3.2.3 Ultrasound assisted digestion

Ultrasonic treatment of waste activated sludge aims to facilitate the dissolution or hydrolysis of organic matter during anaerobic digestion, which is commonly used during activated sludge management in a wastewater treatment plant. Tiehm et al. (2001) observed more effective disintegration at a low frequency, as well as enhanced degradation of volatile solids and biogas production by ultrasound [44]. Later, El-Hadj et al. (2007) observed a more pronounced naphthalene removal in anaerobic digestion of waste activated sludge under mesophilic conditions [92]. Naddeo et al. (2009) reported a positive correlation between ultrasonic intensity and organic solubilization within a short ultrasonication period (< 30 min) [93]. For municipal solid waste, ultrasound also promotes the solubilization of organic solids and subsequent biogas production during anaerobic digestion [94].

2.3.2.4 Synergistic removal of contaminants

Harnessing synergistic effects seems to be an efficient and economic strategy for ultrasonic remediation of soils and sediments [95-98]. Technologies that have been combined with ultrasonic irradiation include: 1) AOPs; 2) electrokinetic processes; 3) thermal desorption; and 4) biodegradation processes.
Recently, Flores et al. (2007) examine different catalysts (i.e., iron sulfate, copper sulfate and iron chloride) in an ultrasound-assisted Fenton-like system. They observe that copper sulfate exhibited the highest catalytic activity for removal of toluene and xylenes from contaminated soils [99]. The improved soil remediation indicates that ultrasound not only facilitates toluene or xylene desorption from solids to the aqueous phase, but also promotes ·OH production that was responsible for the contaminant oxidation. Xu et al. (2010) and Cesaro and Belgiorno (2013) observe a synergistic effect from the combination of ultrasonication and ozonation which improves the organic hydrolysis and anaerobic digestion of activated sludge or municipal solid wastes [45, 100].

Electrokinetics is an effective remediation technology for low permeable soils, during which low-intensity direct currents are applied to extract and transport contaminants from the anode to the cathode [101]. The combination of ultrasonication with electrokinetics has shown increased removal rate for lead and hexachlorobenzene (10 – 80%) [28, 101]. There are two transport phenomena involved, electrophoresis for metal ions (i.e., lead) and electroosmosis for organic compounds (i.e., hexachlorobenzene) [28]. The application of ultrasonic waves increases soil permeability and pore flow. This subsequently improves the migration of ions or organic contaminants in the porous media, sustaining a higher current and mass transfer efficiency. Furthermore, the free radicals produced from cavitation could oxidize organic contaminants, further improving remediation effectiveness.

Thermal desorption is a method to utilize high temperature to vaporize and collect contaminants (e.g., mercury and PAH) from soils and sediments [102, 103]. Lesa et al.
(2009) report a 90 – 99% mercury removal at 570 K in ultrasound-assisted thermal desorption [22]. Microwaves are commonly used as a thermal desorption method utilizing an alternative electric field to provoke frictional vibration between polar molecules and release heating rapidly [104]. Hernoux-Villière et al. (2013) successfully convert 46% starch-based industrial solid wastes into sugar in a microwave-ultrasound system, providing a sufficient and sustainable solution for solid waste management [104].

Bioremediation process utilizes micro-organisms to remove or degrade contaminants in soils, sediments and solid wastes [105]. However, biodegradation is usually challenged by low permeability at the remediation site and limited mass transfer from solids to aqueous solutions where bio-uptake occurs [105]. The high hydrophobicity of HOCs such as PAHs do not favor bioavailability either [106]. He et al. (2011) combined techniques of ultrasound and algal biomass (2AMT-2) and observed enhanced mercury release from the sediments tested and effective bio-sorption of released mercury in the aqueous phase [27]. Anjum et al. (2010) reported enhanced fungal biomass growth under ultrasonication and attributed the increased metal leaching to the higher production of organic acids from Aspergillus niger acting as a chelating reagent [72].

In addition, hot water elution has been combined with ultrasound to improve the heavy oil removal from soils [77]. Ultrasound and freeze/thaw also displayed an oil recovery up to 80% from oily sludge [107]. Meegoda and Veerawa (2002) obtained as high as 99% removal of $p$-terphenyl from harbor sediments in their 20 kHz system combined with a vacuum [25]. Gotoh et al. (2014) in their recent publication showed that coupling ultrasound and mechanical shaking exhibited increased the cleaning efficiency
for soiled textile [108]. Such innovative combinations illustrate notable synergistic effects in the clean-up processes.

2.3.3 Scale-up Consideration for Ultrasonic Treatment of Slurries

The mechanisms unveiled for contaminant desorption and degradation in laboratory experiments have provided fundamental insights for scale-up design and potential full-scale application of the ultrasound technology. Different sono-reactor designs have been developed to improve the sonochemical performance [32]. Even though prominently improved cavitation effects were observed in these designed reactors, the overall energy efficiency and potential for industrial application are still limited due to the unsatisfactory design of current ultrasonic systems. In particular, a typical ultrasonic horn, usually in a two or three stepped shape [88-91, 109], has shrinking cross-sectional areas that concentrate energy at a small tip, resulting in a non-uniform cavitation field and a dense bubble cloud near the horn tip that reduces its effectiveness. Such design has hindered the scale-up of sono-processes. Peshkovsky and Peshkovshy (2007) characterized a barbell-shaped ultrasonic horn to integrate the piezoelectric transducer to water for increased cavitation compared to traditional systems [48]. Recently, Wei et al. (2015) designed a horn with a multiple-step configuration and a cone-shaped tip increasing the energy-emitting surfaces, reactive areas, and cavitation volumes [47]. However, more innovative designs are needed for energy-efficient and low-cost treatments using ultrasound.
To achieve a large-scale ultrasonic treatment, integrated systems that array multiple horns have been developed. Russel (2000) describes a sonic (104 Hz) apparatus (solid steel cylinder, 35 cm × 4.25 m, 3000 kg in weight) for a large-scale application in the conditioning and pacification of ash from combustion [110]. This apparatus may be utilized for mineral extraction and solid washing. Mason et al. (2004) introduce a processing tube with a series of mounted horns on the wall for sludge disintegration [33]. Mason (2007) describes a large-scale vibrating bar acoustic processor in audible frequency, which delivers sufficient vibrational energy in resonant bending modes and thus effective PCB removal (910 ppm to < 0.2 ppm) from contaminated soils [42]. In addition, Abramov et al. (2009) design a pilot-scale ultrasonic flow-type tubular reactor which shows a speed-up of oil extraction [111]. Furthermore, the full-scale application of ultrasonication for pretreatment of activated sludge for anaerobic digestion is also developed based on some pilot-scale studies [112, 113]. The ultrasonication process improves 40 – 50% in biogas production [114]. Mason (2007) also gives an industrial scale example for ultrasonic processing of sewage sludge using a multiple-probe system [42]. Despite the successful implementation of scaled-up systems, many challenges remain before ultrasound will see wide-spread full-scale application.
2.4 Treatment in Porous Media

There are fewer studies of porous media (Table 2.4) as compared to batch slurry experiments (Tables 2.1 – 2.3). Fundamentals of ultrasound in the porous media are different from those in slurries. The propagation and attenuation of ultrasound waves in porous media are critical factors in determining the reactive region of treatment. At the same time, presence of ultrasonic waves has a great impact on characteristics of porous media (e.g., permeability and pore flow). The fundamental section is devoted to explain wave characteristics and media alteration due to ultrasound. Relevant column studies (Table 2.4) and field tests (Table 2.5) are briefly introduced before discussing design criteria for a large-scale application of ultrasound in soil or sediment remediation.

2.4.1 Ultrasound Fundamentals in Porous Media

2.4.1.1 Ultrasound propagation in porous media

Propagation principles

A sound wave is a mechanical wave in a medium (e.g., fluid or solid) associated with reception and transmission of energy [36]. The molecules of media absorb sound energy and vibrate, then transmit the vibration to adjacent molecules. It is this repeating movement that enables the propagation of sound waves and energy. In homogeneous media, the spatial and temporal change of the sound wave is governed by the wave equation as follows [36, 115]:

\[ \nabla^2 P - \frac{1}{c^2} \frac{\partial^2 P}{\partial t^2} = 0 \]  

(2.3)
where $P$ is the acoustic pressure (Pa) and $c$ is the speed of sound in the homogeneous media ($m \, s^{-1}$). The energy ($E$) transported through the homogeneous media is composed of kinetic energy ($E_k$) and potential energy ($E_p$) [36]:

$$E_k = \frac{1}{2} \rho V_0 u^2 \quad (2.4)$$

$$E_p = -\int_{V_0}^{V} P \, dV \quad (2.5)$$

where $\rho$ is the density of the media ($kg \, m^{-3}$) that sound waves travel through, $V_0$ is the initial micro-volume of vibrating molecules, $V$ is the final micro-volume ($dV = -\frac{V_0}{\rho} \, d\rho = -\frac{V_0}{\rho} \, \frac{dP}{c^2}$), so $E_p = \int_{V_0}^{V} \frac{V_0 P}{\rho} \, dP = \frac{1}{2} \rho c^2 V_0$, and $u$ is the velocity of the micro-volume ($m \, s^{-1}$). If substituting $u = \frac{P}{\rho c}$ into Eq. (2.5), $E_p = E_k = \frac{1}{2} \rho V_0 u^2$. Thus, the energy density ($\epsilon$) is calculated as:

$$\epsilon = \frac{E}{V_0} = \frac{E_k + E_p}{V_0} = \rho u^2 \quad (2.6)$$

Sound intensity ($I$, $W \, m^{-2}$), which is the power ($W \, J \, s^{-1}$) of a sound wave per unit area, is derived as follows:

$$I = \frac{W}{A} = \frac{Ec}{V_0} = \epsilon c = \rho u^2 c = \frac{P^2}{\rho c} \quad (2.7)$$

For a planar source, the one direction propagation exhibits one half of the intensity ($\frac{P^2}{2\rho c}$). According to Eq. (2.7), the sound intensity is related to the applied sound
pressure and media density ($\rho$). Usually, the impedance ($Z = \frac{p}{u} = \rho c$, Pa s m$^{-1}$) of sound is used to describe the characteristic of the medium (e.g., acoustic attenuation capacity). The acoustic impedance is an intrinsic nature of the medium and is not affected by the sound waves.

**Attenuation mechanisms**

In the derivation of the wave equation, it is assumed that energy loss is negligible. In fact, the sound energy is dissipated by many mechanisms resulting in the attenuation (i.e., reduction in magnitude) of sound. For example, as shown in Figure 2.1c, sound intensity slowly decreases as sound waves propagate through an elastic medium with mechanical resistance (i.e., ability to resist motion) [52]:

$$I = I_0 \exp(-\alpha d)$$  \hspace{1cm} (2.8)

where $I_0$ is the acoustic intensity at the sound source (W m$^{-2}$), $\alpha$ is the attenuation coefficient, and $d$ is the distance from the source (m). This attenuation is related to the intrinsic nature of the medium. In particular, the sound energy is dissipated by viscous effect, heat conduction, and molecular processes (i.e., kinetic and potential energy). Attenuation also arises when sound waves approach another medium or encounter an obstacle, where reflection, scattering, transmission, refraction, and diffraction of sound waves occur [36, 116, 117]. At the boundary, these divergent sound waves are ultimately converted to random thermal energy.

The same attenuation rules also apply to porous media. A porous medium consists of a rigid solid and an interconnected void [118]. The void can be filled by one phase
(e.g., a single fluid) or two phases (e.g., a liquid and a gas). In porous media, the most characterized parameter, porosity, is defined as the ratio of void volume to total volume of a medium. Acoustic attenuation in fluid saturated porous media occurs in the following ways:

1) Absorption of sound energy at the solid-liquid, solid-gas, and liquid-gas interfaces [119, 120]. At a surface boundary, the absorbed sound energy is first converted to dynamic energy for element vibration (i.e., matrix of solid particle and pore water) and ultimately to heat [36, 116].

2) Reflecting and scattering of sound waves at the interface [115, 119, 120]. The excited oscillation of elements after absorbing sound energy emits a secondary wave in a direction different from the incident wave. This emitted secondary wave is called a scattered wave [115]. The scattering waves, together with reflecting waves, are subsequently absorbed at interfaces they encounter and eventually converted to heat. Fine particles with large surface areas could lead to more reflecting or scattering of sound waves and thus higher sound attenuation.

3) Energy dissipation by fluid viscosity and friction between particles [119, 120]. Ultrasound propagation is the transmission of vibration between elements. However, friction between particles and fluid viscosity both dissipate the dynamic energy of elements and convert it to heat eventually.

4) Acoustic cavitation. A cavitation bubble is initiated from the absorption of sound energy. During bubble collapse, the absorbed energy is utilized for endothermic reaction (e.g., free radical formation) and transformed to cavitation heating [12].
Cavitation if present consumes most of the acoustic energy.

**Biot-Stoll theory**

A commonly used theory model for compress wave propagation in the porous media was developed by Biot in the 1950s [121-123]. Later, Stoll further developed Biot’s theory by considering frictional loss at grain-grain contacts [124, 125]. In the Biot-Stoll theory, it is assumed that the dilatational waves propagate ($< 10^6$ Hz) in an isotropic homogeneous medium and sound waves traveling in the porous media are still considered as elastic waves consisting of fast waves and slow waves. The dilation of elements in fluid saturated porous media is synchronized with sound signal (i.e., driven at the frequency of sound source), which is called in phase motion featuring the fast waves. When the porous matrix moves out of phase (i.e., same frequency but different velocities), the slow waves arise. According to the Biot-Stoll theory, there are coupled propagation equations, one for the liquid and the other for the solid:

$$\nabla^2 (He - C_\xi) = \frac{\partial^2}{\partial t^2} (pe - \rho_c \xi)$$  \hspace{1cm} (2.9)

$$\nabla^2 (Ce - M_\xi) = \frac{\partial^2}{\partial t^2} (\rho_c e - \rho_s \xi) - \frac{\eta}{k} \frac{\partial \xi}{\partial t}$$  \hspace{1cm} (2.10)

where $e$ and $\xi$ are the dilation of bulk material and the relative dilation of fluid, respectively; $C$, $H$, and $M$ are elastic coefficients related to the porosity $\beta$, the bulk modulus $K_s$ of bulk material, and the shear $\mu_b$ and bulk moduli $K_b$ of the porous frame; $\eta$ is the fluid viscosity (Pa s); $k$ is the permeability of porous media ($m^2$); $\rho_f$ and $\rho_s$ are densities ($kg m^{-3}$) for the fluid and the solid, respectively, and the aggregate density...
\[ \rho = (1 - \beta)\rho_s + \beta \rho_f \; ; \; \rho_c = \frac{a \rho_f}{\beta} \rho_c \] and \[ a = 1 + \frac{1 - \beta}{2\beta} \]. The attenuation expression for low-frequency harmonic waves is:

\[ \alpha \propto \frac{1 - \beta}{d \beta} (\omega \eta)^{\frac{1}{2}} \]  \hspace{1cm} (2.11)

where \( d \) is spherical diameter of grains (m) and \( \omega \) is angular frequency of waves (rad s\(^{-1}\)) [126]. According to Eq. (2.11), the attenuation depends on the features of sound (e.g., frequency) and porous media (e.g., fluid viscosity and porosity), which is consistent with the discussed attenuation mechanisms.

2.4.1.2 Ultrasonic effects on porous media

**Enhanced pore flow**

When fluid flow through porous media is in steady-state, the flow rate is proportional to the pressure gradient, which is Darcy’s Law [127]:

\[ Q = \frac{-kA}{\eta} \times \frac{\Delta h}{L} \]  \hspace{1cm} (2.12)

where \( Q \) is the flow rate (m\(^3\) s\(^{-1}\)), \( \Delta h \) is the head difference (Pa), and \( L \) is the longitudinal distance (m). The presence of sound waves has shown to enhance pore water movement in the porous media [17, 18]. Sound waves deform pore spaces [18, 128] and release dissolved air [129, 130], resulting in a change of permeability or porosity (Figure 2.3). In addition, cavitational heating increases temperature of pore fluid which can reduce surface tension and fluid viscosity, further contributing to enhanced pore flow and hydraulic conductivity [131]. Several studies assumed Darcy flow in porous media in the
presence of sound waves [18, 132]. However, hydrodynamics with respect to porous media in an acoustic field is not well studied. Future experimental works are necessary to fill the knowledge gap.

**Enhanced mass transfer**

In porous media, dispersion of a compound is a combination of mechanical dispersion due to fluid flow and molecular diffusion due to concentration gradient [133]. If the compound is non-reactive and non-sorbing, convection-diffusion equation (CDE) describes its transport in porous media [17, 134]:

\[
\frac{\partial C_m}{\partial t} = -v \frac{\partial C_m}{\partial x} + D \frac{\partial^2 C_m}{\partial x^2}
\]  
(2.13)

where \(C_m\) is the aqueous concentration of the compound (M), \(x\) is the distance (m), \(v\) is the seepage flow velocity (m s\(^{-1}\)), and \(D\) is the hydrodynamic dispersion coefficient (m\(^2\) s\(^{-1}\)). Presence of ultrasound leads to the increased \(v^*\) and \(D^*\) as follows [17]:

\[
v^* = v + v_{us}
\]  
(2.14a)

\[
D^* = D + D_{us}
\]  
(2.14b)

where \(v_{us}\) and \(D_{us}\) are enhancements of seepage velocity and dispersion coefficient due to ultrasound, respectively. Vogler and Chrysikopoulos (2002) observe enhanced bromide tracer breakthroughs which are inversely related to the applied frequencies from 50 to 250 Hz [17]. However, studies investigating the possible enhancement of mass transfer in the presence of ultrasound waves are lacking. Therefore, experimental work focuses on quantification of ultrasonic enhancement for compound transport in porous media is encouraged.
**Ultrasonic vibration compaction**

Ultrasound with alternating pressures mobilizes particles in the media, during which small particles tend to percolate into the void between large particles and push those large particles outwards [135, 136]. Ultrasonic vibration rearranges particles in a column and compacts the porous media resulting to a reduced porosity. The ultrasound assisted compaction has also been applied to increase the density of compacted powder [137]. The following equation describes the volume change of porous media with respect to applied pressure (i.e., acoustic pressure for ultrasonic compaction) [137]:

\[
\log P = -M_1 \frac{V_m}{V_{m,0}} + M_2
\]

(2.15)

where \(M_1\) and \(M_2\) are parametric constants, \(V_{m,0}\) and \(V_m\) are the volumes of porous media before and after ultrasonication. According to Eq. (2.15), a higher ultrasonic amplitude or pressure corresponds to a higher density or low porosity. However, low frequency stress waves are observed to increase porosity and permeability within the oil reservoir [129, 138]. Therefore, power ultrasound with a high energy output can deliver a better compaction of porous media as compared to sound waves at low frequency.

**2.4.2 Laboratory-Scale Column Studies in Porous Media**

In the 1950s, stimulation of oil recovery by lower frequency stress waves is studied in the laboratories soon after engineers observed increased oil production after earthquakes (10 – 100Hz seismic waves) [131]. Environmental application of ultrasound follows in the 1990s. Beresnev and Johnson (1994) [131] review the laboratory studies
exploring the effects of sonic/ultrasonic waves on improving oil production in porous media. Table 2.4 lists relevant column studies in sonic/ultrasonic treatment of sand, soil and sandstone after 1991. Most studies listed in the table investigate enhanced oil recovery (EOR) using sound waves with frequencies from as low as 1 Hz to well above megahertz (MHz). The following mechanisms have been proposed for EOR in porous media:

1) Deformation of pores and removal of fines and clays during sonication increase the relative permeability and porosity within the oil reservoir [129, 138].

2) Non-linear acoustic effects such as acoustic streaming and cavitation initiate the oscillation of capillary trapped oil drops [139-141], coalescence of oil drops through the Bjerknes forces [142], and peristaltic transport of the oil to adjacent pores [143, 144].

3) Ultrasound reduces the adherence of wetting films onto solid surface [145].

4) Mechanical vibrations liberate trapped gas in the porous media, thereby avoiding the clog of pore channels by gas bubbles [130].

5) The ultrasonic heating reduces surface tension and viscosity for enhanced pore flow [146-148].

These mechanisms agree well with the Biot-Stoll theory. It is observed that a high frequency limits remediation volume while low frequency is not applicable to compact remediation [149, 150]; sand media with high permeability yields a higher recovery rate as compared to sandstones with low permeability [151-154]. In a site with a large amount of dissolved gases, pulsing the sonication (e.g., 15 – 60s every 15min over 7h) stimulated
the gas evolution and avoided massive cavitation, thereby increasing the oil mobility in the porous media [129]. Majority of the listed studies in Table 2.4 attribute the enhanced mobility of non-aqueous phase liquids (NAPLs) to the increased porosity or permeability of porous media. Iovenitti et al. (1996) [155] report a 100% increase in dissolution of p-xylene by sound waves, further contributing to the enhanced mobility of contaminants.

2.4.3 Field Application of Ultrasound in Porous Media

Current research on ultrasonic remediation remains at the laboratory-scale, and there are very few field studies available in the scientific literature. Table 2.5 lists the full-scale tests in sonic/ultrasonic stimulation of remediation (1 case) and oil production (7 cases). Even though the study of ultrasonic stimulation on oil production dates back to 1950s, the first field test was 20 years later [131]. Again, frequency plays an important role in wave dispersion and heat dissipation. The lower frequency waves with a much larger effective range (approaching hundreds of meters) are useful in stimulating oil recovery in a reservoir, whereas the higher frequency waves have a local effect (on the order of a few meters) and are sufficient for well cleaning. The field studies suggest a range of 5 – 50 kHz as optimal frequencies to clean wellbore [131]. It is noted that the optimal frequency is site-specific and is related to the resonance frequency of natural soils [156]. In most recent studies, Abramov et al. (2013) [157] and Abramova et al. (2014) [158] describe an implementation of ultrasonic equipment in a tested field at Western Siberia and observe a 40 – 100% increase in oil recovery. The increased fluid
production, together with oil production, once again confirms the stimulation role of sound/ultrasound waves for pore fluid and mass transfer [131, 156].

2.4.4 Design Criteria for Large-Scale Application

The success in scale-up developments suggests a potential large-scale application of sound/ultrasound waves in soil and sediment remediation. Since initiation of a degradation reaction is desired at contamination sites, high frequency ultrasonic waves are preferred because ultrasound-induced cavitation produces heating and reactive radicals that can improve contaminant transport and oxidation. Figure 2.4 describes a conceptual application of sound waves for enhanced soil remediation. It is a combination of pump-and-treat and sonication/ultrasonication processes, through which the transport and degradation of contaminated plume in aquifer is enhanced. Specifically, sonic waves that can propagate to a long distance are applied at the upstream to facilitate the transport of contaminated plume; the plume then passes through a region where ultrasonication is applied, enabling sonochemical degradation of contaminants; the treated plume is finally pumped out through an extraction well. To improve remediation, chemical oxidants such as hydrogen peroxide and persulfate can be added at the ultrasonication region. Employing ultrasound in sediment remediation will be different from soil remediation due to the underwater environment and loose packed characteristics. A potential field application of ultrasound for sediment remediation is to “scan” the contaminated sediment floor with a moving sonicator. Before seeing field applications, however,
mechanistic insights of the physical and chemical effects of ultrasound waves on soil/sediment and careful engineering designs are needed.

2.6 Future Work

It is clear that the future management of wastes should undergo green and sustainable paths which usually require interdisciplinary efforts. Ultrasonic technology combines the fundamentals of physics, chemistry, and engineering in the practice of environmental remediation. Such cross-disciplinary technology provides extensive room to support environmental remediation and sustainable development. A good grasp of the theory and mechanism involved is essential to develop the ultrasound technology to fulfill the potentials. Hence, the following areas are needed to allow technology to be developed further: 1) novel ultrasonic system designs (e.g., sufficient electromechanical conversion in transducer and horn configurations) to improve energy efficiency and treatment effectiveness; 2) characterization of ultrasound waves (e.g., cavitation detection and hydrodynamics) in porous media for mechanistic insights into contaminant fate and transport; and 3) combination with other technologies (e.g., nanotechnology and biotechnology) to pursue synergistic treatments.

The ability of ultrasonic technology to address the engineering challenges with great effectiveness, coupled with the rising demand for a clean environment, yields exciting opportunities for high impact research and applications. It is hoped that this systematic review is beneficial to fundamentally understand ultrasonic treatments and
sufficiently deliver recent technology development and scientific insights to scientists and engineers. With no doubt, such a broad and exciting field is also inspiring the researchers to exploit the ultrasound technology in but not limited to the environmental remediation.

2.7 Acknowledgments

This work was supported by the Ohio Sea Grant College Program.
### Table 2.1 Ultrasonic treatment of heavy metal in soils, sediments and solid wastes

<table>
<thead>
<tr>
<th>#</th>
<th>Reference</th>
<th>Freq., kHz</th>
<th>Power/Intensity</th>
<th>Duration, min</th>
<th>Solids</th>
<th>Target Contaminants</th>
<th>Observed results</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Newman et al. (1997) [64]</td>
<td>20</td>
<td>–</td>
<td>30</td>
<td>Granular pieces of brick</td>
<td>Copper oxide</td>
<td>40% reduction of copper content as compared to 6% by conventional shaking.</td>
</tr>
<tr>
<td>2</td>
<td>Meegoda and Perera (2001) [24]</td>
<td>20</td>
<td>1500W</td>
<td>5, 10, 15</td>
<td>Sediments from NY/NJ harbor</td>
<td>Chromium</td>
<td>As high as 83% removal from the silt fraction while insensitive to clay fraction.</td>
</tr>
<tr>
<td>3</td>
<td>Collasiol et al. (2004) [20]</td>
<td>–</td>
<td>10-120W</td>
<td>1.5-2</td>
<td>Certified marine sediment sample, Buffalo River sediment, Montana soil, and non-certified river sediment sample</td>
<td>Mercury</td>
<td>Adequate mercury extraction by ultrasonication to the conventional digestion method.</td>
</tr>
<tr>
<td>4</td>
<td>Kyllönen et al. (2004) [159]</td>
<td>22</td>
<td>100-500W</td>
<td>0.5-60</td>
<td>Soil from former military shooting range</td>
<td>Lead, copper</td>
<td>Improved heavy metal release in all fraction range of soil particles.</td>
</tr>
<tr>
<td>5</td>
<td>He et al. (2005) [15]</td>
<td>20</td>
<td>36W cm(^{-2})</td>
<td>60</td>
<td>Aluminum oxide</td>
<td>Mercury</td>
<td>Mercury release increases then decreases with time; low pH is favored for release.</td>
</tr>
<tr>
<td>C6</td>
<td>Chung et al. (2006) [101]</td>
<td>30</td>
<td>200W</td>
<td>175</td>
<td>Jumunjin sand</td>
<td>Lead, ethylene glycol</td>
<td>Combined treatment showed best removal even through electrokinetics is better for lead and ultrasonication for ethylene glycol; ultrasonication also enhanced 60 – 67% of pore flow.</td>
</tr>
<tr>
<td>7</td>
<td>Elik (2007) [160]</td>
<td>50–60</td>
<td>175W</td>
<td>35</td>
<td>Sediments from Kizil river (2m depth) and Hafik pond (3m depth)</td>
<td>Copper, lead, Manganese, Nickel, and Zinc</td>
<td>Accelerated leaching by ultrasound and at low pH</td>
</tr>
<tr>
<td></td>
<td>Author(s) and Year</td>
<td>Power (W)</td>
<td>Ultrasonic Time (min)</td>
<td>Sample Description</td>
<td>Extracted Metals</td>
<td>Leaching Effectiveness</td>
<td></td>
</tr>
<tr>
<td>---</td>
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<td>--------------------</td>
<td>------------------</td>
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<td></td>
</tr>
<tr>
<td>8</td>
<td>Güngör and Elik (2007) [21]</td>
<td>50-60</td>
<td>–</td>
<td>10-65</td>
<td>Sediments from Kizil river</td>
<td>Lead, Copper, Manganese, Nickel, and Zinc</td>
<td>Leaching effectiveness similar to acid bomb and conventional digestion methods but with reduced treatment time.</td>
</tr>
<tr>
<td>9</td>
<td>He et al. (2007a) [81]</td>
<td>20</td>
<td>36W cm²</td>
<td>60</td>
<td>Aluminum oxide, cinnabar</td>
<td>Mercury</td>
<td>Mercury release increases then decreases with time; chloride and organic matter enhance release; low pH is favored for release.</td>
</tr>
<tr>
<td>10</td>
<td>He et al. (2007b) [83]</td>
<td>20</td>
<td>36W cm²</td>
<td>180-300</td>
<td>Cinnabar</td>
<td>Mercury</td>
<td>Dissolution of cinnabar, sulfur oxidation, and release of dissolved mercury by ultrasonication.</td>
</tr>
<tr>
<td>C10</td>
<td>Lesa et al. (2009) [22]</td>
<td>20</td>
<td>250W</td>
<td>10</td>
<td>Lagoon sediment with silt (63.5%) and clay (22.5%)</td>
<td>Mercury</td>
<td>Mercury desorption increases with time and temperature.</td>
</tr>
<tr>
<td>11</td>
<td>Deng et al. (2009) [161]</td>
<td>20</td>
<td>300-2000W</td>
<td>0-20</td>
<td>Sewage sludge</td>
<td>Lead, Copper, and Zinc</td>
<td>Increase in heavy metal extraction with ultrasonication time and nitric acid concentration.</td>
</tr>
<tr>
<td>12</td>
<td>Anjum et al. (2010) [72]</td>
<td>40</td>
<td>–</td>
<td>7</td>
<td>Grounded black shale ore</td>
<td>Aluminum, Cobalt, Copper, Iron, and Zinc</td>
<td>Maximum leaching of Al (92%), Fe (83%), Cu (92%), Zn (87%) and Co (71%) within 24 days under culture filtrate and ultrasonication.</td>
</tr>
<tr>
<td>13</td>
<td>Cheikh et al. (2010) [162]</td>
<td>20</td>
<td>150W</td>
<td>15, 30, 45, 60</td>
<td>Black sludge from an industrial blast furnace (iron-smelting plant)</td>
<td>Lead and Zinc</td>
<td>Ineffective leaching with or without EDTA at all tested pH probably due to the reduction in grain size.</td>
</tr>
<tr>
<td>C14</td>
<td>He et al. (2011) [27]</td>
<td>20</td>
<td>20W cm²</td>
<td>60</td>
<td>Aluminum oxide, cinnabar and certified marine sediment sample</td>
<td>Mercury</td>
<td>Ultrasound enhances mercury release from sediment and transgenic C. reinhardtii effectively recover Hg(II) released.</td>
</tr>
</tbody>
</table>
Table 2.1 Continued

| 15 | Rivero-Huguet and Marshall (2011) [66] | 20 | – | 20 | Soil | Arsenic, chromium, copper, pentachlorophenol (PCP), polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs). Combination of chelant/surfactant and ultrasound released 70% of arsenic, 75% of chromium, 80% of copper, 90% of PCP, and 79% of PCDDs and PCDFs. |

Note: C — combined methods.
Table 2. 2 Ultrasonic treatment of organic contaminants in soils, sediments, and solid wastes

<table>
<thead>
<tr>
<th>#</th>
<th>Reference</th>
<th>Freq., kHz</th>
<th>Power/ Intensity</th>
<th>Duration, min</th>
<th>Solids</th>
<th>Target Contaminants</th>
<th>Observed results</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Sun et al. (1998) [70]</td>
<td>40</td>
<td>200W</td>
<td>30</td>
<td>Soil at an industrial area</td>
<td>PAHs</td>
<td>Higher in extraction efficiency and more economic and easily operated as compared to Soxhlet extraction.</td>
</tr>
<tr>
<td>2</td>
<td>Tiehm et al. (2001) [44]</td>
<td>41, 207, 360, 616, 1068, 3217</td>
<td>0.1-1.4W cm²</td>
<td>7.5-150</td>
<td>Waste activated sludge</td>
<td>–</td>
<td>Most effective at low frequency for sludge disintegration, enhanced degradation of volatile solids, and increased biogas production.</td>
</tr>
<tr>
<td>3</td>
<td>Lu et al. (2002) [84]</td>
<td>20 (horn), 16, 20 (plate)</td>
<td>460W L⁻¹, 53.3 W L⁻¹</td>
<td>60</td>
<td>Silica particles (diameters 2, 60 and 130 μm); Two alumina particles (diameter 130 μm) with surface areas of 200 and 155 m²/g</td>
<td>–</td>
<td>Ultrasonication decreases grains size; humic acid adds complexity to the system.</td>
</tr>
<tr>
<td>4</td>
<td>Lu and Weavers (2002) [16]</td>
<td>20</td>
<td>460 W L⁻¹</td>
<td>20-50</td>
<td>Silica particles (diameters 2, 60 and 130 μm); two alumina particles (diameter 130 μm) with surface areas of 200 and 155 m²/g</td>
<td>4-Chlorobiphenyl</td>
<td>Increase in 4-CB desorption with ultrasonication time; small mass concentration and less humic acid enhance 4-CB desorption.</td>
</tr>
<tr>
<td>5</td>
<td>Mecozzi et al. (2002) [23]</td>
<td>35</td>
<td>30, 60</td>
<td></td>
<td>Sediment from Italian coast</td>
<td>Humic substance</td>
<td>Accelerated extraction of humic substance by ultrasound.</td>
</tr>
</tbody>
</table>

Continued
### Table 2.2 Continued

<table>
<thead>
<tr>
<th></th>
<th>Researcher and Year</th>
<th>Power (W)</th>
<th>Time (s)</th>
<th>Sample Type</th>
<th>Contaminant</th>
<th>Methodology</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>Meegoda and Veerawa (2002) [25]</td>
<td>20</td>
<td>1500</td>
<td>3-60</td>
<td>Sediments from NY/NJ harbor</td>
<td>p-Terphenyl</td>
</tr>
<tr>
<td>8</td>
<td>Banjoo and Nelson (2005) [19]</td>
<td>50-60</td>
<td>–</td>
<td>30, 60</td>
<td>Sediment from Gulf of Paria</td>
<td>PAH</td>
</tr>
<tr>
<td>9</td>
<td>Collings et al. (2006) [88]</td>
<td>–</td>
<td>1000–1500W, 4000W</td>
<td>5-60</td>
<td>Fine glass beads, sand spiked with contaminants, contaminated soil and riverine sediment</td>
<td>PCBs, polycyclic aromatic hydrocarbons and organochlorides</td>
</tr>
<tr>
<td>10</td>
<td>Choshi et al. (2007) [91]</td>
<td>200</td>
<td>100</td>
<td>60</td>
<td>80 mass-% of silica and 20 mass-% of cellulose powders as a model sediment (d=28μm)</td>
<td>Hexachlorobenzene (HCB)</td>
</tr>
<tr>
<td>11</td>
<td>El-Hadj et al. (2007) [92]</td>
<td>20</td>
<td>70</td>
<td>–</td>
<td>Waste activated sludge</td>
<td>Naphthalene and pyrene</td>
</tr>
<tr>
<td></td>
<td>Author(s) and Year</td>
<td>Frequency</td>
<td>Power (W)</td>
<td>Treatment Time</td>
<td>Media</td>
<td>Contaminants</td>
</tr>
<tr>
<td>---</td>
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</tr>
<tr>
<td>13</td>
<td>Thangavadivel et al. (2009) [90]</td>
<td>1.6 MHz</td>
<td>150 W L⁻¹</td>
<td>90</td>
<td>River sand</td>
<td>1,1,1-trichloro-2,2-bis(p-chlorophenyl) ethane (DDT)</td>
</tr>
<tr>
<td>C14</td>
<td>Pham et al. (2009) [28]</td>
<td>24, 30</td>
<td>100, 200 W</td>
<td>10, 15 d</td>
<td>Kaolin</td>
<td>Hexachlorobenzene (HCB), phenanthrene (PHE) and fluoranthene (FLU)</td>
</tr>
<tr>
<td>15</td>
<td>Naddeo et al. (2009) [93]</td>
<td>20</td>
<td>0.05-0.2 W mL⁻¹</td>
<td>15, 30, 45</td>
<td>Waste activated sludge</td>
<td>–</td>
</tr>
<tr>
<td>16</td>
<td>Shrestha et al. (2009) [164]</td>
<td>30</td>
<td>100 W</td>
<td>6 h</td>
<td>Natural farm soil, kaolin, synthetic clay</td>
<td>Hexachlorobenzene (HCB) and phenanthrene (PHE)</td>
</tr>
<tr>
<td>17</td>
<td>Collings and Gwan (2010) [89]</td>
<td>20</td>
<td>150 W</td>
<td>10, 30</td>
<td>Sand from coast</td>
<td>DDT, chlordane, atrazine, 2,4,5-T and endosulfan</td>
</tr>
<tr>
<td>18</td>
<td>Pham et al. (2010) [82]</td>
<td>24, 30</td>
<td>100, 200 W</td>
<td>1, 6 h</td>
<td>Kaolin</td>
<td>phenanthrene, fluoranthene and hexachlorobenzene</td>
</tr>
<tr>
<td></td>
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</tr>
<tr>
<td></td>
<td>Ambedkar et al. (2011) [165]</td>
<td>20, 25, 58, 192, 430</td>
<td>500W</td>
<td>15, 60</td>
<td>Lignite coal</td>
<td>sulfur</td>
</tr>
<tr>
<td>21</td>
<td>Cesaro et al. (2012) [43]</td>
<td>20</td>
<td>0.1, 0.2, 0.4W mL⁻¹</td>
<td>30, 60</td>
<td>Municipal solid waste</td>
<td>–</td>
</tr>
<tr>
<td>22</td>
<td>Song et al. (2012) [166]</td>
<td>20</td>
<td>–</td>
<td>30</td>
<td>Soil</td>
<td>Phenanthrene</td>
</tr>
<tr>
<td>C24</td>
<td>Hernoux-Villière (2013) [104]</td>
<td>20.1</td>
<td>17W (Acoustic power)</td>
<td>120</td>
<td>Potato starch, wet potato sludge, and dry potato sludge</td>
<td>–</td>
</tr>
<tr>
<td>26</td>
<td>Pee et al. (2014) [26]</td>
<td>20</td>
<td>430W L⁻¹</td>
<td>6-80</td>
<td>Contaminated sediments</td>
<td>Naphthalene, phenanthrene, pyrene</td>
</tr>
</tbody>
</table>

Note: C — combined methods.
Table 2.3 Ultrasonic treatment of oil in soils, sands, and solid wastes

<table>
<thead>
<tr>
<th>#</th>
<th>Reference</th>
<th>Freq., kHz</th>
<th>Power/Intensity</th>
<th>Duration, min</th>
<th>Solids</th>
<th>Target Contaminants</th>
<th>Observed results</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>Sadeghi et al. (1990) [80]</td>
<td>40</td>
<td>12 W cm⁻²</td>
<td>4min - 6h</td>
<td>Tar sand</td>
<td>Oil</td>
<td>Surfactant clean-up accelerated by the introduction of ultrasonic free radicals.</td>
</tr>
<tr>
<td>2</td>
<td>Feng and Aldrich (2000) [73]</td>
<td>30</td>
<td>20-100 W cm⁻²</td>
<td>5</td>
<td>Chemical grade sea sand</td>
<td>Diesel</td>
<td>98.5% diesel removal after a six-stage treatment, more effective than high-speed mechanical agitation in the soil washing.</td>
</tr>
<tr>
<td>3</td>
<td>Kim and Wang (2003) [75]</td>
<td>20</td>
<td>0-140 W</td>
<td>–</td>
<td>Ottawa sand, a fine aggregate, and a natural soil</td>
<td>Oil</td>
<td>Increased pollutant extraction with increasing sonication power but deceasing flushing rate.</td>
</tr>
<tr>
<td>4</td>
<td>Ye et al (2008) [74]</td>
<td>10</td>
<td>0.38W cm⁻²</td>
<td>5</td>
<td>Crude oil</td>
<td>Oil</td>
<td>92.6% dewatering and 87.9% desalting of crude oil.</td>
</tr>
<tr>
<td>5</td>
<td>Abramov et al. (2009) [111]</td>
<td>22</td>
<td>100, 1000W</td>
<td>60</td>
<td>Tar sand from Canada and the model mixtures prepared from different fractions of river sand and high-paraffinaceous oil or residual fuel oil</td>
<td>Oil</td>
<td>Speeded up oil extraction from both laboratory and pilot scale results.</td>
</tr>
<tr>
<td>6</td>
<td>Xu et al. (2009) [76]</td>
<td>28, 40</td>
<td>–</td>
<td>20</td>
<td>Oily sludge</td>
<td>Oil</td>
<td>Up to 55.6% deoiling with ultrasound at 40 °C.</td>
</tr>
<tr>
<td>7</td>
<td>Ji and Guo (2010) [77]</td>
<td>28</td>
<td>0 to 100W L⁻¹</td>
<td>18</td>
<td>Soil</td>
<td>Oil</td>
<td>Significant negative correlation between elution and increasing ultrasonic power density and close relation from elution and the number of C atoms in the marker.</td>
</tr>
<tr>
<td>C8</td>
<td>Sui and Ji (2010) [79]</td>
<td>28</td>
<td>0.1.274 W cm⁻²</td>
<td>18</td>
<td>Soil</td>
<td>Oil</td>
<td>More readily elution for smaller molecules and improved elution of large molecules at higher power intensities.</td>
</tr>
<tr>
<td>C</td>
<td>Authors</td>
<td>Power</td>
<td>Frequency</td>
<td>Ultrasound type</td>
<td>Sample Type</td>
<td>Oil Type</td>
<td>Notes</td>
</tr>
<tr>
<td>-----</td>
<td>--------------------------</td>
<td>---------</td>
<td>-----------</td>
<td>-----------------</td>
<td>-------------</td>
<td>----------</td>
<td>----------------------------------------------------------------------</td>
</tr>
<tr>
<td>C9</td>
<td>Wulandari (2010) [78]</td>
<td>20</td>
<td>462, 528, 616W</td>
<td>Soil</td>
<td>Diesel</td>
<td>Increased oil recovery in the presence of ultrasound; decreased oil recovery with decreased particle size, soil density, and water flow rate.</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>Ji et al. (2011) [167]</td>
<td>28</td>
<td>0 to 100W L⁻¹</td>
<td>Soil</td>
<td>Super heavy oil</td>
<td>13 – 14% increase in the elution of super heavy oil by ultrasound and 62% improvement of first-stage dissolution and dispersion in an ultrasound-enhanced five-stage gradient elution system.</td>
<td></td>
</tr>
<tr>
<td>C11</td>
<td>Son et al. (2011) [168]</td>
<td>35</td>
<td>1.0W</td>
<td>Joomunsin sand</td>
<td>Oil</td>
<td>Much higher removal efficiency by ultrasonic soil-washing (74.7%) than mechanical soil-washing (31.0%); addition of sodium dodecyl sulfate increases the ultrasonic removal efficiency to 76.1%.</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>Zhang et al. (2012) [107]</td>
<td>20</td>
<td>66W</td>
<td>Oily sludge</td>
<td>Oil</td>
<td>Up to 80.0% oil recovery rate for the combined ultrasonic and freeze/thaw treatment.</td>
<td></td>
</tr>
<tr>
<td>C13</td>
<td>Li et al. (2013) [169]</td>
<td>20</td>
<td>600W</td>
<td>Ottawa sand, fine soils that contained 27.6% and 55.3% of silt and clay contents</td>
<td>Crude oil</td>
<td>Highest and lowest desorption for coarse soil (i.e., Ottawa sand) and finer soil (i.e., soil with clay content), respectively.</td>
<td></td>
</tr>
</tbody>
</table>

Note: C — combined methods.
Table 2.4 Summary of laboratory studies on sonic/ultrasonic treatment of porous media

<table>
<thead>
<tr>
<th>#</th>
<th>Reference</th>
<th>Freq., kHz</th>
<th>Power/ Intensity</th>
<th>Duration, min</th>
<th>Solids</th>
<th>Target Contaminants</th>
<th>Observed results</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cleveland and Garg (1993) [170]</td>
<td>Ultrasonic</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>Homogenize soil at small scale and significantly affect permeability; stimulate contaminant/fine particle migration.</td>
</tr>
<tr>
<td>T2</td>
<td>Simkin (1993) [130]</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>Porous media</td>
<td>Oil</td>
<td>Liberates a great amount of dissolved and adsorbed gas clogging the pore channels, displacing the fluid from them and changing the phase permeability of the water and oil containers.</td>
</tr>
<tr>
<td>3</td>
<td>Reddi and Challa (1994) [148]</td>
<td>60Hz</td>
<td>–</td>
<td>15-20</td>
<td>Sand</td>
<td>Hexadecane</td>
<td>Mobilization of NAPL ganglia trapped in pore spaces in sand; increased soil porosity but decreased viscosity and buoyant pressure.</td>
</tr>
<tr>
<td>4</td>
<td>Iovenitti et al. (1995) [149]</td>
<td>50-5000Hz</td>
<td>100kW/m²</td>
<td>–</td>
<td>Sand, silt, clay, soil</td>
<td>–</td>
<td>High frequency limits remediation volume; low frequency is not applicable to compact remediation volume; non-linearities, acoustic scattering and heterogeneities contribute to a practical upper bound on the acoustic intensity.</td>
</tr>
<tr>
<td>5</td>
<td>van Ellen et al. (1995) [154]</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>Sand</td>
<td>Diesel oil</td>
<td>70% in reduction of oil concentration in the soil after flushing 140 times in 5 days.</td>
</tr>
<tr>
<td>6</td>
<td>Venkitaraman (1995) [128]</td>
<td>20-80</td>
<td>20-250 W/m²</td>
<td>110-1100</td>
<td>Berea sandstone</td>
<td>Brine; mud (4% bentonite and 2% NaCl); decane</td>
<td>Increase in permeability by as much as a factor of six in mud damaged cores.</td>
</tr>
</tbody>
</table>

Continued
Table 2.4 Continued

<table>
<thead>
<tr>
<th></th>
<th>Author(s) &amp; Year</th>
<th>Frequency &amp; Power</th>
<th>Porosity</th>
<th>Medium</th>
<th>Treatment</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>Iovenitti et al. (1996) [155]</td>
<td>7.5 &gt;70 W/m²</td>
<td>–</td>
<td>Sand</td>
<td>1,1,1-trichloroethane (TCA); p-xylene</td>
<td>Increased dissolution of p-xylene (~100%) and enhanced hydraulic conductivity.</td>
</tr>
<tr>
<td>T9</td>
<td>Aarts and Ooms (1998) [143]</td>
<td>kHz level</td>
<td>–</td>
<td>Porous media</td>
<td>–</td>
<td>A mathematical model and solution proposed for peristaltic transport mechanism; the model predicts a strong dependence on the power output W and on the shear modulus G of the porous medium.</td>
</tr>
<tr>
<td>10</td>
<td>Kouznetsov et al. (1998) [171]</td>
<td>100-200 Hz</td>
<td>–</td>
<td>Sandstone, quartz, and bentonite</td>
<td>Kerosene</td>
<td>Increased oil recovery and oil-water ratio in both laboratory and pilot-field tests; increase of the rate of kerosene displacement; degas by vibration; higher oil recovery in the presence of CO₂; increased then decreased oil recovery with water salinity.</td>
</tr>
<tr>
<td>11</td>
<td>Aarts et al. (1999) [144]</td>
<td>20 400W 800s</td>
<td>Rubber</td>
<td>–</td>
<td>Flow is induced by ultrasound and increases with power.</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>Roberts et al. (2001) [150]</td>
<td>25-100 Hz</td>
<td>–</td>
<td>48h</td>
<td>Sand core</td>
<td>Trichloroethylene (TCE)</td>
</tr>
<tr>
<td>13</td>
<td>Poesio et al. (2002) [18]</td>
<td>20; 40 700, 2000 W 6-40</td>
<td>Berea sandstone</td>
<td>Brine</td>
<td>Decrease in pressure gradient but increase in permeability with acoustic waves.</td>
<td></td>
</tr>
</tbody>
</table>

Continued
Table 2.4 Continued

<table>
<thead>
<tr>
<th>No.</th>
<th>Authors and Year</th>
<th>Type</th>
<th>Power or Frequency</th>
<th>Duration</th>
<th>Media</th>
<th>Fluids</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>14</td>
<td>Ariadji (2005) [151]</td>
<td>0-200Hz</td>
<td>–</td>
<td>–</td>
<td>Sandstone and cement</td>
<td>Oil</td>
<td>Improve the porosity up to 15.3% and absolute permeability up to 2.2%; decrease the residual oil saturation up to 53.6%.</td>
</tr>
<tr>
<td>T15</td>
<td>Dunin and Nikolaevskii (2005) [141]</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>Porous media</td>
<td>Oil</td>
<td>Analyze nonlinear equations that describe the waves propagating in saturated porous media.</td>
</tr>
<tr>
<td>16</td>
<td>Hamida and Babadagli (2005) [152]</td>
<td>20; 40, 5-250 W/cm(^2), 5000</td>
<td>Berea sandstone and Indiana limestone</td>
<td>Mineral oil and kerosene</td>
<td>Enhance capillary imbibition recovery of oil (up to 15% increase).</td>
<td></td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>Nikolaevskii and Stepanova (2005) [129]</td>
<td>Ultrasonic 50, 100W, 15–60s every 15min over 7h.</td>
<td>Sand</td>
<td>Oil</td>
<td>Stimulated gas evolution from natural oil and increased mobility of the residual oil.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>19</td>
<td>Hamida and Babadagli (2007) [153]</td>
<td>20; 40, 250 W/cm(^2), 2000W</td>
<td>Berea sandstone and Indiana limestone</td>
<td>Mineral oil and kerosene</td>
<td>A considerable enhancement in recovery (up to 23%) and recovery rate (up to 65%) by ultrasound for most experiments; improved recovery rate with surfactant by up to 20%.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>Naderi and Babadagli (2008) [172]</td>
<td>5-84 W/m(^2), 120-10000</td>
<td>Berea sandstone</td>
<td>Oil</td>
<td>Increased recovery in capillary imbibition experiments; more significant effects on oil recovery for oil-wet samples.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>21</td>
<td>Naderi and Babadagli (2010) [147]</td>
<td>45-84 W/m(^2), 20000</td>
<td>Berea sandstone</td>
<td>Oil</td>
<td>Increases in recovery; effect of ultrasound is less with higher viscosity but more significant in oil-wet cases; higher frequency shows higher rate of recovery.</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Continued
Table 2.4 Continued

<table>
<thead>
<tr>
<th></th>
<th>Hamidi et al. (2012) [146]</th>
<th>25; 40</th>
<th>1-500W</th>
<th>100-600h</th>
<th>Berea sandstone cores</th>
<th>Mineral oil</th>
<th>Increase in oil recovery with low viscosity, high frequency, and high power; enhanced percolation rate, higher mobility of oil droplet, and changing in interfacial tension and wettability.</th>
</tr>
</thead>
</table>

Note: T — theoretical evaluation.
Table 2. 5 Summary of field studies on sonic/ultrasonic treatment

<table>
<thead>
<tr>
<th>#</th>
<th>Reference</th>
<th>Freq., kHz</th>
<th>Power/ Intensity</th>
<th>Duration, min</th>
<th>Field location</th>
<th>Target Contaminants</th>
<th>Observed results</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Shaw Resource Services, Inc. (1992) [173]</td>
<td>200Hz - 10kHz</td>
<td>3-5kW</td>
<td>4-6h; 1 month</td>
<td>Bakersfield, California; Ventura County, California</td>
<td>oil</td>
<td>Up to 45% increase in oil production; treatment effect lasts up to one month.</td>
</tr>
<tr>
<td>2</td>
<td>Beresnev and Johnson (1994) [131]</td>
<td>58 MHz</td>
<td>48 kW</td>
<td>several min</td>
<td>Odessa, Texas</td>
<td>oil</td>
<td>Average increase in oil production of 29% and an increase of 25% in fluid production.</td>
</tr>
<tr>
<td>3</td>
<td>Beresnev and Johnson (1994) [131]</td>
<td>12.5-16.5</td>
<td>1.2-5.0 kW/m²</td>
<td>&gt;5d</td>
<td>Western Siberia</td>
<td>oil</td>
<td>Almost doubled the oil production.</td>
</tr>
<tr>
<td>4</td>
<td>Beresnev and Johnson (1994) [131]</td>
<td>5-50</td>
<td>1-10 kW/m²</td>
<td>several h</td>
<td>Western Siberia</td>
<td>oil</td>
<td>Increased production immediately after treatment; improved production lasted for a couple of months to more than a year.</td>
</tr>
<tr>
<td>5</td>
<td>Guo et al. (2004) [174]</td>
<td>High frequen cy</td>
<td>–</td>
<td>–</td>
<td>Daqing, Heilongjiang; Dongying, Shandong; and many other oilfields in China</td>
<td>heavy oil</td>
<td>High frequency vibration leads to an increase in oil and fluid in heavy oil reservoir.</td>
</tr>
<tr>
<td>6</td>
<td>Hartog and Westerhoff (2010) [156]</td>
<td>12-196Hz</td>
<td>–</td>
<td>5h</td>
<td>Rotterdam harbour area, Netherlands</td>
<td>PCE, TCE, DCE</td>
<td>Stimulated NAPL dissolution, not mobilization; optimal frequency is related to the resonance frequency of natural soils and is site-specific.</td>
</tr>
</tbody>
</table>

Continued
<table>
<thead>
<tr>
<th></th>
<th>Abramov et al. (2013) [157]</th>
<th>25</th>
<th>5, 10kW</th>
<th>–</th>
<th>Western Siberia</th>
<th>oil</th>
<th>Enhance oil recovery by 30 – 50%; the effect of ultrasonic treatment lasts from 3 to 12 months or longer; significant higher production for ultrasound treatment combined with chemicals.</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>Abramova et al. (2014) [158]</td>
<td>18</td>
<td>2-3kW</td>
<td>–</td>
<td>Western Siberia and Samara Region</td>
<td>oil</td>
<td>Increase in oil production by 40-100%.</td>
</tr>
</tbody>
</table>
Figure 2.1 Acoustic vibration and wave propagation (a — molecule oscillation; b — harmonic wave; c — attenuated wave)
Figure 2. 2 Acoustic cavitation and its effects (a — cavitation bubble; b — particle)
Figure 2. 3 Acoustic effects on porous media (gray — particle; brown — NAPL; black — colloid; ))) — sound waves; arrow — flow)
Figure 2.4 Conceptual design for acoustically enhanced soil remediation
CHAPTER 3

CHARACTERING ULTRASONIC CAVITATION AND
HYDRODYNAMICS IN DIFFERENT SIZED POROUS MEDIA

58
3.1 Abstract

Optimizing ultrasonic remediation requires mechanistic insights into acoustic properties in relation to porous media. However, there is a dearth of information on both cavitation and pore flow hydrodynamics in porous media in the presence of acoustic fields. In this study, a flow-through packed-media column coupled with a 20 kHz ultrasonic system was designed and utilized to investigate i) propagation of ultrasonic waves in two different porous silica media, glass beads and sand; ii) location of ultrasonic cavitation; and iii) hydrodynamic properties resulting from sonication of these media. The acoustic pressure measured by a hydrophone was found to decay exponentially with distance in both media, and a higher attenuation of the sound propagation was observed for sand, which had a wider size distribution than the spherical glass beads. The cavitation featured a locally detected broadband signal in the frequency spectra and produced heating that enhanced pore flow due to reduced fluid viscosity. A Darcy model incorporating ultrasonic effects (i.e., acoustic pressure and cavitation heating) on pore flow revealed that acoustic pressure immediately increased flow velocity at the beginning of sonication and viscous effect then played a dominant role in the enhancement for pore flow. Column hydrodynamics of bromide breakthrough tests, estimated using CXTFIT software, indicated enhanced dispersion of the tracer by ultrasound. These results indicate that ultrasonically enhanced pore flow and mass transfer could be utilized to facilitate soil/sediment remediation.

Keywords: porous media, hydrophone, cavitation, Darcy flow, hydrodynamics
Nomenclature

A  cross-sectional area of column (m$^2$)
A_m  unit area (m$^2$)
c  speed of the sound wave (m s$^{-1}$)
C  solute concentration (M)
C_0  initial tracer concentration in (M)
d  spherical diameter of grains (m)
D  hydrodynamic dispersion coefficient (m$^2$ s$^{-1}$)
D_{ac}  enhanced dispersion coefficient due to sonication (m$^2$ s$^{-1}$)
D_e  effective dispersion coefficient (m$^2$ s$^{-1}$)
E  acoustic energy (J)
I  acoustic intensity (W m$^{-2}$)
I_0  acoustic intensity at sound source (W m$^{-2}$)
k  permeability of porous media (m$^2$)
k_{ave}  weighted-average permeability (m$^2$)
K  hydraulic conductivity (m s$^{-1}$)
L  longitudinal distance from acoustic source (m)
p  fluid pressure (Pa)
P    acoustic pressure (Pa)
P_0  acoustic pressure at sound source (Pa)
Q    flow rate (mL min^-1)
Re   Reynolds number
t    time (s)
T    temperature (K)
u    molecule vibration velocity (m s^-1)
v    superficial flow velocity (m s^-1)
v_{ac} enhanced seepage velocity due to sonication (m s^-1)
v_c  effective seepage velocity (m s^-1)
v_s  seepage velocity (m s^-1)
V_0  micro-volume of molecules (m^3)
W    power of acoustic waves (J s^-1)
z    elevation head (m)

Greek letters
\(\alpha\)    attenuation coefficient for acoustic intensity
\(\alpha_m\)  tracer dispersivity (m)
\(\zeta\)     average distance of tracer movement (m)
\(\eta\)     fluid viscosity (Pa s)
\(\rho\)     media density (kg m^{-3})
\(\rho_l\)   fluid density (kg m^{-3})
\( \rho_s \) solid density (kg m\(^3\))

\( \tau \) hydraulic tortuosity

\( \phi \) porosity

\( \omega \) angular frequency of wave (rad s\(^{-1}\))
3.2 Introduction

Contaminant transport in porous media is an important design factor for subsurface remediation. Traditional pump-and-treat methods are ineffective in reducing or removing non-aqueous phase liquids (NAPLs) such as chlorinated solvents due to their high hydrophobicity and low mobility [175]. Thus, sound waves at Hz to MHz levels have been used to effectively remediate contaminated groundwater and soils [9]. The lack of chemical additions in acoustic treatments leads to less secondary contamination risk as compared to surfactant or cosolvent (e.g., humic substance) enhanced mobilization of hydrophobic NAPLs [17] further enhancing its appeal.

In bench-scale studies, acoustic treatments can deform pore spaces [18, 128, 151], liberate trapped gas [129, 130], reduce viscosity of pore fluid [18, 146, 176], and dissolve NAPLs [177, 178]. These combined effects result in enhanced pore flow and contaminant transfer in porous media. However, these proposed mechanisms either fail to account for or overlook some critical phenomena, such as cavitation, in the porous media that might significantly impact contaminant fate and transport. Exploring mechanisms for enhanced pore flow due to sonication necessitates quantitative differentiation between cavitation heating and pressure waves; meanwhile, the fate and transport of sonochemically formed hydroxyl radical, which may oxidize NAPLs in the pore fluid, are not clear. Thus, characterization of cavitation with respect to magnitude and range may help to identify effective regions of cavitation in the porous media and clarify the mechanisms contributing to acoustically enhanced treatment.
Acoustic cavitation, usually generated by ultrasound (≥ 20 kHz) [9], refers to the initiation, growth, and collapse of bubbles [13]. It is different from the geomechanical definition of cavitation which only includes initiation of vapor bubbles in porous media [179]. Traditional aqueous-based tests used to characterize cavitation effects (e.g., dosimetry and sonochemiluminescence) may be influenced by potential adsorption of chemicals onto grain surfaces in the porous media leading to an under-estimation of cavitation effects. The hydrophone technique, which has been used to measure acoustic pressures and determine sound wave propagation in aqueous solution, may help delineate these acoustic effects in porous media. The acoustic emission method based on hydrophone measurements detects and analyzes physical signals from bubble oscillations [180]. At low intensity, bubbles oscillate linearly at the driving frequency of the ultrasonic source [180]. Bubble motion at higher intensities departs from linearity and generates multiple sub- and ultra-harmonic frequencies [181]. Chaotic micro-jets or shock waves from bubble collapse, together with the harmonic motion sources, generate a broadband sound signal, which is indicative of transient cavitation [182, 183]. Similar to the aqueous tests, acoustic cavitation in water-saturated porous media is expected to be detected and characterized by spectral analysis of sound signals.

The enhancement of interstitial water/solute transport due to cavitation heating or oscillatory pressure is potentially limited by heterogeneity of porous media, which is commonly confronted in subsurface remediation [184]. The examination of acoustic effects in different porous media is helpful to anticipate how sound waves enhance solute transport and to improve remediation in heterogeneous media. For example, variation in
particle sizes may lead to different flow and transport properties in the presence of sound waves due to different attenuation capacities exhibited by the various particles. However, limited reports have investigated the effect of particle characteristics on enhancement of solute transport due to sonication [17].

Therefore, the primary goal of the present study is to examine ultrasonic cavitation in different porous media in order to improve our understanding of the mechanisms responsible for enhanced pore flow and mass transfer due to ultrasound. We utilized a flow-through packed-media column coupled with an ultrasonic system to measure ultrasound and hydrodynamics. Two types of silica media, glass beads and sand, were sieved into different size ranges, enabling us to investigate the effects of particle size on cavitation, pore flow and solute transport. Using the column setup, we first measured sound propagation and acoustic cavitation in water-saturated porous media with a hydrophone. We then measured pore flow velocity and fit the data using Darcy’s Law in porous media. Finally, we evaluated the column hydrodynamics using bromide breakthrough tests and investigated the mechanism for the enhancement of solute transport in the presence of ultrasound.
3.3 Materials and Methods

3.3.1 Materials

Potassium bromide (KBr) was purchased from Sigma Aldrich. Sodium biocarbonate (NaHCO₃), purchased from Fisher Scientific, was used as solution buffer. Calcium chloride (CaCl₂), an electrolyte, was also purchased from Fisher Scientific. All chemicals were reagent grade. Stock solutions were prepared using deionized (DI) water (Milli-Q, Millipore) with a resistivity of 18.2 MΩ cm.

Glass beads (Fisher Scientific, Pittsburg, PA) and Ottawa sand (Unimin, Ottawa, MN) were used as packing media. The mean diameters of the three tested glass beads were 0.5 mm (small), 1.0 mm (medium), and 2.0 mm (large), respectively. Ottawa sand was sieved into three size fractions (50 – 100, 30 – 40, and 16 – 20 mesh, ASTM sieves), which correspond to mean grain diameters of 0.316 ± 0.011 mm (small), 0.547 ± 0.012 mm (medium), and 0.760 ± 0.005 mm (large), respectively. Prior to testing, the glass beads and quartz sand were cleaned thoroughly to remove metal oxides (Fe and Al) and organics coated on the surface of grain particles [185], excluding their potential interference in experiments.

3.3.2 Experimental Setup

An experimental setup (Figure 3.1) coupling an ultrasonic system and a media-packed column was designed to investigate cavitation, pore flow, and solute transport in porous media. As shown in Figure 3.1, a 20 kHz ultrasonic probe (Sonic Dismembrator
550, Fisher Scientific) with a tip area of 1.2 cm² introduced acoustic pressure and cavitation to the water-saturated porous media. A plexiglass column (2.5 cm i.d. × 15.0 cm length) was fabricated to fit the probe. A stainless steel cap connected the probe to the column. A stainless steel filter (50 μm in pore size) was used to retain packed particles and a stainless steel end-cap was milled to accommodate the Teflon tubing (0.32 cm i.d.). A series of 7 openings 1.5 cm apart on the side of the column were drilled to contain hydrophones (Reson TC4013) and thermocouple probes. All unused column openings were sealed with rubber stoppers during the experiment.

As shown in Figure 3.1, a background solution containing an electrolyte (1.0 mM CaCl₂) and a pH buffer (0.006 mM NaHCO₃) or bromide tracer (1.0 mM) flowed into the column through a T-valve. The column effluent was diverted to either a graduated cylinder for measurements of flow or to a fraction collector (Retriever® 500, Teledyne Isco, Inc.) for sampling.

3.3.3 Experimental Procedure

The porosity of the medium was calculated from the ratio of the volume of water required to saturate a packed medium in the column to the total volume of the column. Although glass beads exhibit a slightly higher porosity than did the corresponding quartz sand, there was no significant difference in porosity among the same particle types (see Table 1). Prior to each experiment, the column was flushed with background solution (ionic strength = 3.0 mM, pH = 7.5) following dry packing of sand or glass beads to a height of 13 cm. The background solution was stored in a tank providing a constant head
(h) of 50 cm. This applied water head provided fast pore flow (>10⁻³ m s⁻¹) for sufficient heat transfer through the column. During hydrophone measurements, the hydrophone position was changed by inserting it into different openings on the side of the column. The influence of the hydrophone insertion on pore flow was negligible. The hydrophone was connected to a TDS 5000 Tektronix oscilloscope (Tektronix Inc., USA) with a sampling frequency of 125 kHz. Similarly, thermocouple probes were placed at 7 different locations of the column through the side openings and temperatures were monitored at 10 s intervals in each experiment. Duplicate experiments were carried out for each particle type and size range.

The breakthrough tests using 1.0 mM KBr as a nonreactive tracer were conducted both with and without ultrasound for all six particle types. Effluent samples were collected every 5 s using the fraction collector. The Br⁻ concentrations were analyzed using a Dionex ICS – 2100 ion chromatograph (Dionex Corp.) equipped with an AS-19 column. The eluent (KOH) flow rate 1.0 mL min⁻¹ and a 5 – 45 mM eluent gradient in 25 min were set for the anion analysis. The particle size distribution in the column and in the effluent was measured in select experiments using a MasterSizer (Malvern Instruments Ltd.).
3.3.4 Theory

3.3.4.1 Sound wave propagation in poroelastic media

The acoustic wave equation describes wave motion in elastic media [6, 115]:

\[ \nabla^2 P - \frac{1}{c^2} \frac{\partial^2 P}{\partial t^2} = 0 \]  (3.1)

where \( P \) is the acoustic pressure (Pa), \( c \) is the speed of sound (m s\(^{-1}\)), and \( t \) is time (s). The acoustic energy (\( E \); J) associated with wave motion in poroelastic media is a function of the vibration velocity (\( u \); m s\(^{-1}\)) for micro-volume of the media (\( V_0 \) m\(^3\); see Figure 3.S1a) [36]:

\[ E = \rho V_0 u^2 \]  (3.2)

where \( \rho \) is the media density (kg m\(^{-3}\)). Meanwhile, the acoustic intensity (\( I \); W m\(^2\)) is defined as the power (\( W \); J s\(^{-1}\)) of a sound wave per unit area (\( A_m \); m\(^2\)) [6, 115]:

\[ I = \frac{W}{A_m} = \frac{P^2}{\rho c} \]  (3.3)

Eq. (3.3) describes the acoustic intensity for a point source emitting waves spherically. Our ultrasound source was a planar emitting surface that emits into a hemispherical space. Therefore, the intensity for our ultrasonic system is half of the total intensity (\( \frac{P^2}{2\rho c} \)).

Attenuation of acoustic intensity in the poroelastic media follows exponential decay [52]:

69
\[ I = I_0 \exp(-2\alpha L) \]  \hspace{1cm} (3.4)

where \( I_0 \) is the acoustic intensity at the sound source (W m\(^{-2}\)), \( \alpha \) is the attenuation coefficient, and \( L \) is the longitudinal distance from the ultrasound source (m).

3.3.4.2 Pore flow in an acoustic field

In most cases, fluid flow through porous media such as an aquifer is very slow (Reynolds number, \( \text{Re} < 1.0 \)) \cite{186}, allowing the use of Darcy’s Law to calculate the flow \cite{187}:

\[ Q = KA \frac{\Delta h}{L} \]  \hspace{1cm} (3.5)

where \( Q \) is the volumetric flow rate (m\(^3\) s\(^{-1}\)), \( K = k \frac{\rho g}{\eta} \) is the hydraulic conductivity (m s\(^{-1}\)), \( k \) is the permeability of porous media, m\(^2\); \( g \) is the gravitational acceleration, 9.81 m s\(^{-2}\); \( \eta \) is the fluid viscosity, Pa s), and \( A \) is the cross-sectional area of the column (5.06 \times 10^{-4} m\(^2\)). \( h \) is the piezometric head (m), as shown in Figure 3.S1b:

\[ h = z + \frac{p}{\rho g} \]  \hspace{1cm} (3.6)

where \( z \) is the elevation head (m) and \( p \) is the fluid pressure (Pa). Typically, the “head” is considered as the mechanical energy per unit mass of fluid in the porous media \cite{187}. More specifically, the mechanical energy (\( h_{\text{total}} \)) for the pore flow consists of potential
energy, pressure energy, and kinetic energy, which correspond to elevation head \( z \), pressure head \( \frac{p}{\rho g} \), and velocity head \( \frac{v^2}{g} \), respectively [187]:

\[
h_{\text{total}} = z + \frac{p}{\rho g} + \frac{v^2}{g}
\]

(3.7)

where \( v = \frac{Q}{A} = \phi v_s \) (\( \phi \) is media porosity and \( v_s \) is seepage velocity, m s\(^{-1} \)) is the superficial flow velocity (m s\(^{-1} \)) [188]. The term “flow velocity” indicates superficial flow velocity in this study, unless noted otherwise. We designated a homogeneous flow velocity over the column for all experiments.

In the presence of an acoustic field, pore flow in the porous media is typically considered as Darcy flow [18, 132]. Since pore flow is slow, the velocity head term is much smaller than the pressure head term and Eq. (3.7) becomes:

\[
h_{\text{total}} = z + \frac{p}{\rho g} + \frac{P}{\rho g} = h + \frac{P}{\rho g}
\]

(3.8)

where \( \frac{P}{\rho g} \) is the acoustic pressure head. Due to the exponential decay of acoustic pressure, different compressing effects were expected at different locations of the column, resulting in variable permeability over the column. If we consider the packed media in the column is comprised of several layers and \( k \) is homogeneous in each layer, the weighted-average permeability (\( k_{\text{ave}} \)) for the column system can be calculated as follows [189]:
\[
 k_{\text{ave}} = \frac{\sum_{j=1}^{n} k_j h_j}{\sum_{j=1}^{n} h_j} \tag{3.9}
\]

where \( n \) equals the number of layers. We divided the packed media into \( n = 7 \) layers with the centers of the side openings as boundaries, as shown in Figure 3.S1b.

### 3.3.4.3 Solute transport in an acoustic field

A convection-diffusion equation (CDE) was used to describe the transport of a non-reactive and non-sorbing solute (e.g., bromide) in porous media \([17, 134]\):

\[
 \frac{\partial C}{\partial t} = -v_e \frac{\partial C}{\partial x} + D_e \frac{\partial^2 C}{\partial x^2} \tag{3.10}
\]

where \( C \) is the solute concentration (M), \( x \) is the distance (m), \( v_e \) is the effective seepage velocity of tracer, and \( D_e \) is the effective hydrodynamic dispersion coefficient (m\(^2\) s\(^{-1}\)). In the presence of an acoustic field, \( v_e \) and \( D_e \) are defined as follows, respectively \([133]\):

\[
 v_e = v_s + v_{ac} \tag{3.11a}
\]

\[
 D_e = D + D_{ac} \tag{3.11b}
\]

where \( v_{ac} \) and \( D_{ac} \) are enhancements of seepage velocity and dispersion coefficient due to sonication, respectively. In porous media, tracer dispersion is a combination of mechanical dispersion in a flow field and molecular diffusion coefficient due to concentration gradient (\( D^* \); m\(^2\) s\(^{-1}\)) \([17]\):
\[ D_e = \alpha_m v_e + \frac{D^*}{\tau} \]  

(3.12)

where \( \alpha_m \) is the tracer dispersivity (m) in porous media, \( \tau = \frac{\langle \zeta \rangle}{L} \) is the hydraulic tortuosity that is determined as the ratio of average distance (\( \langle \zeta \rangle \)) of tracer movement to longitudinal length (L) [190]. The longer diffusion pathways for tracer in tortuous micro-channels of porous media result in \( \tau > 1.0 \). The value of \( \tau \) depends on the nature of porous media. By fitting experimental data into the CDE equilibrium model using software CXTFIT, the tracer velocities and dispersion coefficients in the different media were estimated.

3.4 Results and Discussion

3.4.1 Ultrasound Propagation in Porous Media

Ultrasound was first detected and measured in silica particles using the hydrophone. Ultrasound signal captured by oscilloscope was converted to acoustic pressure in root mean square (see conversion in the SI). The propagation of 20 kHz ultrasound observed in the column containing large sand particles (0.760 ± 0.005 mm) at different power intensities is shown in Figure 3.2. At low intensities of ultrasound, the acoustic pressure distribution was relatively even, whereas a high pressure region (in red) arose starting at power level 2 (1.16 W cm\(^{-2}\)). The red region extended with increasing power intensities. However, regions with acoustic pressure above 50 kPa were all within
4.0 cm. The acoustic pressure was distributed similarly in the column packed with the other two sand particles and three glass beads (Figure 3.S2-S6). The mathematical expression of acoustic pressure in poroelastic media is obtained by substituting Eq. (3.3) into Eq. (3.4):

$$P = P_0 \exp(-\alpha L)$$  \hspace{1cm} (3.13)

where $P_0$ is the acoustic pressure at the sound source (Pa). The acoustic pressure values were fit to the exponential decay model to obtain the attenuation coefficient for each medium. Table 3.1 lists the characteristics and attenuation abilities of the tested particles.

Sound attenuation in porous media is mainly attributed to three mechanisms. First, when sound waves approach a particle-liquid, particle-air, or liquid-air interface, absorption, reflection and scattering occur [119, 120]. Second, acoustic energy is dissipated by fluid viscosity (relative motion between fluid and skeletal frame of aggregated sand/glass beads) and frictional loss between sand/glass beads. [119]. Third, cavitation, if it occurs, consumes most of the acoustic energy by forming free radicals and releasing heat [191]. Thus, physical properties of porous media such as porosity, grain size, fluid viscosity, and trapped air all can affect sound propagation and attenuation. As shown in Table 3.1, the acoustic attenuation increased as the particle size decreased for sand or glass beads, which was consistent with previous results [121, 123]. The larger surface areas of the smaller particles resulted in more absorption of acoustic energy and subsequent increase in attenuation. The attenuation exhibited by sand particles was overall higher than glass beads. The irregular shapes and heterogeneous surface of sand appeared to cause a higher frictional loss during ultrasound propagation [119].
3.4.2 Cavitation in Porous Media

The acoustic emission method is usually employed in aqueous solution to characterize cavitation effects induced by ultrasound in a range from kHz to MHz [180, 181, 183]. After electromechanical conversion of sinusoidal alternating current (AC) to mechanical vibrations, the emitted waves from ultrasonic devices remain sinusoidal in shape when there is no interruption during their propagation through water [192]. In this case, bubble dynamic motion is linear and in the driving frequency of the ultrasonic device (i.e., 20 kHz in our system) [180]. However, under high power intensities the bubbles start to oscillate nonlinearly in the unstable environment. At the same time, bubbles of different size are generated and vibrate in different frequencies as secondary emitters of sound signals [180]. This introduces many harmonic frequencies and a broad range of frequencies that give rise to a broadband signal (i.e., an elevated baseline). It is generally accepted that a broadband signal indicates transient cavitation [180]. It is noted here that stable cavitation also appears in this case, but to a lesser degree. The broadband signal is an indication of a statistical predominance of transient cavitation in a sonicating system [193].

Figure 3.3 shows 20 kHz ultrasound waveforms and frequency spectra during sonication of DI water in the column setup. At lower power intensity (0.04 W cm$^{-2}$), the sound signal captured and shown in the oscilloscope was approximately sinusoidal (Figure 3.3a), indicating the dominance of one frequency. The large peak at 20 kHz in the frequency spectrum (Figure 3.3b) was consistent with this waveform observation [192]. At high intensity (6.26 W cm$^{-2}$), the waveform became featureless and several harmonic
frequencies (e.g., 3/2 $f_0$ and $2f_0$) of the fundamental frequency ($f_0$) appeared in the frequency spectrum (Figure 3.3c). This was consistent with previous observations of acoustic emissions in water [180]. As shown in Figure 3.3d, the observed broadband signal indicates the occurrence of cavitation at the intensity of 6.26 W cm$^{-2}$. As a matter of fact, the measured threshold for cavitation to occur was 0.74 W cm$^{-2}$ in water. Therefore, this high intensity of 6.26 W cm$^{-2}$ is likely to generate cavitation in water-saturated porous media.

We adapted the acoustic emission method to detect and characterize cavitation in the porous media at 6.26 W cm$^{-2}$. Figure 3.4 shows the frequency spectra as a function of distance in the column packed with large sand. At 1 cm, the baseline was elevated to around 10 (arbitrary units), indicating the presence of broadband and thus transient cavitation. However, at locations further from the probe tip (2.5 – 10.0 cm), no broadband was observed. It appeared that cavitation only occurred at a location close to the probe in the porous sand, which was similar to sonication in water [7]. The extent of baseline elevation and magnitude of featured peaks in Figure 3.4 were significantly lower (up to 1 order of magnitude) than those in water (Figure 3.3), suggesting cavitation in porous media was less intense than that in water. This decrease may be attributed to the higher attenuation of acoustic intensity for the porous sand as compared to water, as shown in Figure 3.S7.

To correlate the relationship between particle size and cavitation, experiments with different particles were carried out. Figure 3.5 shows the frequency spectra observed from the different porous media. Since the spectra were the same at locations $> 2.5$ cm,
data for only the 2.5 cm distance was plotted to compare to that at 1.0 cm. As shown in Figure 3.5, the observation of broadband at the location of 1 cm once again confirmed the localized cavitation. The finest sand with a larger surface area significantly attenuated the acoustic intensity resulting in a low level of cavitation at 1.0 cm (baseline at 1.0 as compared to 10 – 20 for other particles). In addition, low level cavitation was also observed at 2.5 cm for 1.0 mm and 2.0 mm glass beads. The localized cavitation was consistent with the acoustic pressure measurements in those porous media (Figure 3.2 and Figure 3.S2-S6).

3.4.3 Ultrasound Enhanced Pore Flow

Figure 3.6 shows the flow velocity \( v = \frac{Q}{A}; \) m s\(^{-1}\) measured volumetrically as a function of sonication time in the large sand (0.760 ± 0.005 mm) packed column. As shown there, the flow velocity increased immediately after applying sonication and reached a stable value after 30 seconds. Figure 3.7 shows the pore flow velocities for the tested particles under different power intensities (W cm\(^{-2}\)). The flow velocity increased up to 0.73 × 10\(^{-3}\) m s\(^{-1}\) with increasing power intensity and exhibited linear relationships for all tested particles \((r^2 > 0.90)\).

High acoustic pressure in the column may facilitate the movement of interstitial water which absorbed acoustic energy and converted it into dynamic energy. The exponential decay model, as shown in Eq. (3.7), described the acoustic pressure distribution along the column. The high acoustic pressure near the ultrasonic horn drove interstitial water to move in the micro-channels of the porous media; however,
compression of the porous media due to acoustic pressure resulted in reduced permeability ($10^{-14}$ as compared to $10^{-12}$ m$^2$ in the absence of ultrasound) counteracting the ultrasonic promotion of fluid movement. Therefore, homogeneous velocity along the column was assumed even though the acoustic pressure was exponentially distributed. The weighted-average permeability values (Table 1) for the different media in the column were calculated to be smaller than those without sonication, suggesting that acoustic pressure may not continuously enhance the pore flow velocity in the porous media as expected. The decrease in flow velocity (Figure 3.8) after long-time sonication (i.e., > 5min) indicated reduced permeability of packed media due to ultrasonic consolidation in the column.

In addition to the contribution of mechanical waves, heating of the fluid due to cavitation, as shown in Figure 3.9, may reduce fluid viscosity and thus increase the flow velocity. A similar increase in temperatures at different locations along the column (data not shown) suggests that fast fluid flow efficiently transferred the heat through the porous media leading to a homogeneous temperature distribution. In order to investigate the relationship between pore flow and cavitational heating, flow velocities at different initial temperatures in large sand packed column were measured. Figure 3.8 shows a smaller reduction in viscosity was observed at higher initial temperature, which corresponded to the lower level of velocity enhancement. This linear relationship between flow velocity and temperature confirmed cavitational heating enhanced pore flow. However, the temperature change at the outlet (10 cm away from horn tip) in Figure 3.6 was out of phase as compared to velocity in the tested time period indicating a non-correlation to
each other. The fast increase of flow velocity immediately after sonication suggests that the acoustic pressure facilitated interstitial water movement through the porous media in the column. This was supported by the unchanged temperature at the start of sonication (< 20 s). At the same time, the media permeability varied little during such a short period sonication. After long-time sonication (>300 s in Figure 3.S7), the permeability was reduced due to the ultrasonic compression. However, the constant higher level of flow velocity seemed to support the theory that cavitational heating resulting in reduced fluid viscosity was the major contribution to the enhanced pore flow in a long-period sonication process. This observation is consistent with previously reported results [18].

The energy flow in the sonicated column was estimated to verify that cavitational heating dominated pore flow enhancement. The calculated mechanical energy using Eq. (3.7) for the pore flow was < 1.3% of total ultrasonic energy, suggesting almost all of the ultrasonic energy was eventually converted into thermal energy that increased the temperature of pore water and possibly the sand/glass bead particles. This energy distribution confirmed cavitational heating enhanced flow velocity in the porous media. Therefore, the higher acoustic pressure and pore water temperature under higher power intensities led to faster pore flow in the tested porous media, as shown in Figure 3.7.

Tested particles featuring different pore size and surface friction affected the flow differently. As shown in Table 3.1, the small pore spaces between the small particles resulted in a slower pore flow in glass beads and sands [127]. In addition, smaller particles with larger surface area generated more frictional resistance for the water movement [194]. This high flow resistance for the small particles was consistent with
their acoustic attenuation abilities. The overall smaller velocity for sand particles as compared to glass beads could be attributed to the wider particle distribution. The smaller diameter sand particles might fill voids between larger particles due to gravitational and sonicating effects, resulting in smaller porosity and thus slower movement of interstitial water. As compared to spherical glass beads, the heterogeneous surface of sand particles might also account for more frictional loss during propagation of acoustic vibration and thus higher flow resistance [194].

3.4.4 Ultrasound Enhanced Solute Transport

Nonreactive tracer tests were conducted to assess column hydrodynamics (e.g., tracer velocity and dispersion coefficient). Figure 3.9 shows the bromide breakthrough curves for tested particles in the absence and presence of ultrasound. For all breakthrough curves, the recoveries of bromide approached 100% confirming little affinity between tracer and particles and negligible bromide oxidation by hydroxyl radicals due to short contact time. The shift of breakthrough curves to the left and reduced slope under sonication suggested increases in both the velocity and dispersion for bromide during sonication[195]. In order to obtain hydrodynamic parameters, the breakthrough data was fitted using the CDE equilibrium modeling in CXTFIT ($R^2 > 0.96$).

Table 3.1 shows the fitted tracer velocities ($v_e$) for different particles. The increasing tracer velocities with increasing particle size were consistent with the measured seepage velocities ($v$) except for the 2.0 mm glass beads. The tracer velocities were 66.5 – 96.5% of seepage velocities, suggesting that the pathway of tracer was
tortuous in the micro-channels of porous media. The Reynolds number for 2.0 mm glass beads was 5.24 (Table 3.1), which was $2 - 10$ times of other tested particles resulting in more turbulence in the pore flow. This may cause a more tortuous pathway, or a larger $\zeta$, for tracer in the 2.0 mm glass bead packed column. Therefore, a smaller tracer velocity was obtained for the largest glass beads. In the presence of ultrasound, the enhanced tracer velocity could be again attributed to the increased fluid temperature (i.e., viscous contribution) and acoustic pressure (i.e., kinetic contribution).

The dispersion of tracer in the column was a combination of mechanical dispersion due to flow velocity and molecular diffusion due to concentration gradient, as shown in Eq. (3.12). Without sonication, larger tracer dispersion coefficients were observed in the media with large grain size and seepage velocity, suggesting mechanical dispersion was dominant. In the presence of ultrasound waves, the dispersion coefficient was found to be up to 6 times larger than the original values (Table 3.1). The higher dispersion coefficient for medium glass bead/sand as compared to small glass bead/sand was attributed to the faster pore flow; however, the dispersion coefficients for large glass bead/sand was slightly decreased probably due to the high tortuosity of tracer in the column. Figure 3.10 compares the viscous and kinetic contributions to enhanced tracer dispersion in tested media. The viscous contribution due to increased temperature was estimated using the following expression derived from Stokes–Einstein–Sutherland equation [196]:

$$\frac{D_{T_1}}{D_{T_2}} = \frac{T_1 \eta_{T_1}}{T_2 \eta_{T_2}}$$  (3.14)
As shown in Figure 3.10, the viscous contribution varied little due to the small difference in fluid temperature in the column packed with different particles (Table 3.1). In contrast, the kinetic contribution was complex. For glass beads, the enhancement in dispersion was inversely related to particle size; an obvious enhancement due to pore flow was observed for the medium sand, while the viscous effect was the main contribution to enhanced dispersion for small and large sand. Generally, the high attenuation exhibited by small glass beads/sand resulted in a limited enhancement for tracer dispersion. Flow velocity increased as particle size increased and the enhancement of dispersion due to ultrasound became more obvious for medium glass beads/sand. However, high tortuosity of tracer in the presence of ultrasound waves led to reduced dispersion in large glass bead and sand media.

3.5 Conclusion

This study resulted in a practical method to detect and characterize ultrasonic cavitation in porous media using hydrophone technology. Although the intensity of ultrasound dropped quickly due to absorption and scattering by the particles, the localized cavitation increased pore water temperature resulting in reduced water viscosity. This, in conjunction with the presence of alternating ultrasound waves, increased the superficial flow velocity in the porous media. The acoustic pressure promoted pore flow immediately after sonication, whereas viscous effects in long-time sonication were the major reason for enhancement of pore flow in porous media. The calculation from Darcy
model agrees well with fitted hydrodynamic values from bromide breakthrough tests in CXTFIT.

This examination of the behavior of ultrasound in porous media shows promising results for ultrasonic remediation of porous soils or sediments. The ultrasonically enhanced pore flow could potentially facilitate mass transfer of chemical reagents and fine particles that are used for in-situ remediation such as pump-and-treat technologies. Furthermore, excitation and oscillation of pore fluid by acoustic vibration at $\mu$m to mm pore scales could solve the problem of clogging pores that commonly occurs in soil remediation. However, long-time sonication compacted the porous media and reduced the permeability. Utilizing low frequency sound waves and pulsing the sound signals may mitigate these compression effects, thereby improving the acoustic remediation.

3.6 Acknowledgments

This work was supported by the Ohio Sea Grant College Program.
Table 3. 1 Characteristics, attenuation abilities, and hydrodynamics of pore flow for tested particles.

<table>
<thead>
<tr>
<th>Particle</th>
<th>$d_{10}$, mm</th>
<th>$\phi$</th>
<th>$\alpha$</th>
<th>$T$, °C</th>
<th>$\sqrt{\frac{\eta}{\rho}}$, Pa s</th>
<th>$v_{f} \times 10^{3}$ m s$^{-1}$</th>
<th>$k \times 10^{12}$ m$^2$</th>
<th>$D_{c} \times 10^{5}$ m$^2$ s$^{-1}$</th>
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<tr>
<td>Small glass beads</td>
<td>0.50</td>
<td>0.403±0.017</td>
<td>0.654±0.175</td>
<td>28.6±0.1</td>
<td>0.828</td>
<td>1.43±0.02/1.28±0.01</td>
<td>2.89</td>
<td>0.62±0.04/0.86 (1.08)</td>
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<td></td>
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<td>1.79±0.02/1.29±0.01</td>
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<td></td>
<td></td>
<td>2.06±0.01/1.64±0.02</td>
<td>4.01</td>
<td>1.03±0.11/2.24 (2.40)</td>
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<td></td>
<td></td>
<td>4.44</td>
<td>1.75±0.14/4.65 (5.24)</td>
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<td></td>
<td>3.73±0.28/5.34 (6.32)</td>
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<tr>
<td>Medium glass beads</td>
<td>1.00</td>
<td>0.390±0.009</td>
<td>0.645±0.134</td>
<td>26.9±0.3</td>
<td>0.860</td>
<td>2.06±0.03/1.48±0.01</td>
<td>2.36</td>
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<td></td>
<td>2.32±0.05/1.54±0.01</td>
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<td>4.44</td>
<td>1.75±0.14/4.65 (5.24)</td>
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<td></td>
<td>3.73±0.28/5.34 (6.32)</td>
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<tr>
<td>Large glass beads</td>
<td>2.00</td>
<td>0.415±0.005</td>
<td>0.510±0.149</td>
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<td>0.886</td>
<td>1.23±0.02/1.00±0.01</td>
<td>2.36</td>
<td>0.88±0.13/0.50 (0.49)</td>
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<td>1.22±0.01/1.03±0.01</td>
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<td></td>
<td>2.36</td>
<td>1.75±0.14/4.65 (5.24)</td>
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<td></td>
<td></td>
<td>3.73±0.28/5.34 (6.32)</td>
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<tr>
<td>Small sand</td>
<td>0.316±0.011</td>
<td>0.378±0.026</td>
<td>2.857±0.231</td>
<td>31.0±1.3</td>
<td>0.786</td>
<td>1.62±0.04/1.23±0.02</td>
<td>3.29</td>
<td>1.21±0.31/1.06 (1.07)</td>
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<td>1.64±0.01/1.57±0.04</td>
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<td>3.29</td>
<td>1.21±0.31/1.06 (1.07)</td>
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<td></td>
<td></td>
<td>5.77±0.94/7.07 (7.77)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Medium sand</td>
<td>0.547±0.012</td>
<td>0.362±0.019</td>
<td>1.136±0.056</td>
<td>28.1±0.3</td>
<td>0.836</td>
<td>1.76±0.02/1.40±0.05</td>
<td>3.55</td>
<td>6.53±1.49/1.61 (1.70)</td>
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<td>Large sand</td>
<td>0.760±0.005</td>
<td>0.354±0.009</td>
<td>0.820±0.123</td>
<td>28.5±0.8</td>
<td>0.829</td>
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1 Average diameter for tested particles;
2 Estimated value based on averaged temperature;
3 Flow velocity measured from volumetric method/ tracer velocity fitted using CXTFIT;
4 Weighted-average values using Eq. (3.9);
5 Estimated value using CXTFIT, and Reynolds number was calculated using equation of $Re = \frac{\rho vd}{\eta}$. 
Figure 3. 1 Schematic of experimental setup
Figure 3.2 Propagation of ultrasound from source in column with large sand (mean diameter of 0.760 ± 0.005 mm; color key in kPa; numbers indicate power intensity in W cm⁻²)
Figure 3.3 Ultrasound waveforms (a and c) and frequency spectrum (b and d) observed from water at different power intensities.
Figure 3.4 Frequency spectrum at different locations for large sand (mean diameter of 0.760 ± 0.005 mm; power intensity of 6.26 W cm⁻²)
Figure 3.5 Frequency spectrum observed from different porous media (—1cm; —
2.5cm; power intensity of 6.26 W cm⁻²)
Figure 3. 6 Temperature (□) and flow velocity (■) changes at column outlet for large sand (mean diameter of 0.760 ± 0.005 mm; power intensity of 6.26 W cm\(^{-2}\))
Figure 3. 7 Flow velocities in tested media under different power intensities
Figure 3.8 Enhancement of pore flow (□) and decrease in viscosity (■) at different initial temperatures for large sand (mean diameter of 0.760 ± 0.005 mm; power intensity of 6.26 W cm⁻²).
Figure 3. 9 Bromide breakthrough curves for different media in the presence and absence of 20 kHz ultrasound waves (☐— no sonication; ■ — sonication at power intensity of 6.26 W cm$^{-2}$)
Figure 3.10 Kinetic and viscous contribution to enhanced dispersion coefficients in different media in the presence of ultrasound (power intensity of 6.26 W cm\(^2\))
CHAPTER 4

KINETICS AND MECHANISM OF ULTRASONIC ACTIVATION OF PERSULFATE: AN IN-SITU EPR SPIN TRAPPING STUDY
4.1 Abstract

Ultrasound (US) was shown to activate persulfate (PS) providing an alternative activation method to base or heat as an in-situ chemical oxidation (ISCO) method. The kinetics and mechanism of ultrasonic activation of PS were examined in aqueous solution using an in-situ electron paramagnetic resonance (EPR) spin trapping technique and radical trapping with probe compounds. Using the spin trap, 5,5-dimethyl-1-pyrroline-N-oxide (DMPO), hydroxyl radical (·OH) and sulfate radical anion (SO₄⁻) were measured from ultrasonic activation of persulfate (US-PS). The yield of ·OH was nearly ten-fold greater than that of SO₄⁻. The comparatively high ·OH yield was attributed to the reaction of SO₄⁻ with water in the interfacial region of cavitation bubbles formed from US. Using steady-state approximations, the dissociation rate of PS under sonication was fitted to be two orders of magnitude greater than the ambient temperature control. An effective temperature of ~ 330 K at the bubble-water interface was estimated from the Arrhenius equation. A double layer model based on an energy balance predicted a shell width of ~ 4.0 μm surrounding the cavitation bubble and featured a steep temperature gradient and rapidly decreasing dissociation rate of PS within the shell. Comparative studies using the probe compounds tert-Butyl alcohol and nitrobenzene verified the bubble-water interface as the location for PS activation and elucidated a role for ·OH in activating PS to SO₄⁻. The mechanisms unveiled in this study provide a basis for optimizing the US-PS system in the remediation process.

Keywords: ultrasound, persulfate, EPR, DMPO, bubble-water interface
4.2 Introduction

*In-situ* chemical oxidation (ISCO) has shown promise for remediating non-aqueous phase liquids (NAPLs; e.g., chlorinated solvent) in groundwater and soils [30]. Activated persulfate (PS) [31] has recently gained use as an alternative ISCO. PS has a long half-life (600 days at 25 °C) [197] allowing for transport of the reactant from an injection point to locations of contamination. Within the remediation region, the activation of PS to sulfate radical anion (SO$_4$$^{2-}$), a strong oxidant, is achieved through thermal treatment [198, 199], base injection [200, 201], or catalyst addition (e.g., Fe$^{2+}$ and Co$^{2+}$) [202]. PS activation has also been achieved by reaction with natural organic matter (NOM) [203, 204] and naturally occurring minerals [197], as well as by electrokinetic reaction [205] and UV irradiation [206, 207].

In limited studies, ultrasound (US) has been shown to activate PS [208-214]. Activation by US is thought to occur in two possible ways. In both mechanisms, the activation begins by the sonication of aqueous solution inducing cavitation bubbles. Collapse of those bubbles generates localized “hot spots” where temperature and pressure are as high as 5000 K and 1000 atm, respectively [215]. This high localized temperature has been reported as one mechanism for PS dissociation in US systems. In the second mechanism, hydroxyl radical (·OH) generated from dissociation of water molecules in cavitation bubbles attacks PS ions forming SO$_4$$^{2-}$, bisulfate ion, and oxygen [211]. However, these proposed mechanisms of ultrasonic activation of PS have not been confirmed in experiments.
To characterize radical formation from PS dissociation, \( \text{SO}_4^{2-} \) is usually estimated through an indirect measurement of a decrease in PS concentration \([197, 199, 216]\). This indirect measurement may over-estimate the activation process because PS may undergo reactions other than the assumed cleavage of the peroxide bond to form \( \text{SO}_4^{2-} \). Electron paramagnetic resonance (EPR) has been widely used as a method to directly detect free radicals through use of a spin trap such as 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) \([204, 217]\). The addition of \( ^\cdot \text{OH} \left( 2.8 \times 10^9 \text{ M}^{-1} \text{s}^{-1} \right) \) \([218]\) or \( \text{SO}_4^{2-} \) (this study) to the spin trap is rapid as compared to radical production in the ultrasound-persulfate (US-PS) system, so the detection of DMPO adducts in EPR is almost a simultaneous reflection of radical formation.

This study was designed to investigate the mechanisms of ultrasonic activation of PS in aqueous solution. In order to elucidate reaction pathways in the US-PS system, an ultrasonic reactor coupled to an EPR spectrometer through a flow cell was designed to detect and quantify radical formation. We hypothesized that the persulfate ion undergoes thermal dissociation and \( ^\cdot \text{OH} \) activation into \( \text{SO}_4^{2-} \) at the high temperature (~1900 K \([219]\)) of bubble-water interface. To test this hypothesis, batch sequential experiments and theoretical modeling were conducted. Using the spin trap DMPO, \( ^\cdot \text{OH} \) and \( \text{SO}_4^{2-} \) production were first determined in the US and US-PS systems, respectively. Next, a kinetic model was developed to fit the PS dissociation rate at the interface, since it was challenging to directly probe PS activation in the interfacial region. The fitted rates were compared to values from controls at ambient temperature (293 K). Modeling of the
bubble-water interface based on an energy balance and steady-state heat transfer was used to determine the width of the interfacial shell surrounding cavitation bubbles and predict temperature and PS reactivity distributions at the interface. To gain insight into the role of \(^\cdot\)OH in PS activation, two probe compounds, tert-Butyl alcohol (TBA) and nitrobenzene (NB), were employed to manipulate and verify the reaction pathway involved in the PS activation.

4.3 Materials and Methods

4.3.1 Materials

The spin trap reagent, 5,5-dimethyl-1-pyrroline-\(N\)-oxide (DMPO; > 99.0%), purchased from Dojindo Molecular Technologies and the radical standard, 2,2,6,6-tetramethylpiperidine (TEMPO; 98.0%), purchased from Fisher Scientific were used without further purification. Sodium persulfate (\(\text{Na}_2\text{S}_2\text{O}_8\); > 98.0%), tert-Butyl alcohol (> 99.9%), and nitrobenzene (99.5%) purchased from Fisher Scientific were used as received. All stock solutions were prepared using Milli-Q deionized (DI) water buffered with sodium dihydrogen phosphate (\(\text{NaH}_2\text{PO}_4\)) and disodium hydrogen phosphate (\(\text{Na}_2\text{HPO}_4\)) at \(\text{pH} = 7.4\).
4.3.2 Experimental Setup

Figure 4.1 shows the experimental setup. A horn-type ultrasonic system (Sonic Dismembrator 550, Fisher Scientific) with a tip area of 1.2 cm² was used to activate PS in a water-jacketed glass rosette reactor. A cooling bath (1006S, Fisher Scientific) was used to maintain the solution temperature at 20 °C in the reactor. The sonicated solution was pumped into an Aqua-X multi-bore designed sample tube with closely spaced capillaries (Bruker), which was placed in the cavity of a Bruker EMX Plus EPR spectrometer; the solution was circulated back to the reactor by a peristaltic pump (8 Roll Masterflex Pumphead, Cole-Parmer).

4.3.3 Sonication and EPR Experiments

Twenty-five mL batch experiments were conducted at different PS (0.1 – 100.0 mM) and DMPO (1.0 – 80.0 mM) concentrations. Prior to each experiment, a reactant solution was transferred into the reactor and purged with argon (99.9999%) for 5 min. Oxygen removal minimizes the formation of superoxide radical (’O₂⁻) and excludes its interference in experiments. The purging gas was turned off before sonication to avoid gas bubbles becoming entrained in the Aqua-X tube. The ultrasonic power density (PD) was set at 1.5 W mL⁻¹ with a sonication period of 10 – 30 min. The radical adduct signals were acquired and analyzed using WINEPR software. All scans were carried out at room temperature with the following instrument settings for EPR: sweep width, 120 G; attenuator, 13 dB; power, 10.02 mW; modulation amplitude, 1.00 G; time constant,
81.92 ms; conversion time, 40 ms; sweep time, 40.96 s; resolution in X, 1024; and resolution in Y, 20 – 40. The spin trap, DMPO, reacts with the short-lived radicals (i.e., ‘OH and SO₄⁻) that are generated in the US-PS system, thus forming spin adducts with longer, measureable life-times:

\[
\text{N}^+\text{O}^- + \text{R}^\cdot \rightarrow \text{N}^+\text{O}^\cdot\text{R}^- \tag{4.1}
\]

where R indicates trapped radicals such as ‘OH and SO₄⁻. A typical EPR spectrum obtained containing DMPO–OH and DMPO–SO₄⁻ is shown in Figure 4.2. Hyperfine coupling constants (hfcc) for nitrogen and hydrogen atoms were obtained by fitting spectra using the WinSim package (NIEHS, NIH, USA). To quantify spin adducts in the US-PS system, TEMPO was used as a stable nitrooxide radical standard. A 7-point calibration curve of TEMPO was prepared in buffer (0.0005, 0.001, 0.005, 0.01, 0.1, 0.5, and 1.0 mM). The spin adduct concentrations in samples were then calculated by comparing integrated areas of all detected peaks with the best-fit linear regression fit of TEMPO peak areas.
4.4 Results and discussion

4.4.1 Radical Production in US-PS System

Formation of radical species during sonication at different DMPO and PS concentrations was determined first. Figure 4.3 shows the DMPO-radical adduct formation with respect to DMPO concentration. DMPO•−OH and DMPO′−SO₄⁻ formation reached a plateau at 10 and 40 mM, respectively. The different DMPO concentrations in which the plateau occurs indicates that the trapping rate of SO₄⁻ by DMPO might not be as fast as •OH. To ensure that DMPO adequately trapped both radicals, 40 mM of DMPO was utilized in this study unless noted otherwise. Figure 4.4 illustrates adduct formation with sonication time in the absence and presence of persulfate. DMPO•−OH and DMPO′−SO₄⁻ concentrations reached a plateau between 200 and 400 s of sonication indicating that formation and decomposition of adducts were in equilibrium. Overall, the DMPO•−OH yield was higher than the corresponding DMPO′−SO₄⁻ yield in this US-PS system, which was consistent with the observation in Figure 4.3. Additionally, the DMPO•−OH yield in the presence of persulfate is nearly 3 times that in the US system, suggesting a source of •OH production other than dissociation of water molecules in the gas phase of cavitation bubbles. Even though a higher concentration of trapping reagent was required to trap •SO₄⁻, DMPO′−SO₄⁻ (~ 200 s) adduct formation reached steady-state faster than DMPO•−OH (~ 400 s), as shown in Figure 4.4.
Table 4.1 summarizes principal reactions in the US-PS system (R# indicates the assigned reaction number). According to these reactions, 'OH and SO$_4^{2-}$ are major radical species expected to be formed, which was confirmed in Figure 4.2. The higher 'OH yield in the presence of PS as compared to the US-only system was attributed to R13 (SO$_4^{2-}$ + H$_2$O $\rightarrow$ H$^+$ + SO$_4^{2-}$ + 'OH). The reaction rate constant ($k_{13a}$ = 6.0 $\times$ 10$^1$ s$^{-1}$) for R13a may be much improved in the interfacial region of cavitation bubbles. Water in a supercritical state may exist at the reported high temperature and pressure of the interface, thereby increasing the reactivity of water with SO$_4^{2-}$ [220]. Two other radicals possibly present include 'H and 'O$_2$'/HO$_2$. Negligible levels of 'H were detected due to insufficient trapping by DMPO, or instability of the DMPO'–H adduct [221]. Additionally, the relatively high PS concentration may compete with DMPO for consumption of 'H through R10 (S$_2$O$_8^{2-}$ + 'H $\rightarrow$ HSO$_4^{-}$ + SO$_4^{2-}$), resulting in the very small amount of DMPO'–H formation. At pH 7.4 used in these experiments, 'HO$_2$ deprotonated to 'O$_2^{-}$. In the argon-purged system, 'HO$_2$ cannot form through 'H + O$_2$ $\rightarrow$ 'HO$_2$. Therefore, 'O$_2^{-}$ is formed as the daughter species of 'OH and SO$_4^{2-}$ through R5 and R16. Since 'OH and SO$_4^{2-}$ were both sufficiently trapped by DMPO (Figure 4.3), no DMPO'–O$_2^{-}$ was observed in the EPR spectrum. Furthermore, formed DMPO'–O$_2^{-}$ quickly decomposes due to its reported short half-life (35-91s) [222].
4.4.2 Spin Adduct Decay

In order to evaluate the potential effect of adduct decomposition, we monitored adduct evolution with time after sonication was terminated. As shown in Figure 4.5, concentrations of DMPO$^\cdot$−SO$_4^-$ and DMPO$^\cdot$−OH adducts decreased over time, with faster decay of DMPO$^\cdot$−OH compared with DMPO$^\cdot$−SO$_4^-$. The decay followed first-order kinetics ($R^2 > 0.95$) during the time period tested; rate constants ($k_{21}$ and $k_{22}$) are given in Table 4.2. Marriott et al. (1980) [223] also reports first-order decay for DMPO$^\cdot$−OH at concentrations below $4 \times 10^{-5}$ M. For DMPO$^\cdot$−SO$_4^-$, a 16% decrease was previously observed in a time span of 10 min, but no rate constant is reported in that study [217]. In our system, nearly 50% of DMPO$^\cdot$−SO$_4^-$ was decomposed in the same time span. We attributed the variation in observation to the different initial conditions used in the experiments. In spite of the difference, the obvious decay of spin adducts observed in Figure 4.5 indicates that decay of the spin trap adducts cannot be ignored in the US-PS system.

4.4.3 Thermal Activation at the Bubble-Water Interface

PS dissociation is negligible in bulk solution at ambient temperature [198]. In addition, PS is non-volatile. Thus, observed formation of SO$_4^{\cdot-}$ is likely to occur in *OH rich and elevated temperature regions at or near the bubble-water interface. The probe compound, TBA, was used to verify the activation location of PS. TBA reacts slowly with SO$_4^{\cdot-}$ ($k = 4.0 \times 10^5$ M$^{-1}$ s$^{-1}$; R24) [224] but is an efficient scavenger of *OH ($k = 6.0$
× 10^8 M^{-1} s^{-1}; R25) [225]. At a high concentrations of TBA, the role of \(^{•}\)OH radical on SO\(_4^{−}\) formation is expected to be negligible, leaving only R8 as the source of SO\(_4^{−}\).

Although a portion of TBA added into the sonicated solution will enter into the gas phase of the bubble and lower the gaseous collapse temperature (to 2800 K in the presence of 100 mM TBA [226]), the corresponding reduced temperature at the interface is still far beyond the requirement for PS dissociation. We observed no change in SO\(_4^{−}\) production due to TBA (see Figure 4.S1). The insensitivity in SO\(_4^{−}\) production to TBA supports the hypothesis that R8 was the dominant reaction forming SO\(_4^{−}\) at the bubble-water interface.

In order to quantify PS dissociation, a kinetic model was developed to probe the activation reaction and fit the dissociation rate in the interfacial region of the cavitation bubbles. For this analysis, the 40 mM DMPO concentration used assured the free radicals in the US-PS system were fully trapped. Under this high level of DMPO, the recombination of free radicals was negligible, leaving only R1, R8-11, 13, and 17-19 to be considered. Therefore, the following kinetic expressions were derived:

\[
\frac{d[^{•}\text{OH}]}{dt} = k_1 - k_{2}[S_2O_8^{2−}][^{•}\text{OH}] + k_{13}[\text{SO}^{•}_4] - k_{18}[\text{DMPO}[^{•}\text{OH}]
\] (4.2)

\[
\frac{d[^{•}\text{H}]}{dt} = k_1 - k_{10}[S_2O_8^{2−}][^{•}\text{H}] - k_{19}[\text{DMPO}[^{•}\text{H}]
\] (4.3)

\[
\frac{d[\text{SO}^{•}_4]}{dt} = k_8 + k_9[S_2O_8^{2−}][^{•}\text{OH}] + k_{10}[S_2O_8^{2−}][^{•}\text{H}]
\]

\[
- k_{11}[S_2O_8^{2−}][\text{SO}^{•}_4] - k_{13}[\text{SO}^{•}_4] - k_{19}[\text{DMPO}[\text{SO}^{•}_4]]
\] (4.4)
Using steady-state approximations \( \frac{d[^*\text{OH}]}{dt} \approx 0, \frac{d[^*\text{H}]}{dt} \approx 0, \text{and} \frac{d[^*\text{SO}_4^-]}{dt} \approx 0 \), the radical concentrations were calculated:

\[
[^*\text{OH}] = \frac{k_1 + k_{13}[\text{SO}_4^\cdot]}{k_9[S_2\text{O}_8^{\cdot2^-}] + k_{18}[\text{DMPO}]} \tag{4.5a}
\]

\[
[^*\text{H}] = \frac{k_1}{k_{10}[S_2\text{O}_8^{\cdot2^-}] + k_{19}[\text{DMPO}]} \tag{4.6a}
\]

\[
[\text{SO}_4^\cdot] = \frac{k_8 + \left( \frac{k_9[S_2\text{O}_8^{\cdot2^-}]}{k_{18}[\text{DMPO}]} + \frac{k_{10}[S_2\text{O}_8^{\cdot2^-}]}{k_{19}[\text{DMPO}]} \right) k_1}{k_{13} + \frac{k_9[S_2\text{O}_8^{\cdot2^-}]}{k_{18}[\text{DMPO}]} + k_{17}[\text{DMPO}]} \tag{4.7a}
\]

Given \( k_{9,10} \) and \( k_{18,19} \) in Table 4.1, \([S_2\text{O}_8^{\cdot2^-}] = 1.0 \text{ mM}\) and \([\text{DMPO}] = 40 \text{ mM}\), we calculated \( k_9[S_2\text{O}_8^{\cdot2^-}] \ll k_{18}[\text{DMPO}] \) and \( k_{10}[S_2\text{O}_8^{\cdot2^-}] \ll k_{19}[\text{DMPO}] \). Thus, Eqs. (4.5-7a) simplify to:

\[
[^*\text{OH}] = \frac{k_1 + k_{13}[\text{SO}_4^\cdot]}{k_{18}[\text{DMPO}]} \tag{4.5b}
\]

\[
[^*\text{H}] = \frac{k_1}{k_{14}[\text{DMPO}]} \tag{4.6b}
\]

\[
[\text{SO}_4^\cdot] = \frac{k_8 + \left( \frac{k_9[S_2\text{O}_8^{\cdot2^-}]}{k_{18}[\text{DMPO}]} + \frac{k_{10}[S_2\text{O}_8^{\cdot2^-}]}{k_{19}[\text{DMPO}]} \right) k_1}{k_{13} + k_{17}[\text{DMPO}]} \tag{4.7b}
\]

The formation rate of DMPO−SO\(_4^\cdot\) is written as follows:

\[
\frac{dC_{\text{DMPO-SO}_4^\cdot}}{dt} = \left( \frac{dC_{\text{DMPO-SO}_4^\cdot}}{dt} \right)_{\text{formation}} - \left( \frac{dC_{\text{DMPO-SO}_4^\cdot}}{dt} \right)_{\text{hydrolysis}} \tag{4.8a}
\]
where \( \left( \frac{dC_{DMPO-SO4\text{-}}}{dt} \right)_{\text{formation}} = k_{17}[\text{DMPO}[SO_4^\cdot]] \) and

\[
\left( \frac{dC_{DMPO-SO4\text{-}}}{dt} \right)_{\text{hydrolysis}} = k_{21}[\text{DMPO}^\cdot - SO_4^\cdot] \]

was a calculated value using change of \([\text{DMPO}^\cdot - SO_4^\cdot]\) over the reaction period in the adduct decay experiments (Figure 4.5).

Due to the rapid trapping of \( SO_4^\cdot \) by DMPO (40 mM), \([SO_4^\cdot]\) was very low under this steady-state condition. Therefore, the formation of \( \text{DMPO}^\cdot - SO_4^- \) was independent of both \([\text{DMPO}]\) and \([SO_4^\cdot]\), leading to pseudo-zero-order kinetics at the initiation of the reaction (Figure 4.4). If we let \( k'_{17} = k_{17}[\text{DMPO}[SO_4^\cdot]] \) and \( k_{\text{hydrolysis}} = k_{21}[\text{DMPO}^\cdot - SO_4^\cdot] \), Eq. (4.8a) simplified to:

\[
\frac{dC_{DMPO-SO4\text{-}}}{dt} = k'_{17} - k_{\text{hydrolysis}} = k_{\text{obs,DMPO-SO4}}. \tag{4.8b}
\]

The observed initial zero-order kinetics (\( k_{\text{obs,DMPO-SO4}} \)) is consistent with chemical dosimetry tests for \( \cdot\text{OH} \) measurements [227]. Combining Eq. (4.7b) and Eqs. (4.8a), we obtain:

\[
k_{\text{obs,DMPO-SO4}} = \frac{k_{17}k_{\text{US}}}{k_{13} + k_{17}[\text{DMPO}]} \left( k_9 + \frac{k_{10}}{k_{19}} \right) \times [S_2O_8^{2-}] + \left( \frac{k_{17}k_{\text{heat}}[\text{DMPO}]}{k_{13} + k_{17}[\text{DMPO}]} - k_{\text{hydrolysis}} \right)
\tag{4.9a}
\]

If we define \( M = \frac{k_{17}k_{\text{US}}}{k_{13} + k_{17}[\text{DMPO}]} \left( k_9 + \frac{k_{10}}{k_{19}} \right) \) and \( N = \frac{k_{17}k_{\text{heat}}[\text{DMPO}]}{k_{13} + k_{17}[\text{DMPO}]} - k_{\text{hydrolysis}} \), then

\[
k_{\text{obs,DMPO-SO4}} = M \times [S_2O_8^{2-}] + N \tag{4.9b}
\]
Therefore, the formation rate constant of DMPO$^-$–SO$_4^-$, $k_{\text{obs,DMPO-SO}_4^-}$, is linearly correlated to PS concentration. By altering the persulfate concentration, we obtained different $k_{\text{obs,DMPO-SO}_4^-}$ values in batch studies, as shown in Figure 4.6a. The observed data was fitted into Eq. (4.9b) and parameter constants M and N were obtained. The value of $k_8$ for PS dissociation was then calculated, as shown in Table 4.2. Similarly, the formation rate of DMPO$^-$–OH ($k_{\text{obs,DMPO-OH}}$) is:

$$
\frac{dC_{\text{DMPO-OH}}}{dt} = \left( \frac{dC_{\text{DMPO-OH}}}{dt} \right)_{\text{formation}} - \left( \frac{dC_{\text{DMPO-OH}}}{dt} \right)_{\text{hydrolysis}} = k_{\text{obs,DMPO-OH}} = M'[S_2O_8^{2-}] + N'
$$

(4.10)

where $\left( \frac{dC_{\text{DMPO-OH}}}{dt} \right)_{\text{hydrolysis}} = k_{22}[\text{DMPO}^–\text{–OH}]$ was measured in adduct decay experiments (Figure 4.5), $M' = \frac{k_{13}}{k_{17}[\text{DMPO}]^2} \left( \frac{k_9 + k_{10}}{k_{18} k_{19}} \right)$ and $N' = \left( \frac{k_{\text{heat}}}{k_{17}[\text{DMPO}]} + k_{\text{US}} - k_{\text{hydrolysis}} \right)$. Eq. (4.10) suggests a linear relationship for $k_{\text{obs,DMPO-OH}}$ and PS concentration, as illustrated in Figure 4.6b. Since $k_{13a}$ in Table 4.1 may be under-estimated and there is no experimentally reported value for $k_{17}$, both rate constants in our system were fitted using Eq. (4.10) and are listed in Table 4.2.

4.4.4 Role of Free Radicals in Activation

The radical recombination shown in Table 4.1 may also alter SO$_4^{2-}$ production and subsequent contaminant oxidation. For example, excess 'OH may reduce SO$_4^{2-}$ formation due to the reaction of the two radical species (R14, SO$_4^{2-}$ + 'OH $\rightarrow$ HSO$_5^-$ $\rightarrow$ H$^+$ + SO$_4^{2-}$).
+ 1/2O₂). To evaluate the effects of \( \cdot \)OH on SO₄²⁻ formation (R9, \( S₂O₈^{2-} + \cdot \)OH → H⁺ + SO₄²⁻ + SO₄⁻ + 1/2O₂, and R14), the probe compound NB was used. Based on its high Henry’s Law constant, we assume that NB accumulates on the bubble-water interface and scavenges \( \cdot \)OH (R27) there [228]. NB is not expected to scavenge SO₄⁻ due to the low reaction rate constant (R26). Thus, the presence of NB in solution (e.g., 1mM) interrupts R9 and R14 and ultimately alters DMPO−SO₄⁻ formation. Additionally, at a high DMPO concentration, radical concentrations are very low and R14 is negligible compared with R9. Thus, a DMPO concentration (1 mM) that fell in the linear section in Figure 4.3 was used to determine if both R9 and R14 played roles in SO₄⁻ production.

Figure 4.7 illustrates adduct formation in the absence and presence of NB. An obvious reduction was observed for both adducts with NB present. The decrease in DMPO−OH concentration was expected due to scavenging of \( \cdot \)OH by NB. The reduced DMPO−SO₄⁻ concentration is attributed to a decrease in R9 with reduced \( \cdot \)OH. The decrease in DMPO−SO₄⁻ concentration at two initial NB concentrations was not significantly different confirming that NB did not react with SO₄⁻. R14 did not appear to play an important role here, otherwise an increased DMPO−SO₄⁻ concentration would have been observed. A comparable role for R9 and R14 was also excluded. No or negligible change in DMPO−SO₄⁻ yield was expected if R9 and R14 were comparable. Even under a low concentration of spin trap reagent, the concentrations of \( \cdot \)OH and SO₄⁻ were relatively low as compared to PS. Therefore, R9 has a higher reaction rate and out-
competes R14 in spite of a higher reaction rate constant for the latter reaction. This comparative study verified the *OH activation of PS through R9.

4.4.5 Modeling Reactivity at the Bubble-Water Interface

Both thermal and radical activation of PS occurred at the bubble-water interface with an unknown spatial size. The size of interface was a key factor in determination of the temperature gradient that affected the reaction rate and pathway. To determine the size of interface, a simple model describing the spatial distribution of temperature and reactivity surrounding a cavitation bubble was developed.

Assumptions for model development

- All cavitation bubbles are spherical. 
  
  *This is a commonly used assumption which allows one to simplify the multi-bubble system. In a 20 kHz system, Colussi et al. (1998) [229] assigned $R_0 = 2.0 \mu m$ and $R_{max} = 30.0 \mu m$ to achieve a collapse temperature of 5000 K. In our calculations, we utilized the same bubble radius.*

- Heat transfer is instantaneous across the interface.

  *Suslick and Flannigan (2008) [215] report a cooling rate of $\sim 10^{12} K \text{s}^{-1}$ inside the bubble, suggesting that the energy from bubble collapse is released instantaneously. Thus, the modeling of heat transfer can be simplified to an energy balance problem. The values of 5000 K [14, 215], 2260 K (see calculation in the SI) and 293 K were*
assigned as the temperature of gas phase, bubble-water interface and bulk solution, respectively.

- 10% of the bubble radius serves as a first approximation of the interfacial region ($R_{\text{interface}} = 1.1R_0$).

Kamath et al. (1993) estimated the reactive region to be 10-20% of initial bubble size in an argon-purged system (21kHz) [230]. For our 20 kHz system, we selected a value equal to 10% of the bubble radius as the interfacial region. The corresponding 200 nm scale is similar to previous reports of the interfacial thickness (200 – 270nm) in 20 kHz horn type systems [14, 231].

- The physics resulting in asymmetric bubble dynamics, such as bubble interactions, are negligible.

**Kinetics at the interface**

Both observed and fitted $k$ values in Table 4.2 are a reflection of the total aqueous solution sonicated in the reactor. Thus, a conversion from observed reaction rates to kinetics at the interface, where reactions really occur, is needed before predicting the interface size. The volume of the interfacial region may be quite small, due to the steep temperature gradient and the limited mass transfer of free radicals surrounding cavitation bubbles. We assumed all reactions occurred at the interface and formed adducts were immediately released from the compact interfacial region to bulk solution following collapse of the cavitation bubble. Thus, the following expression was derived to relate $k_{\text{interface}}$ with $k_{\text{obs}}$ on the basis of a mass balance:
\[
\frac{dC_{\text{obs}}}{dt} \times V_{\text{solution}} = \frac{dC_{\text{interface}}}{dt} \times V_{\text{interface}}
\]

(4.11a)

where \( \frac{dC_{\text{obs}}}{dt} = k_{\text{obs}} \) and \( \frac{dC_{\text{interface}}}{dt} = k_{\text{interface}} \), or

\[
k_{\text{interface}} = \frac{V_{\text{solution}}}{V_{\text{interface}}} k_{\text{obs}}
\]

(4.11b)

where \( V_{\text{solution}} \) is the total solution volume (25 mL), \( V_{\text{interface}} = \frac{4}{3} \pi (R_{\text{interface}}^3 - R_0^3) \times N \) is the volume of interfacial shell surrounding cavitation bubbles. The estimation method from Colussi et al. (1998) [229] and an acoustic emission method including fast fourier transform (FFT) and inverse FFT [232] were used to estimate the cavitation bubble number \( (N) \) and total bubble number \( (N_t) \), respectively. These methods are explained in the supporting information (SI). For our operational conditions, the cavitation bubble number was calculated to be \( 1.56 \times 10^7 \) s\(^{-1} \), which falls within the predicted range of \( 10^6 - 10^8 \) for a horn type ultrasonic system driven at 20 kHz [233-235]. At \( R_0 = 2.0 \) μm and \( R_{\text{interface}} = 2.2 \) μm, \( V_{\text{interface}} = 1.73 \times 10^{-4} \) mL. Therefore, the rate constants at the interface, \( k_{\text{interface}} \), were calculated to be 5 orders of magnitude \( (25\text{mL}/1.73 \times 10^{-4} \text{mL} \approx 10^5) \) greater than the observed and fitted values in aqueous solutions (Table 4.2).

The interfacial rate constants calculated using Eq. (4.11b) agree well with the observation of DMPO adduct formation. For example, \( k_{13b} \) was almost 3 orders of magnitude greater than that in ambient temperature, which supports the conclusion that the reaction between water and \( \text{SO}_4^{2-} \) was much enhanced at the bubble-water interface.
resulting in higher \(^{\cdot}\text{OH}\) yields (Figures 4.3 and 4.4). As shown in Table 4.1, \(k_{17}\) was much smaller than \(k_{18}\), which was consistent to the low DMPO\(^{-}\text{−SO}_4\)\(^{-}\) but high DMPO\(^{-}\text{−OH}\) yields. The interfacial value of \(5.49 \times 10^{-6}\ \text{s}^{-1}\) for \(k_{8,\text{int}}\) was 2 orders of magnitude higher than \(1.01 \times 10^{-8}\ \text{s}^{-1}\) at 20 °C [198]. According to [198], the Arrhenius equation to estimate the dissociation rate of PS during thermal activation is:

\[
\ln k_a = \ln A - \frac{E_a}{RT}
\]

(4.12)

where \(\ln A = 33.6\), \(E_a = 134\ \text{kJ M}^{-1}\), \(R = 8.314\ \text{J K}^{-1}\ \text{M}^{-1}\), and \(T\) is temperature (K). Using Eq. (4.12), the corresponding temperature for \(k_{8,\text{int}}\) was calculated to be \(~ 330\ K\), which is considered as the effective temperature of the interfacial region surrounding cavitation bubbles. After submitting these re-calculated \(k\) values into Eqs. (4.5-7a), the concentrations of \(^{\cdot}\text{OH}, ^{\cdot}\text{H}, \text{and SO}_4^{-}\) were calculated as \(4.25 \times 10^{-11}\ \text{M}\), \(3.13 \times 10^{-11}\ \text{M}\), and \(1.94 \times 10^{-10}\ \text{M}\) at the bubble-water interface, respectively. The low concentration of free radicals indicates the steady-state assumptions in the kinetic calculations are valid.

**Determination of interface size**

With given model assumptions and recalculated kinetics at the interface, we present a double layer model to approximate the heat transfer across the interfacial region, as shown in Figure 4.9. The inner layer and outer layer were demarcated with the calculated effective temperature of 330 K. The inner layer (5000 – 330 K) can be considered as the typical bubble-water interface in the hot-spot theory, and the outer layer has temperature dropping from 330 K to 303 K which is the lowest temperature
requirement for observed PS dissociation [198]. The shell volume of inner layer is quite small, so in spite of its high temperature PS dissociates adequately as compared to outer layer with low temperature but large shell volume.

We estimated the energy (\(E_b\)) of a single bubble is \(\sim 1.18 \times 10^{-7} \) J (see calculation in the SI), which was similar to the reported value of \(1.03 \times 10^{-8} \) J in a 52 kHz ultrasonic system [236]. This energy released from bubble collapse first heat up the inner layer (Figure 4.9) surrounding the bubble, resulting in a temperature decrease (\(\Delta T\)) from bubble to interface:

\[
E_b = \rho_w VC_p \Delta T
\]

(4.13)

where \(\rho_w\) is the water density (1000 kg m\(^{-3}\); volume of supercritical water in the inner layer is relatively small as compared to the double-layer interface, so the density change under supercritical conduction [237] is neglected and 1000 kg m\(^{-3}\) is used for a consistent calculation in this model), \(V = \frac{4\pi}{3}(r^3 - R^3)\) is the shell volume (m\(^3\); \(r\) is the interface radius, m), and \(C_p\) is the heat capacity for water (\(4.2 \times 10^3\) J kg\(^{-1}\) K\(^{-1}\)). Given the collapse temperature of bubble (5000 K [215]) and effective temperature of interface (330 K), the thickness of inter layer was calculated as 111 nm. In the inner layer, we assumed the cooling rate was still extremely high due to the large temperature gradient. Thus, we can again use Eq. (4.16) to calculate the thickness of outer layer (4.148 \(\mu\)m) where temperature dropped from 330 K to 303 K. The total thickness of 4.259 \(\mu\)m for interfacial region (two layers) was more than 20 times of previous reported thickness and
twice of the original bubble radius. The interfacial region for PS dissociation extended a much larger distance due to the instability of PS even at a relatively low temperatures (303 K) [198]. This calculation suggests that the interfacial region, or reactive region, varies depending on the specific reaction. A reaction which requires a high temperature and is diffusion limited necessitates a relatively small interfacial region, or vice versa. Therefore, this extended reactive region is applicable to PS dissociation, but not to radicals diffusing from cavitation bubbles.

**Temperature and reactivity distribution**

The energy-balance model cannot estimate the temperature change with distance in a layer. Since the heat transfer occurs instantaneously, we considered the steady-state heat transfer for a reasonable predication of temperature distribution at the interface. Typically, heat transfer in a homogeneous medium is governed by the following equation [220, 238, 239]:

\[
\frac{\partial T}{\partial t} = \kappa \nabla^2 T \tag{4.14}
\]

where \( \kappa = \frac{\lambda}{\rho C_p} \) is the thermal diffusivity (m\(^2\) s\(^{-1}\)); \( \lambda \) is the thermal conductivity, W m\(^{-1}\) K\(^{-1}\); \( \rho \) is the fluid density, kg m\(^{-3}\)). For a spherical shell surrounding a cavitation bubble with a radius \( r \), Eq. (4.14) can be simplified to:

\[
\frac{\partial}{\partial r} \left( r^2 \frac{\partial T}{\partial r} \right) = 0 \tag{4.15}
\]
The solution for Eq. (4.15) is:

\[ T = \frac{A}{r} + B \]  \hfill (4.16)

where A and B are parametric constants. With the given initial values (5000 K at 2.000 μm, 330 K at 2.111 μm and 303 K at 4.259 μm), Eq.(4.16) becomes:

\[
\begin{cases}
T = \frac{1.77 \times 10^{-1}}{r} - 8.37 \times 10^{-4} \text{(inner layer)} \\
T = \frac{8.89 \times 10^{-5}}{r} + 2.89 \times 10^{-2} \text{(outer layer)}
\end{cases}
\]  \hfill (4.17)

Given Eq. (4.17), we calculated the spatial temperature distribution and corresponding dissociation rate of PS using Eq. (4.12) at the bubble-water interface, as shown in Figure 4.8. The temperature dropped exponentially with respect to distance from the gas phase of the cavitation bubble and finally reached ambient temperature. This prediction agrees with previous results of temperature distribution at the interface [230]. The temperature in the inner layer (< 2.111 μm) may be beyond the critical point for supercritical water [220], thus providing evidence for a high fitted \( k_{13} \) value and contribution of R13 to high \(^\cdot\text{OH} \) yield in the US-PS system. The PS dissociation rate decreased quickly due to the steep temperature gradient at the interface. The trend for dissociation rates mirrors the temperature change in the interfacial region.

It is possible that the double layer model based on energy balance may overestimate the interfacial region size since instantaneous heat transfer from inner layer to outer layer was assumed. The combination of double layer model and steady-state heat
transfer delivers a more complete modeling of the temperature and reactivity distribution in the interfacial region surrounding a cavitation bubble.

4.5 Environmental Application

PS has seen increased use in ISCO applications. Meanwhile, unique physical and chemical effects of US have been utilized to oxidize contaminants in aqueous solution, desorb contaminants from particle surfaces, and facilitate mass transfer in porous media [17, 18], which all may contribute to improvement of ISCO remediation efforts. Thus, US offers an interesting option to activate PS because the combination of US and PS results in benefits beyond activation of PS. The US devices may be implemented downstream so that US can activate the PS mixed in a contaminant plume, thereby enhancing the contaminant degradation at the implementation site. Likewise, sonication in the direction of plume flow may facilitate the contaminant transport resulting in a faster remediation. The 'OH oxidation will be a dominant reaction pathway at the contamination site based on the mechanisms examined in this study. Future studies including optimization of operational conditions (e.g., US power level, US frequency, and PS dosage) and designs of scale-up treatments are necessary before seeing an economical application of US-PS for contaminant remediation.
4.6 Acknowledgements

Funding from Ohio Sea Grant College Program is gratefully acknowledged.
Table 4.1 Principal reactions in US-PS system

<table>
<thead>
<tr>
<th>R#</th>
<th>Reaction</th>
<th>Rate constant, M⁻¹ s⁻¹</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H₂O → 'OH + 'H</td>
<td>4.8×10⁻³ s⁻¹</td>
<td>this study</td>
</tr>
<tr>
<td>2</td>
<td>'OH + 'H → H₂O</td>
<td>7.0×10⁹</td>
<td>[225]</td>
</tr>
<tr>
<td>3</td>
<td>'OH + 'OH → H₂O₂</td>
<td>5.5×10⁹</td>
<td>[225]</td>
</tr>
<tr>
<td>4</td>
<td>'H + 'H → H₂</td>
<td>7.8×10⁹</td>
<td>[225]</td>
</tr>
<tr>
<td>5</td>
<td>'OH + H₂O₂ → H₂O + 'OH</td>
<td>2.7×10⁷</td>
<td>[225]</td>
</tr>
<tr>
<td>6</td>
<td>'H + H₂O₂ → H₂O + 'OH</td>
<td>9.0×10⁶</td>
<td>[225]</td>
</tr>
<tr>
<td>7</td>
<td>'OH + H₂ → H₂O + 'H</td>
<td>4.2×10⁷</td>
<td>[225]</td>
</tr>
<tr>
<td>8</td>
<td>S₂O₈²⁻ → 2 SO₄⁻</td>
<td>5.5×10⁶ s⁻¹</td>
<td>this study</td>
</tr>
<tr>
<td>9</td>
<td>S₂O₈²⁻ + 'OH → H⁺ + SO₄⁻ + SO₄⁻ + 1/2O₂</td>
<td>&lt;1×10⁶</td>
<td>[225]</td>
</tr>
<tr>
<td>10</td>
<td>S₂O₈²⁻ + 'H → H⁺ + SO₄⁻² + SO₄⁻</td>
<td>2.5×10⁷</td>
<td>[240]</td>
</tr>
<tr>
<td>11</td>
<td>S₂O₈²⁻ + SO₄⁻ → SO₄⁻² + S₂O₈⁻</td>
<td>6.6×10⁵</td>
<td>[240]</td>
</tr>
<tr>
<td>12</td>
<td>2 SO₄⁻ → S₂O₈⁻</td>
<td>4.4×10⁵</td>
<td>[241]</td>
</tr>
<tr>
<td>13a</td>
<td>SO₄⁻ + H₂O → H⁺ + SO₄⁻ + 'OH</td>
<td>6.0×10⁵ s⁻¹</td>
<td>[242]</td>
</tr>
<tr>
<td>13b</td>
<td>SO₄⁻ + H₂O (SC) → H⁺ + SO₄⁻² + 'OH</td>
<td>3.2×10⁴ s⁻¹</td>
<td>this study</td>
</tr>
<tr>
<td>14</td>
<td>SO₄⁻ + 'OH → HSO₅⁻ → H⁺ + SO₄⁻² + 1/2O₂</td>
<td>9.5×10⁹</td>
<td>[241, 242]</td>
</tr>
<tr>
<td>15</td>
<td>SO₄⁻ + 'H → H⁺ + SO₄⁻²</td>
<td>1.0×10⁶</td>
<td>[225, 241]</td>
</tr>
<tr>
<td>16</td>
<td>SO₄⁻ + H₂O₂ → 2H⁺ + SO₄⁻² + 'O₂⁻</td>
<td>1.2×10⁷</td>
<td>[242]</td>
</tr>
<tr>
<td>17</td>
<td>DMPO + SO₄⁻ → DMPO^−−SO₄⁻</td>
<td>2.8×10³</td>
<td>this study</td>
</tr>
<tr>
<td>18</td>
<td>DMPO + 'OH → DMPO^−−OH</td>
<td>2.8×10⁹</td>
<td>[218]</td>
</tr>
<tr>
<td>19</td>
<td>DMPO + 'H → DMPO^−−H</td>
<td>3.8×10⁹</td>
<td>[225]</td>
</tr>
<tr>
<td>20</td>
<td>DMPO + 'O₂⁻ → DMPO^−−O₂⁻</td>
<td>1.0×10⁴</td>
<td>[243]</td>
</tr>
<tr>
<td>21</td>
<td>DMPO^−−SO₄⁻ + H₂O → DMPO^−−OH + H⁺ + SO₄⁻²</td>
<td>1.5×10⁸ s⁻¹</td>
<td>this study</td>
</tr>
<tr>
<td>22</td>
<td>DMPO^−−OH+ H₂O → Product</td>
<td>1.8×10² s⁻¹</td>
<td>this study</td>
</tr>
<tr>
<td>23</td>
<td>CH₃SOCH₃ + SO₄⁻ → CH₃(CH₃)SO⁺ + H⁺ + SO₄⁻²</td>
<td>3.0×10⁹</td>
<td>[244]</td>
</tr>
<tr>
<td>24</td>
<td>(CH₃)₂COH + SO₄⁻ → Product</td>
<td>4.0×10⁵</td>
<td>[224]</td>
</tr>
<tr>
<td>25</td>
<td>(CH₃)₂COH + 'OH → Product</td>
<td>6.0×10⁸</td>
<td>[225]</td>
</tr>
<tr>
<td>26</td>
<td>(C₆H₅)NO₂ + SO₄⁻ → Product</td>
<td>&lt;10⁸</td>
<td>[245]</td>
</tr>
<tr>
<td>27</td>
<td>(C₆H₅)NO₂ + 'OH → Product</td>
<td>3.9×10⁹</td>
<td>[225]</td>
</tr>
</tbody>
</table>

Note: Argon purged solution, pH = 7.4, pKₐ of HSO₄⁻ = 1.92, pKa of 'HO₂ = 4.5, and SC indicates supercritical state; M s⁻¹, s⁻¹, and M⁻¹ s⁻¹ are units for zero-, first-, and second-order reaction rate constants, respectively.
Table 4. Observed and fitted reaction rate constants in aqueous solution

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate constant</th>
<th>Condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_1$</td>
<td>$1.75 \times 10^{-8}$ M s$^{-1}$</td>
<td>Observed (40 mM DMPO)</td>
</tr>
<tr>
<td>$k_8$</td>
<td>$2.02 \times 10^{-11}$ s$^{-1}$</td>
<td>Fitted</td>
</tr>
<tr>
<td>$k_{13}$</td>
<td>$1.19 \times 10^{-1}$ s$^{-1}$</td>
<td>Fitted</td>
</tr>
<tr>
<td>$k_{17}$</td>
<td>$1.03 \times 10^{-2}$ M$^{-1}$ s$^{-1}$</td>
<td>Fitted</td>
</tr>
<tr>
<td>$k_{21}$</td>
<td>$8.35 \times 10^{-3}$ s$^{-1}$</td>
<td>Observed (5 mM DMPO)</td>
</tr>
<tr>
<td>$k_{22}$</td>
<td>$9.99 \times 10^{-4}$ s$^{-1}$</td>
<td>Observed (5 mM DMPO)</td>
</tr>
<tr>
<td>$k_{obs, DMPO-OH}$</td>
<td>$4.85 \times 10^{-8}$ M s$^{-1}$</td>
<td>Observed (40 mM DMPO)</td>
</tr>
<tr>
<td>$k_{obs, DMPO-SO4^-}$</td>
<td>$3.00 \times 10^{-9}$ M s$^{-1}$</td>
<td>Observed (40 mM DMPO)</td>
</tr>
</tbody>
</table>

Note: M s$^{-1}$, s$^{-1}$, and M$^{-1}$ s$^{-1}$ are units for zero-, first-, and second-order reaction rate constants, respectively.
Figure 4. 1 Experimental setup for *in-situ* EPR measurements of sonicated solution

1 — Transducer  
2 — Horn  
3 — Argon gas inlet  
4 — Reactor  
5 — OH  
6 — SO₄⁻  
7 — DMPO  
8 — EPR spectrometer  
9 — Aqua-X tube  
10 — Spectrum
Figure 4. 2 EPR spectrum of sonicated persulfate (PS = 100 mM; DMPO = 40 mM; PD = 1.5 W mL⁻¹, □ — DMPO•−OH, a_N = 15.01, a_β-H = 14.72; ■ — DMPO•−SO_4^−, a_N = 13.67, a_β-H = 10.24, a_γ-H1 = 1.52, a_γ-H2 = 0.79)
Figure 4. 3 Adduction formation at different DMPO concentrations (PS = 1 mM; 
\[ PD = 1.5 \text{ W mL}^{-1} \])
Figure 4.4 DMPO adduct formation with sonication time (□—DMPO•−OH at 100 mM persulfate; ■—DMPO•−SO₄⁻ at 100 mM persulfate; △—DMPO•−OH at 1 mM persulfate; ▲—DMPO•−SO₄⁻ at 1 mM persulfate; ○—DMPO•−OH under sonication only; DMPO = 40 mM; PD = 1.5 W mL⁻¹).
Figure 4.5 Hydrolysis of DMPO adducts with time (□ — DMPO$^\cdot$OH; ■ — DMPO$^\cdot$SO$_4^-$; PS = 100 mM; DMPO = 5 mM; PD = 1.5 W mL$^{-1}$)
Figure 4. 6 Linear relationship between initial zero-order formation rate constants and persulfate concentrations for DMPO$^\cdot$SO$_4^-$ (a) and DMPO$^\cdot$OH (b; DMPO = 40 mM; PD = 1.5 W mL$^{-1}$)
Figure 4. 7 Adduct formation in the absence and presence of nitrobenzene (DMPO = 1Mm; PS = 1 mM; PD = 1.5 W mL⁻¹; P-value < 0.05 for DMPO•−OH suggests significant difference and P-value = 0.36 for DMPO•−SO₄⁻ suggests no significant difference)
Figure 4.8 Predicting spatial temperature distribution and corresponding dissociation rate of persulfate at the bubble-water interface ($R_0 = 2.0 \, \mu m$ in argon purged solution; bubble temperature $= 5000 \, K$ and $T_{\text{min}} = 303 \, K$; small graph depicts temperature change in outer layer)
Figure 4.9 Schematic of double layer model for interfacial region
CHAPTER 5

DESIGNING AND CHARACTERIZING A MULTI-STEPPED ULTRASONIC HORN FOR ENHANCED SONOCHEMICAL PERFORMANCE

(Ultrasonics Sonochemistry, 2015, 27, 325–333)
5.1 Abstract

The commonly used ultrasonic horn generates localized cavitation below its converging tip resulting in a dense bubble cloud near the tip and limiting diffusion of reactive components into the bubble cloud or reactive radicals out of the bubble cloud. To improve contact between reactive components, a novel ultrasonic horn design was developed based on the principles of the dynamic wave equation. The horn, driven at 20 kHz, has a multi-stepped design with a cone-shaped tip increasing the energy-emitting surface areas and creating multiple reactive zones. Through different physical and chemical experiments, performance of the horn was compared to a typical horn driven at 20 kHz. Hydrophone measurements showed high acoustic pressure areas around the horn neck and tip. Sonochemiluminescence experiments verified multiple cavitation zones consistent with hydrophone readings. Calorimetry and dosimetry results demonstrated a higher energy efficiency (31.3%) and a larger hydroxyl radical formation rate constant (0.36 μM min⁻¹) compared to typical horns. In addition, the new horn degraded naphthalene faster than the typical horn tested. The characterization results demonstrate that the multi-stepped horn configuration has the potential to improve the performance of ultrasound as an advanced oxidation technology by increasing the cavitation zone in the solution.

Keywords: multi-stepped, hydrophone, sonochemiluminescence, calorimetry, dosimetry
Nomenclature

a  displacement acceleration of micro-volume in horn rod (m s$^{-2}$)
A  transfer matrix for equivalent circuit
C$_p$  heat capacity of liquid (J kg$^{-1}$ K$^{-1}$)
c  speed of the sound wave (m s$^{-1}$)
d  diameter of cylindrical element in designed horn (m)
E  Young’s Modulus (Pa)
f  frequency of ultrasound (Hz)
k  angular wave number (m$^{-1}$)
M  mass of liquid (kg)
M$_p$  magnification factor of ultrasonic horn
P$_{ac}$  calorimetrically determined acoustic power (W)
P$_{to}$  total electrical power consumed by generator (W)
S  cross-sectional area of any given horn along x-axis (m$^2$)
T  temperature of the liquid (K)
t  time (s)
u  particle displacement in the horn due to longitudinal vibration along the x-axis (m)
<table>
<thead>
<tr>
<th>Greek letters</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$</td>
<td>parameter for the equivalent circuit</td>
</tr>
<tr>
<td>$\rho$</td>
<td>density of horn material (kg m$^3$)</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>stress acting on any given micro-volume of the horn (Pa)</td>
</tr>
<tr>
<td>$\omega$</td>
<td>angular frequency (rad s$^{-1}$)</td>
</tr>
</tbody>
</table>
5.2 Introduction

A typical ultrasonic system used to obtain cavitation effects is composed of a power supply, a transducer, and a horn (Figure 5.1a) [7, 87]. The horn component, typically a solid metal rod in one of a variety of tapered shapes (e.g., stepped, conical, exponential, and catenoidal) [48, 85, 89, 90, 109, 246], amplifies the mechanical vibration generated by the electromechanical transducer [7, 48, 87, 247]. Horns in common use have shrinking cross-sectional areas that concentrate energy at a small tip, resulting in a non-uniform acoustic field and localized cavitation in solution. The concentration of cavitation near the horn tip limits the degradation efficiency of a contaminant compared to more distributed cavitation zones [7, 34, 35]. The dense bubble cloud near the tip also limits the mass transfer of hydroxyl radical (·OH) in the reactor, consequently restricting contaminant reaction by oxidation.

Different strategies have been tested to improve the degradation efficiency of commonly used horns. These include optimizing the geometries of reactors [85, 248, 249], applying different operational conditions (e.g., frequency, power input, and pulsing the ultrasonic signal) [250-253], and modifying sonication media (e.g., additives and purging oxygen) [252, 254-256]. A redesign of the horn configuration provides an alternative solution that potentially increases energy-emitting surfaces, reactive areas, and cavitation volumes [7, 48, 257].

Therefore, for this study, a horn with a multiple-step configuration and a cone-shaped tip (Figure 5.1b) was designed to enhance both cavitation effects and energy efficiency. The dynamic wave equation and equivalent circuit method were used in the
design and calculation processes. Performance of the new horn was evaluated by different physical and chemical methods. First, hydrophone measurements and sonochemiluminescence (SCL) imaging were conducted to demonstrate and verify how the designed horn increased energy-emitting surfaces and created multiple cavitation zones. Next, the acoustic power and 'OH yield were measured through calorimetry and dosimetry experiments. Finally, sonochemical degradation of naphthalene, a polycyclic aromatic hydrocarbon (PAH), was conducted to evaluate the capability of the designed horn for use in a larger-scale advanced oxidation process (AOP). We also compared the performance of the designed horn against that of a typical horn driven at 20 kHz.

5.3 Ultrasonic Horn Design

5.3.1 Design Principles

Horn design theory is based on the longitudinal vibration equation of a variable cross-section rod (Figure 5.2a) [48, 87, 247]. Microscopically, molecules in the solid rod vibrate after absorbing acoustic energy from a transducer, cause adjoining molecules to oscillate before returning to their original position due to the elastic restoring force [36, 115, 258]. The molecule displacement ($u$) is parallel to the direction of longitudinal sound wave propagation in the rod [116]. Macroscopically, any small volume element ($dV = S \cdot dx$) in the variable cross-section rod forming the horn (Figure 5.2a) repeats the same vibration and transmits the oscillation to the next micro-element when the stresses of the acoustic waves are uniformly distributed over the rod’s cross section. Based on
Newton’s Second Law, a dynamic equation of vibration for the small volume element \((dV)\) can be developed such that \([48, 257]\):

\[
\frac{\partial(S \cdot \sigma)}{\partial x} \, dx = S \cdot \rho \frac{\partial^2 u}{\partial t^2} \, dx
\] 

(5.1)

where \(S\) is cross-sectional area \((m^2)\), \(\sigma = E \frac{\partial u}{\partial x}\) is stress \((Pa)\), \(E\) is Young’s Modulus \((Pa)\), \(\rho\) is density of horn material \((kg \ \text{m}^{-3})\), and \(t\) is time \((s)\). The left side of Eq. (5.1) is the force, \(F = S \cdot \sigma\), acting on the small volume element, \(dV\). On the right side of Eq. (5.1),

\[S \cdot \rho \cdot dx = dm,\]

where \(dm\) is the mass of the micro-element, and the expression \(\frac{\partial^2 u}{\partial t^2} = a\), where \(a\) is the displacement acceleration.

Usually, simple harmonic vibration in steady-state mode is used to describe vibration in a micro-element \([36, 115]\). Eq. (5.1) can be modified to:

\[
\frac{\partial^2 u}{\partial x^2} + \frac{1}{S} \cdot \frac{\partial S}{\partial x} \cdot \frac{\partial u}{\partial x} + k^2 u = 0
\] 

(5.2)

where \(k^2 = \frac{\omega^2}{c^2}\), \(k = \frac{2\pi}{\lambda}\) is the angular wavenumber, \(\omega = \frac{2\pi}{T} = 2\pi f\) is the angular frequency, and \(c = \left(\frac{E}{\rho}\right)^{\frac{1}{2}}\) is the propagation velocity of the longitudinal wave within the horn rod.

For a cylindrically shaped horn rod, the area of its cross section remains unchanged; thus, \(\frac{\partial S}{\partial x} = 0\). Therefore, Eq. (5.2) simplifies to:
\[
\frac{\partial^2 u}{\partial x^2} + k^2 u = 0
\]  
(5.3)

The solution of Eq. (5.3) for any single-element cylindrical horn is:

\[
u = A \cos kx + B \sin kx
\]  
(5.4)

With Eq. (5.4), displacement \( u \) and the parametric constants \( A \) and \( B \) can be calculated using the following boundary conditions: (i) forces acting on two free ends are zero; (ii) forces at the joint connection are equal but opposite; and (iii) molecule displacements at the joint connection are the same \([48, 87, 247]\). From these parametric constants, characteristics such as resonance frequency \( (f) \) and magnification factor \( (M_p) \) can be determined for a given single-element horn, or \( M_p \) and \( f \) can be chosen and parametric constants determined.

5.3.2 Horn Configuration Design

Design of the horn occurs sequentially: 1) first, key parameters such as maximum diameter, total length, and \( M_p \) are chosen for an optimal performance that includes planar homogeneous propagation of ultrasound waves through the horn, vibration resonance at the horn output end, and non-concentrated acoustic energy below the tip; 2) next, specific goals such as element number and surface area are determined depending on treatment requirements (e.g., volume of treated water and sonication time); and 3) the final configuration of horn (i.e., diameter and length) is calculated based on the dynamic vibration theory of the horn rod.
5.3.2.1 Design requirements

The horn dimension should not exceed a quarter of the ultrasound wavelength in the horn rod ($\lambda/4 = 280 \text{ mm}/4 = 70 \text{ mm}$) so that the acoustic propagation is planar homogeneous [48, 257]. The half-wave horn, which is multiples of the half-wavelength in length, is chosen to obtain mechanical resonance at the desired frequency. For our horn driven at 20 kHz, a length of one full wavelength (280 mm) of acoustic waves propagating in the stainless steel rod ($c = \sim 5600 \text{ m s}^{-1}$) was used (Figure 5.1b). Then, a $M_p$ of 2.0 was used for the designed horn because a larger value would increase the converging acoustic power at the output end, resulting in a concentrated cavitation volume below the tip and non-uniform acoustic field in the reactor. Lastly, in order to obtain multiple reactive zones, both the multi-stepped neck configuration and the cone-shaped tip were introduced into the design, as illustrated in Figure 5.1b. The multi-stepped neck design was used to introduce more energy-emitting surfaces and larger cavitation volumes [246] since it provides more of the “edge” areas from where the ultrasound waves are emitted [34, 35]. McMurray and Wilson imaged the SCL for both plane-ended and cone-ended horns [35], and observed an elongated cavitation area below the cone-shaped tip and additional light-emission areas surrounding it.

5.3.2.2 Horn configuration calculations

After confirming key parameters, the final horn configuration is determined using the equivalent circuit method [87, 247, 259], since it is easier to calculate parameters of a multi-element horn as compared to the conventional analytical method of solving the
dynamic wave equations [48, 87, 247, 259]. In the equivalent circuit method, any given horn with a single element (e.g., horn in Figure 5.2a) can be considered as a general equivalent circuit (Figure 5.2b) with the following mathematical expression:

\[
\begin{align*}
F_2 &= \alpha_{21} \ddot{u}_1 + \alpha_{22} F_1 \\
\ddot{u}_2 &= \alpha_{11} \ddot{u}_1 + \alpha_{12} F_1
\end{align*}
\]  
\tag{5.5}

where \( F_1 \) and \( F_2 \) are forces acting on the horn input end (left) and the output end (right), respectively; \( \ddot{u}_1 \) and \( \ddot{u}_2 \) are molecule vibration velocities at the input and output ends, respectively; and \( \alpha_{11}, \alpha_{12}, \alpha_{21}, \) and \( \alpha_{22} \) are the parameters for the equivalent circuit model.

The equivalent matrix manipulation for the circuit is:

\[
\begin{bmatrix}
\ddot{u}_2 \\
\ddot{F}_2
\end{bmatrix} =
\begin{bmatrix}
\alpha_{11} & \alpha_{12} \\
\alpha_{21} & \alpha_{22}
\end{bmatrix}
\begin{bmatrix}
\ddot{u}_1 \\
F_1
\end{bmatrix}
\]  
\tag{5.6}

where \( A = \begin{bmatrix} \alpha_{11} & \alpha_{12} \\ \alpha_{21} & \alpha_{22} \end{bmatrix} \) is defined as the transfer matrix for the equivalent circuit, and \( \alpha_{11} \) in the matrix is equal to \( M_p \).

For a multi-element horn, the \( i^{th} \) transfer matrix can be expressed as:

\[
A_i = \begin{bmatrix}
\alpha_{11}^i & \alpha_{12}^i \\
\alpha_{21}^i & \alpha_{22}^i
\end{bmatrix}
\]  
\tag{5.7}

Since \( A_1, A_2, \ldots, A_i \) are multipliable 2×2 matrices, the overall \( A \) for the multi-element horn can be obtained as follows:

139
For any cylindrically shaped element of our designed horn in Figure 5.1b, \( A_i \) determined from Eq. (5.3) is:

\[
A_i = \begin{bmatrix}
\cos (k_i l_i) & - j (\sin (k_i l_i)) \\
-j pcS_i (\sin (k_i l_i)) & pcS_i (\cos (k_i l_i))
\end{bmatrix}
\]  

Therefore, \( A \) for our eight-element cylindrical horn is:

\[
A = \begin{bmatrix}
\cos (k_1 l_1) & - j (\sin (k_1 l_1)) \\
-j pcS_1 (\sin (k_1 l_1)) & pcS_1 (\cos (k_1 l_1))
\end{bmatrix} \times \begin{bmatrix}
\cos (k_2 l_2) & - j (\sin (k_2 l_2)) \\
-j pcS_2 (\sin (k_2 l_2)) & pcS_2 (\cos (k_2 l_2))
\end{bmatrix} \times \cdots \times \begin{bmatrix}
\cos (k_8 l_8) & - j (\sin (k_8 l_8)) \\
-j pcS_8 (\sin (k_8 l_8)) & pcS_8 (\cos (k_8 l_8))
\end{bmatrix}
\]  

Using Eq. (5.10), the two unknowns, \( S \) (expressed in terms of \( d \), 26-38 mm) and \( l \) (12-75 mm) are determined for each element (Figure 5.1b) based on many trials of calculations performed by COMSOL Multiphysics. The selected values of \( d \) and \( l \) in current design generate a more evenly distributed acoustic pressure in the simulation and yield a \( M_p \) value equal to 2.0.

5.4 Materials and Methods

5.4.1 Materials

Terephthalic acid (TA, 98 %) and luminol (3-aminophthalhydrazide, 97 %) were purchased from Sigma Aldrich. Standard 2-hydroxyterephthalic acid (HTA) was prepared following the method described by Mason et al. [260]. Sodium hydroxide (NaOH),
potassium dihydrogen phosphate (KH$_2$PO$_4$), and disodium hydrogen phosphate (Na$_2$HPO$_4$) purchased from Fisher Scientific were used as solution buffers. All stock solutions were prepared using the deionized (DI) water (Milli-Q, Millipore) with a resistivity of $R$ equal to 18.2 MΩ cm.

5.4.2 Ultrasonic System

The designed horn, engineered and fabricated by Etrema Products, Inc., is made of stainless steel and driven at a frequency of 20 kHz. A Branson BCA 900 series power supplier transmits electrical power to a Branson 902R Model ultrasonic transducer, which converts electricity to mechanical vibration. Cold air, filtered through a desiccant and a 5μm Whatman filter, was used to cool the transducer. A cooling bath (Isotherm 95036, Fisher Scientific) was connected to the water jacket of a cylindrical reactor with a spherical bottom (100 mm in diameter, 210 mm in height, and 1.5 L in volume) to control the temperature and to obtain the desired initial solution temperature. A Teflon cap was screwed to the horn at the nodal point of the horn and tightly fit into the glass reactor to: 1) seal the reactor; 2) accurately position the ultrasonic horn; and 3) hold the ultrasonic horn.

A traditional ultrasonic horn system driven at 20 kHz (Sonic Dismembrator 550, Fisher Scientific) was used for comparison. This horn had a tip area of 1.2 cm$^2$ and was used in a 50 mL glass rosette reactor. Temperature control was accomplished by a cooling bath (1006S, Fisher Scientific). Conditions and the surrounding environment were maintained the same throughout all experiments for both ultrasonic systems.
5.4.3 Horn Characterization

5.4.3.1 Acoustic field measurements

Hydrophones, which record underwater sound by receiving pressure signals [261-263], have been used to map the acoustic pressure distribution in sonochemical reactors [261-263]. In our experiments, the piezoelectric materials in a Reson T4013-type hydrophone (Reson A/S) transferred pressure signals to electrical signals that then were captured by a TDS 5000 Tektronix oscilloscope (Tektronix, Inc.) with a sampling frequency of 125 kHz. All root-mean-square values of voltage output from the oscilloscope were recorded by a Tektronix Toolbar for Excel, which is an add-on to Microsoft Excel from Tektronix “OpenChoice™ Solutions Software Developers’ Kit”. With the oscilloscope voltage output and hydrophone sensitivity (–211 dB re V/μPa), the ultrasonic pressure was calculated. All hydrophone measurements were conducted in a large beaker because it was not possible to fit the hydrophone into both glass sono-reactors. The hydrophone was positioned at different locations in the beaker using a manual positioning system. The origin of our system was just below the horn tip (X, Y, Z = 0, 0, 0). Then, we moved the hydrophone in the X-Y plane (horizontal) followed by movement in Z direction (vertical). The acoustic pressure measurements were conducted at 1cm intervals using the manual positioning system. These measurements were then plotted as contours to create an acoustic pressure map for the designed horn. The frequency spectrum analysis was carried out using PeakFit software version 4.12, and contour graphical display was performed with OriginPro 7.5.
5.4.3.2 Sonochemiluminescence

Sonochemiluminescence (SCL) is a phenomenon where the \(^{\cdot}\)OH generated sonochemically oxidizes luminol, thereby producing light emission [35, 264]. Since the SCL of luminol illustrates the spatial distribution of cavitational activities in an aqueous solution, it was used to verify hydrophone measurements. The luminol concentration was \(10^{-3}\) M with a pH of 11.3. When prepared luminol solution was sonicated in the glass reactors, SCL imaging was taken by a Nikon D3100 14.2MP Digital SLR Camera (18-55mm f/3.5-5.6 AF-S DX VR Nikkor Zoom Lens) at an exposure time of 25 seconds.

5.4.3.3 Calorimetry

The acoustic power delivered into aqueous solution was measured using the calorimetry method [255, 265, 266], in which cavitation energy is assumed to be completely converted into heat [191]. A K-type thermocouple (5SRTC-TT-K-20-36, Omega Engineering Inc.) was used to measure the change in water temperature generated by ultrasonic irradiation. The acoustic power \(P_{ac}\) transmitted to the DI water was calculated with the following equation [265, 266]:

\[
P_{ac} = \left(\frac{dT}{dt}\right) \times C_p \times M
\]  

(5.11)

where \(C_p\) is the heat capacity of water (4.2 kJ kg\(^{-1}\) K\(^{-1}\)) and \(M\) is the mass of water irradiated (kg). The total electrical power \(P_{to}\) consumed by the ultrasonic generator was calculated by multiplying the quoted maximum rating power (1000 W and 550 W for designed and typical horns, respectively) by the selected output percentage [266].
In order to fully understand the performance of the designed horn under different operational conditions, the power measurements were carried out in a series of initial temperatures (1.0 °C, 10 °C, 30 °C, 40 °C, 50 °C, and 60 °C) and electrical power inputs (50 %, 60 %, 70 %, 80 %, 90 %, and 100 %). The effect of horn position on cavitation activity was not studied in this experiment because the Teflon clamp did not allow the submerged horn’s position to be varied. All measurements were duplicated.

5.4.3.4 Dosimetry

Terephthalate dosimetry was conducted to quantify ’OH production. During the process, TA scavenges ’OH to form HTA [227, 260, 267-269]. Sonication of the 2mM TA solution at pH 7.4 following the method of Mason et al. [260] was carried out under different calorimetric acoustic powers and initial solution temperatures. HTA in the sonicated and calibration samples was measured by a spectrofluorophotometer (RF-5301PC, Shimazu) with an excitation wavelength of 315 nm and an emission wavelength of 425 nm [270].

5.4.3.5 Sonolysis of naphthalene

Sonolytic degradation of naphthalene at concentrations of 10 and 50 μM was conducted with both designed and typical horns at room temperature (20 °C). All reaction solutions were adjusted to pH 7.4 with the phosphate buffer. Similar temperature measurements throughout the reactor indicated that sonication provided sufficient mixing. Thus, no external mixing was used. During sonication, a 0.5 mL sample was taken from
the reactor at designated times for analysis. The sample volume taken during the course of sonication did not exceed 1% of the total volume to maintain the same acoustic field and bubble clusters in the reactor. All sonolytic experiments were duplicated.

The analysis of naphthalene was performed using a high-performance liquid chromatograph (HPLC) equipped with a diode array detector (DAD). A mobile phase of 80/20 (v/v) and a flow rate of 0.5 mL min⁻¹ through a C18 Hypersil ODS column was used. The spectrofluorophotometer (RF-5301PC, Shimazu) was also used to observe naphthalene (333 nm) reduction and product (300 nm) formation during the sonolysis experiments.

5.5 Results and Discussion

5.5.1 Hydrophone and Sonochemiluminescence (SCL) Measurements

Physical characterization of the newly designed horn was first conducted to characterize the energy-emitting surface and cavitation volume. The resonant frequency of 20 kHz was verified by spectrum analysis of the hydrophone signal (Figure 5.3). The resonant frequency (f) was dominant in the system. Subharmonic (1/8 f and 1/2 f) and ultraharmonic (2 f and 3 f) frequency vibrations were also observed in the signal.

Figure 5.4 shows the distribution of acoustic pressures for designed and typical horns. The red color indicates the highest voltage output corresponding to the highest acoustic pressure and blue indicates the lowest voltage readings. The typical horn delivers
only one high acoustic pressure area below its tip, whereas our multi-stepped design generates multiple high acoustic pressure regions around the “edges.” A high acoustic pressure region usually suggests a location of intense cavitation.

The existence of cavitation zones was verified by SCL imaging. Sonochemically generated 'OH reacts with luminol resulting in light emission. Figure 5.5 illustrates that intense SCL appears in a relatively large vicinity of the designed horn, but the intense cavitation region of a typical horn is only found below the titanium tip. The greater volume of cavitation in the designed horn, indicated by the intense SCL, is expected to increase 'OH yield and distribute the radicals along the horn neck compared to the dense bubble cloud of the typical horn. Thus, more contaminant molecules are expected to be exposed to the radicals in these cavitation zones, thereby improving contaminant degradation. In addition, the intense SCL, which requires a high acoustic pressure to occur, is consistent with the hydrophone measurements in Figure 5.4a. Both the hydrophone measurements and the SCL images demonstrate that the multi-stepped design and cone-shaped tip introduce more energy-emitting surfaces, multiple reactive zones, and ultimately a larger cavitation volume.

5.5.2 Calorimetry

The calorimetrically determined acoustic power was plotted against initial temperature at different electrical power inputs determined from the dial setting on the Branson BCA 900 series power supplier (Figure 5.6). The higher electrical power applied to the system corresponded to higher acoustic power at different initial temperatures of
DI water. However, a higher initial temperature is not favorable for converting the electrically driven mechanical vibrations into acoustic power. As shown in Figure 5.6, as the initial temperature of DI water increased, the calorimetrically determined acoustic power input into the solution decreased.

As a cavitation bubble collapses, external work performed by the liquid on the bubble is converted into kinetic energy of the bubble-liquid shell, heat of the gas content, enthalpy of chemical reaction, and emission of light [61, 229]. Endothermic bond dissociation of vapor is a major component in the energy balance [229]. When solution temperature increases, the vapor content in the gas phase increases thus decreasing the specific heat ratio ($\gamma$) of the gas mixture in the bubble [11, 219]. Through endothermic reactions and by reducing the heat of the gas mixture, the increased vapor content in the bubble decreases the maximum temperature ($T_{\text{max}}$) of bubble collapse compared to lower solution temperatures [267, 271, 272]. This increased vapor content leads to lower calorimetrically determined acoustic power at higher solution temperatures. In addition, the number of gas nuclei is reduced at higher temperatures due to decreased air solubility in aqueous solution, contributing to the already reduced cavitation intensity [273, 274].

Calorimetry results for the designed horn and other typical horns are shown in Table 5.1. The energy conversion efficiency of an ultrasonic horn is defined as the ratio of calorimetric acoustic power to electrical power input. As shown in Table 5.1, the calculated value of 31.5% for the newly designed horn is higher than typical horns [85, 90, 191, 265, 266, 275-277]. In addition, with an emitting area of 148.7 cm$^2$, the smaller power intensity of 2.1 W cm$^{-2}$ for the designed horn as compared to traditional horns
indicates that the acoustic power is widely distributed along the horn instead of concentrated on the small surface of the tip.

5.5.3 Dosimetry

Similar to the calorimetry observations, as shown in Figure 5.7a, enhanced sonochemical reactivity is observed when the calorimetric acoustic power input increases. In Figure 5.7b, HTA formation is slowest at 40 °C. However, the HTA formation rate at 1.0 °C is in between the values at 20 °C and 40 °C, which is not consistent with the calorimetry trend of higher acoustic power at lower initial temperature.

The vapor content increases with solution temperature. At low temperature, the gas mixture with less vapor content achieves a higher $T_{\text{max}}$ in the bubble, resulting in more dissociation of water vapor into free radicals [11, 61, 219, 273, 274]. This, combined with increased gas solubility in water at lower temperature, generates the faster HTA formation at 20 °C compared to at 40 °C. The lower temperature also increases water viscosity which in turn reduces diffusivity of TA and $\cdot$OH in aqueous solution [267, 278, 279], causing the opposite observation between1.0 °C and 20 °C. This result supports the argument that at low temperature diffusion-controlled chemical reaction played a more profound role in the dosimetry tests. In addition, the low temperature of 1.0°C also reduced water surface tension increasing the threshold of ultrasonic cavitation, which further depresses the $\cdot$OH yield and thus HTA formation.
In order to compare the 'OH production from different systems, the zero-order rate constant for HTA formation in the typical horn was normalized to the rate constant of our designed horn using the following equation [191]:

\[
{k_{nor}} = k_{th} \times \left( \frac{PD_{dh}}{PD_{th}} \right)
\]  

(5.12)

where \(k_{nor}\) is the normalized zero-order rate constant (\(\mu\text{M min}^{-1}\)), \(k_{th}\) is the zero-order rate constant for the typical horn (\(\mu\text{M min}^{-1}\)), \(PD_{dh}\) is the calorimetric power density for the designed horn (\(\text{W L}^{-1}\)), and \(PD_{th}\) is the calorimetric power density for the typical horn (\(\text{W L}^{-1}\)).

Results listed in Table 5.1 show that our designed horn has a 1.6-4.0 fold higher HTA formation rate constant than the tested horn and other typical horns. Enhanced acoustic cavitation, as measured by HTA formation, is attributed to the higher energy and mass transfer efficiencies exhibited by the new horn.

5.5.4 Naphthalene Sonolysis

Finally, contaminant degradation in the designed horn and typical horn were compared using two concentrations of naphthalene. In all conditions, degradation fit apparent pseudo-first-order kinetics, as shown in Figure 5.8. The degradation rate of naphthalene by the typical horn was normalized to the designed horn using Eq. (5.12). At both concentrations the degradation rate was faster in the designed horn by approximately 40%. Similar to HTA results, the higher rate for designed horn is attributed to the larger
cavitation volume generated by the larger emitting surface of the multi-stepped configuration.

The enhancement in naphthalene degradation for designed horn is much less than with HTA formation (Table 5.1). Unlike deprotonated TA, naphthalene, with a high Henry’s Law constant (0.043 kPa m³ M⁻¹) [280], enters into the gas phase of cavitation bubbles and undergoes thermolysis reactions. During sonolysis of TA solutions, Pee (2008) [277] reported similar HTA formation rates (0.090 ± 0.001 mM min⁻¹) in the presence and absence of naphthalene, suggesting that thermolysis in the gas phase is the predominant degradation pathway for aqueous naphthalene. Thus, it appears a smaller fraction of naphthalene vaporizes into the gas phase in the designed horn compared to the typical horn with compact treatment volume, resulting in the lower level of enhancement in naphthalene degradation compared to HTA formation. Hence, our results suggest that as the configuration changes, it alters the ratio of degradation by ·OH and thermolysis pathways. Nevertheless, the faster naphthalene degradation, together with the high HTA formation rate, delivered by the designed horn compared to the typical horn demonstrates that the multi-stepped design is capable of enhancing contaminant degradation.
5.6 Conclusions

A scaled-up ultrasonic horn with a multi-stepped shape and a cone-shaped tip was designed on the basis of the dynamic wave equation and equivalent circuit method. Results of both physical and chemical characterization studies showed that this designed ultrasonic horn improved the sonochemical performance (higher energy efficiency, multiple reactive zones, increased cavitation volume, and faster sonolysis) as compared to the typical horn which is restricted by localized cavitation below its small tip. Enhanced cavitation by the multi-stepped horn leads to the possibility of industrial scale application of ultrasound technology in AOPs.

5.7 Acknowledgments

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Table 5.1 Characteristics of designed and typical horns

<table>
<thead>
<tr>
<th>Ultrasonic horn/Manufacture</th>
<th>Freq. (kHz)</th>
<th>Electrical power input (W)</th>
<th>Reaction volume (mL)</th>
<th>Emitting area (cm²)</th>
<th>Calorimetric acoustic power (W)</th>
<th>¹ Power intensity (W cm⁻²)</th>
<th>¹ Power density (W L⁻¹)</th>
<th>¹ Energy efficiency (%)</th>
<th>Zero-order 'OH formation rate constant (μM min⁻¹)</th>
<th>References</th>
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</thead>
<tbody>
<tr>
<td>Designed Horn</td>
<td>20</td>
<td>1000</td>
<td>1250</td>
<td>148.7</td>
<td>315</td>
<td>2.1</td>
<td>252</td>
<td>31.5</td>
<td>² 0.36</td>
<td>this study</td>
</tr>
<tr>
<td>Typical Horn</td>
<td>20</td>
<td>275</td>
<td>85</td>
<td>1.2</td>
<td>36.6</td>
<td>30.5</td>
<td>430</td>
<td>13.3</td>
<td>² 0.09</td>
<td>this study</td>
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<td>Model 550, Fisher Scientific</td>
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<td>–</td>
<td>50</td>
<td>1.2</td>
<td>23.4</td>
<td>19.5</td>
<td>468</td>
<td>–</td>
<td>² 0.23</td>
<td>[270]</td>
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<td>Model VC 600, Sonics &amp; Materials</td>
<td>22</td>
<td>–</td>
<td>50</td>
<td>0.8</td>
<td>19.6</td>
<td>24.5</td>
<td>392</td>
<td>–</td>
<td>² 0.22</td>
<td>[227]</td>
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<td>VCX-400 Vibracell, Sonics &amp; Materials</td>
<td>20</td>
<td>200</td>
<td>235</td>
<td>1.2</td>
<td>56.1</td>
<td>46.8</td>
<td>239</td>
<td>28.1</td>
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<td>50</td>
<td>1.2</td>
<td>66.5</td>
<td>55.8</td>
<td>1340</td>
<td>27.1</td>
<td>–</td>
<td>[191]</td>
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<td>Model VC-750, Sonics &amp; Materials</td>
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<td>1.13</td>
<td>66.0</td>
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<td>1650</td>
<td>13.5</td>
<td>–</td>
<td>[283]</td>
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<td>450</td>
<td>–</td>
<td>1.33</td>
<td>53.1</td>
<td>40.0</td>
<td>–</td>
<td>11.8</td>
<td>–</td>
<td>[284]</td>
</tr>
</tbody>
</table>

¹ Power intensity = Calorimetric acoustic power /Emitting area; Power density = Calorimetric acoustic power /Reaction volume; Energy efficiency = Calorimetric acoustic power /Electrical power input×100%.

² Value normalized to the rate constant of designed horn using Eq. (5.12).
Figure 5.1 Configurations of a typical horn (a) and the designed horn (b; I — the transitional section; II — the reactive section; all measurement numbers in mm).
Figure 5.2 Schematic diagram of longitudinal vibration of a single-step horn (a) and its equivalent circuit (b).
Figure 5.3 Measured frequency spectrum of the designed horn (1/8f and 1/2f are subharmonic frequencies, f is resonant frequency, and 2f and 3f are ultraharmonic frequencies).
Figure 5. 4 Acoustic field distribution around designed horn (a) and typical horn (b) as determined from hydrophone measurements (color key in volts, initial temperature = 20 °C).
Figure 5.5 Sonochemiluminescence imaging of designed horn (a) and typical horn (b) in the reactor (initial luminol concentration = $10^{-3}$ M, pH = 11.3, and initial temperature = 20 °C).
Figure 5.6 The influence of initial temperature on calorimetrically determined acoustic power input into solution at different electrical power inputs (■ — 500 W; ● — 600 W; ▲ — 700 W; ▼ — 800 W; ◇ — 900 W; ★ — 1000 W as electric input power levels by dial setting using Branson BCA 900 series power supplier).
Figure 5. The influences of calorimetrically determined acoustic power (a; initial temperature = 20 °C, pH = 7.4) and initial temperature (b; calorimetric acoustic power = 147 W, pH = 7.4) on the zero-order rate constant for HTA formation.
Figure 5.8 The first-order sonolytic degradation rate constants of naphthalene by designed horn (grey; power density = 252 W L\(^{-1}\), pH = 7.4) and typical horn (white; power density = 430 W L\(^{-1}\), pH = 7.4; value normalized to the rate constant of designed horn using Eq. 5.12).
CHAPTER 6

COMBINING COMSOL MODELING WITH ACOUSTIC PRESSURE MAPS TO DESIGN SONO-REACTORS
6.1 Abstract

Scaled-up and economically viable sonochemical systems are critical for increased use of ultrasound for contaminant degradation. In this study, computational simulations and hydrophone mapping were used to design a large-scale sono-reactor using a multi-stepped ultrasonic horn. Simulations in COMSOL Multiphysics showed ultrasonic waves emitted from horn neck and tip, generating multiple regions of high acoustic pressure. The size of these regions surrounding the horn neck were larger compared with those below the horn tip. The simulated acoustic field was verified by hydrophone measurements in a plexiglass box filled with water. These hydrophone contour maps revealed an asymmetric and discrete distribution of acoustic pressure due to acoustic cavitation, wave interaction, and water movement by ultrasonic irradiation. The hydrophone contour maps were consistent with the simulation results in terms of the effective scale of cavitation zones (~10cm and < 5cm above and below horn tip, respectively). With the mapped acoustic field and identified cavitation location, a cylindrical shaped sono-reactor with a conical bottom was designed to evaluate the treatment capacity for the designed horn using COMSOL simulations. In this study, verification of simulation results with experiments demonstrates that coupling of COMSOL simulations with hydrophone measurements is a simple, effective and reliable scientific method to evaluate reactor designs of ultrasonic systems.

Keyword: ultrasound, COMSOL Multiphysics, hydrophone, spectra, cavitation
Nomenclature

\( A_i \) \hspace{1cm} \text{amplitude in radius change for } i^{th} \text{ harmonic}

\( c \) \hspace{1cm} \text{speed of ultrasound propagation in the water (m s}^{-1}\text{)}

\( c_E \) \hspace{1cm} \text{elastic coefficients (6×6 matrix; Pa) at constant electric field strength}

\( d \) \hspace{1cm} \text{piezoelectric strain constant (3×6 matrix; m V}^{-1}\text{)}

\( d^T \) \hspace{1cm} \text{transposed piezoelectric strain constant matrix (6×3; m V}^{-1}\text{)}

\( D \) \hspace{1cm} \text{electric flux density vector (3×1 matrix; C m}^{-2}\text{)}

\( e \) \hspace{1cm} \text{dielectric permittivity (3×6 matrix; C m}^{-2}\text{)}

\( e^{ip} \) \hspace{1cm} \text{alternating current (AC)}

\( e^T \) \hspace{1cm} \text{transposed dielectric permittivity matrix (6×3; C m}^{-2}\text{)}

\( E \) \hspace{1cm} \text{electric field intensity vector (3×1 matrix; V m}^{-1}\text{)}

\( f \) \hspace{1cm} \text{frequency of ultrasound (Hz)}

\( f_h \) \hspace{1cm} \text{bubble oscillation frequency (Hz)}

\( f_R \) \hspace{1cm} \text{resonance frequency of bubble oscillation (Hz)}

\( F_V \) \hspace{1cm} \text{force per volume (N m}^{-3}\text{)}

\( m \) \hspace{1cm} \text{integral number}

\( n \) \hspace{1cm} \text{integral number}

\( \mathbf{n} \) \hspace{1cm} \text{unit vector}

\( P \) \hspace{1cm} \text{acoustic pressure (Pa)}

\( P_A \) \hspace{1cm} \text{maximum acoustic pressure (Pa)}

\( P_{\text{stat}} \) \hspace{1cm} \text{hydrostatic pressure (Pa)}

\( P_{\text{vapor}} \) \hspace{1cm} \text{vapor pressure (Pa)}
\( q \) dipole source \((\text{m s}^{-2})\)

\( R \) bubble radius at time \( t \) \((\text{m})\)

\( R_0 \) bubble radius at equilibrium \((\text{m})\)

\( s_E \) elastic compliance \((6\times6 \text{ matrix; m}^2 \text{ N}^{-1})\) in a constant electric field

\( S \) strain vector \((6\times1 \text{ matrix; m m}^{-1})\)

\( T \) stress vector \((6\times1 \text{ matrix; Pa})\)

\( t \) time \((\text{s})\)

\( u \) particle displacement \((\text{m})\)

\( x \) defined power series

Greek letters

\( \alpha \) characteristic exponent

\( \beta \) ratio of driving frequency to bubble oscillation frequency

\( \gamma \) ratio of specific heats

\( \varepsilon_S \) dielectric matrix \((3\times3; \text{ F m}^{-1})\) at constant mechanical strain

\( \varepsilon_T \) dielectric matrix \((3\times3; \text{ F m}^{-1})\) at constant mechanical stress

\( \mu \) fluid viscosity \((\text{Pa s})\)

\( \rho \) water density \((\text{kg m}^{-3})\)

\( \rho_m \) material density \((\text{kg m}^{-3})\)

\( \rho_s \) density of horn rod \((\text{kg m}^{-3})\)

\( \sigma \) surface tension \((\text{N m}^{-1})\)

\( \varphi \) phase difference \((\text{rad})\)
\( \varphi_i \) \hspace{1cm} \text{phase difference for } i^{th} \text{ harmonic (rad)}

\( \omega \) \hspace{1cm} \text{angular frequency (rad s}^{-1}\text{)}
6.2 Introduction

Many laboratory studies have reported the chemical processing of materials, water contaminants, and waste streams using ultrasound [8, 285]. However, few studies report methods to scale-up these bench-scale studies to larger systems. The most commonly used bench-scale device for sonication has low energy efficiency, localized cavitation, and a non-uniform acoustic field in the reactor [7, 34, 35]. A few studies have investigated strategies to design new ultrasonic devices [48], improve reactor performances [249, 252, 256], and scale-up sonication processes [32, 33].

In the design process, computational simulations are used to investigate how different reactor geometries, horn configurations, and operational parameters (e.g., frequency) impact optimizing performance of ultrasonic systems [286-290]. Of the available computational tools, COMSOL Multiphysics applies a finite element method to solve different physics and engineering problems (e.g., acoustic propagation and heat transfer) governed by partial differential equations (PDEs). The numerous modules and corresponding analytical solutions in the software allows it to combine different phenomena into one model, which is required to simulate ultrasonic systems that feature electromechanical and elastic mechanical effects [87, 291]. Therefore, COMSOL Multiphysics has been applied to simulate acoustic fields and sonochemistry in reactors, provided results consistent with laboratory measurements [286, 287, 289].

A hydrophone is a piezoelectric device that can detect sound pressure underwater and convert the pressure signals to electrical signals. Hydrophone measurements are used to determine an acoustic pressure distribution in solution and through frequency
spectral analysis, locate cavitation regions [261-263]. Bubble oscillations in an acoustic field, together with shock waves / micro-jets that follow bubble collapse, introduce many subharmonic/harmonic frequencies and a broad range of frequencies (i.e., background noise) [181, 183, 292, 293]. This emitted broadband signal is indicative of transient cavitation [180]. Measuring the acoustic emissions using a hydrophone has been used to characterize the acoustic field and sonochemical reactivity in many ultrasonic systems [180, 182, 261].

The coupling of computational simulation with mapping the acoustic field using hydrophone measurements provides a method for designing ultrasonic reactors. This work presents a protocol for a sono-reactor design using this coupled method. In this study, the acoustic field surrounding a multi-stepped horn was first simulated in COMSOL Multiphysics to evaluate ultrasound propagation and the cavitation zone in water. The acoustic pressure distribution was then mapped using hydrophone measurements in a plexiglass box, followed by spectral analysis of ultrasound signals to investigate the cavitation region and scope. Finally, the configuration of an approximately sized sono-reactor was proposed and modeled. We proposed this method for reactor design as a rational way to design and characterize sono-reactors.
6.3 Methodology

6.3.1 COMSOL Simulation

An ultrasonic system, composed of a transducer and a horn, involves different physical phenomena [7, 87, 291]. The piezoelectric material in the transducer converts electricity into mechanical vibrations which pass through the ultrasonic horn rod and are amplified at the end of the horn [291]. These amplified mechanical waves (i.e., ultrasound waves) are emitted and propagate through a medium, such as water. Thus, three different modules were selected to simulate these physical effects in COMSOL Multiphysics software (version 4.2): 1) a piezoelectric material module for the transducer; 2) a linear elastic material module for the horn rod; and 3) a pressure acoustics module for water [294, 295]. Each module is governed by its own equations that describe the specific physics as discussed in the following section.

6.3.1.1 Applied physical modules

Piezoelectric effect is a phenomenon that an applied stress on piezoelectric materials induces electric polarization or an applied electric field induces dimension change for piezoelectric materials [296]. In the transducer, the lead zirconate titanate (PZT) ceramics provide an electrical field and a mechanical field at the same time. The electromechanical behaviors of the isotropic PZT are expressed by two linearized constitutive equations [296, 297]:

168
\begin{align*}
\text{Stress} - \text{Charge} & \quad \begin{cases}
T = c_e S - e^T E \\
D = e S + \varepsilon_s E
\end{cases} \quad (6.1a) \\
\text{Strain} - \text{Charge} & \quad \begin{cases}
S = s_e T + d^T E \\
D = d T + \varepsilon_T E
\end{cases} \quad (6.1b)
\end{align*}

where \( T \) is the stress vector (6 \times 1 \text{ matrix; Pa}), \( S \) is the strain vector (6 \times 1 \text{ matrix; m m}^{-1}), \( E \) is the electric field intensity vector (3 \times 1 \text{ matrix; V m}^{-1}), \( D \) is the electric flux density vector (3 \times 1 \text{ matrix; C m}^{-2}), \( c_e \) is the elastic coefficient (6 \times 6 \text{ matrix; Pa}) at constant electric field strength, \( e^T \) is the transposed dielectric permittivity matrix (6 \times 3; C m^{-2}), \( e \) is the dielectric permittivity (3 \times 6 \text{ matrix; C m}^{-2}), \( \varepsilon_s \) is the dielectric matrix (3 \times 3; F m^{-1}) at constant mechanical strain, \( s_e \) is the elastic compliance (6 \times 6 \text{ matrix; m}^2 N^{-1}) in a constant electric field, \( d^T \) is the transposed piezoelectric strain constant matrix (6 \times 3; m V^{-1}), \( d \) is the piezoelectric strain constant (3 \times 6 \text{ matrix; m V}^{-1}), and \( \varepsilon_T \) is the dielectric matrix (3 \times 3; F m^{-1}) at constant mechanical stress.

The vibration generated in the piezoelectric transducer is then transmitted to the horn rod. Assuming both the stainless steel structure of the horn rod and PZT are isotropic and elastic materials, their linear elastic behavior is governed by Newton’s Second Law [294, 295]:

\[-\rho_m \omega^2 u - \nabla \cdot T = F_v e^{i\omega t}\]

where \( \rho_m \) is the material density (kg m^{-3}), \( \omega \) is the angular frequency (rad s^{-1}), \( u \) is the particle displacement (m), \( F_v \) is the force per volume (N m^{-3}), and \( e^{i\omega t} \) indicates the alternating current (AC).
The pressure acoustics module has been used to simulate ultrasound propagation in water. The acoustic wave equation is given as follows [36, 295, 297]:

\[ \nabla \cdot \left( -\frac{1}{\rho} \nabla P + q \right) + \frac{\omega^2 P}{\rho c^2} = 0 \]  

(6.3)

where \( \rho \) is the density of water (kg m\(^{-3} \)), \( c \) is the speed of ultrasound propagation in water (m s\(^{-1} \)), \( P \) is the acoustic pressure (Pa), \( t \) is time (s), and the dipole source \( q \) (m s\(^{-2} \)) is optional. For our setup, there is no polarization (\( q = 0 \)) for the longitudinal ultrasound waves [36].

6.3.1.2 Assigned boundary conditions and initial inputs

The boundary conditions, which refers to COMSOL Modeling Guides [294, 295] and previous simulation studies [287, 289], were set to couple the three modules. A structure-acoustic boundary was set to the interface between the ultrasonic horn and water [295, 298]. Since ultrasonic waves are longitudinal waves, the side of the horn was set as a hard boundary meaning the normal component of the acceleration is zero (there are no particle movements in the direction perpendicular to horn axis) [298]:

\[ \mathbf{n} \cdot \left( -\frac{1}{\rho_s} \nabla P + q \right) = 0 \]  

(6.4)

where \( \mathbf{n} \) is the unit vector and \( \rho_s \) is the density of horn rod. Displacements at the interface between the water and the wall of the tank were also set to zero (\( u = 0 \) or \( P = 0 \)), assuming the tank material with a large acoustic impedance sufficiently absorbed incident ultrasound waves. The particle displacement at the interface of the transducer
and horn was set to the same value [48, 257, 299]. Boundary conditions for surfaces contacting air were set to be \( P = 0 \) [295]. The default temperature was 293.15K. The liquid, horn, and transducer domains were assigned to linear water media, piezoelectric material (PZT-5H), and stainless steel material (AISI 4340), respectively. The input information of these materials is summarized in Table 6.S1 of supporting information (SI).

6.3.2 Experimental Verification

6.3.2.1 Ultrasonic system

As shown in Figure 6.1, a Branson BCA 900 series power supplier (1000W at maximum) was used to transmit electrical power to a Branson 902R Model ultrasonic transducer (20 kHz) which was connected to a multi-stepped horn. The ultrasonic horn was placed at the center of a water tank (61 cm × 61 cm × 45cm, 167.5 L) made of plexiglass. A Reson T4013 type hydrophone (Reson A/S, Denmark) was used to measure acoustic pressure in the water tank. The hydrophone was connected to a TDS 5000 Tektronix oscilloscope (Tektronix Inc., USA) which recorded and displayed the sound signals at a sampling frequency of 125 kHz. Another typical horn-type ultrasonic system (Sonic Dismembrator 550, Fisher Scientific) was used to determine the cavitation threshold following the method of Ashokkumar et al. (2007) [180].
6.3.2.2 Experimental procedure

After filling water to a depth of 40 cm in the plexiglass tank, the multi-stepped horn was submerged to the depth of 16 cm (from horn tip to water surface). The depth right below the horn tip was defined to be $Z = 0$ and horizontal planes were defined as X-Y planes. A manual positioning system with a resolution of 2 cm was used to position the hydrophone accurately during acoustic field mapping. The origin of the hydrophone was just below the horn tip (X, Y, Z = 0, 0, 0). With the manual positioning system, the hydrophone was then moved in the X-Y plane at 2 cm intervals, followed by movements in the Z-direction (vertical) to map another X-Y plane. A full-scan of an X-Y plane was accomplished through line scans in the x- or y-axis. X-Y planes below the horn tip ($Z = -4$ cm), at the horn tip ($Z = 0$ cm), and above the horn tip ($Z = +4$ cm) were scanned to generate acoustic field maps for the multi-stepped horn in the water tank. Hydrophone readings in these scans were acquired as root mean square values by the oscilloscope. Operational conditions such as power input and water volume were constant for all measurements. The temperature of water in the tank varied from 18 °C to 22 °C depending on the length of sonication. Such temperature change was not found to alter hydrophone readings.

6.3.3 Acoustic Emission

The acoustic emission method was used to determine the cavitation region in the hydrophone-mapped acoustic field. Frequency is a critical factor to determine the shape of a sound signal. At low power intensity, a sinusoidal shape for sound signal converted
from AC indicates one dominant frequency, which in our system corresponds to linear vibration of bubbles at a driven frequency of 20 kHz. When a high intensity distorts the linear system, multiples of the driving frequency (i.e., ultraharmonics) are generated [192]. Beyond a threshold value, subharmonics appear [192]. The numerical analysis of bubble oscillation at subharmonic and harmonic frequencies is explained in the SI. Collapse of cavitation bubbles induces shock waves and micro-jets forming a noisy background. These bubble oscillations and collapses generate a broadband signal (i.e., an elevated baseline), which is indicative of transient cavitation [300]. Both the elevated baseline and sharp peaks at the driving, subharmonic, and harmonic frequencies are characteristics of an observed hydrophone spectrum from high power ultrasound.

6.4 Results and Discussion

6.4.1 Acoustic Field Modeling

The simulation was conducted in 2D axisymmetric dimension (i.e., half geometry; Figure 6.S1), where the ultrasonic horn irradiates water in a cylindrical volume with a diameter of 31 cm and a height of 36 cm. Figure 6.2 shows the simulated acoustic pressure distribution in an X-Z plane (vertical) where red or blue indicates a high absolute acoustic pressure. Due to the propagation of ultrasonic waves, the red and blue colors oscillate temporally in those regions. Therefore, the term “high acoustic pressure region” indicates both red and blue areas unless noted otherwise. As shown in Figure 6.2, high acoustic pressure regions surrounding the horn neck and below its tip were observed.
At further regions, ultrasound waves propagate in the water forming ripples. Acoustic attenuation was also observed based on pressure color changing from red to yellow or blue to cyan. Figure 6.3 compares acoustic fields in X-Y planes at different depths, where Plane 3 is at $Z = 0$ cm. Ultrasound waves were emitted out from the horn neck generating a large high acoustic pressure region in Plane 2. Scale of the dark-colored region extended to approximately 10 cm as opposed to $\leq 5$ cm in other X-Y planes. The simulated acoustic pressure mapping indicates that areas surrounding the ultrasonic horn neck ($Z > 0$ cm) were more likely to generate multiple cavitation zones.

The simulation includes several assumptions: 1) there was no energy loss for piezoelectric effects and transmitting of mechanical energy from transducer to horn rod, so the simulation results may overestimate the particle displacements for both piezoelectric material and stainless steel horn rod; 2) the acoustic pressure distribution in the tank was symmetric and exponentially decreasing from center to edges due to the linearity of water media; 3) there were no cavitation bubbles generated in the tank; and 4) water movements in the tank were negligible. Even though this simple simulation does not accurately reflect the real system (up to one order of magnitude in difference from hydrophone measurements), it was a worthy starting step and a valuable reference for experimental designs.

6.4.2 Acoustic Field Mapping

The acoustic pressure in the plexiglass tank was mapped using hydrophone measurements. Hydrophone readings were recorded as root mean square values, so they
only present in positive numbers as opposed to alternating values in simulations. First, the acoustic pressure from \( Z = -15 \text{ cm} \) to \( Z = +15 \text{ cm} \) was measured at different distances to the horn neck (i.e., 2 cm, 5 cm, and 10 cm), as shown in Figure 6.4. Apparently, the radial region of the horn neck (\( 0 \leq Z \leq +15 \text{ cm} \)) exhibited higher acoustic pressure compared with the regions below the horn tip. In addition, the hydrophone readings decayed with distances (\( 2 \text{ cm} > 5 \text{ cm} > 10 \text{ cm} \)), which was consistent with the simulated ultrasound propagation in Figure 6.2. However, the higher power input does not intensify the acoustic pressure. This unexpected observation probably reflects the interference of a large amount of cavitation bubbles on sound propagation and higher energy dissipation due to more violent water movement in the tank under higher intensities. Such a nonlinear relationship between acoustic pressure and power input was also observed in previous studies by Hodnett et al. (2004 and 2007) [261, 301]. They attributed the nonlinearity to the shifting of lower acoustic frequency to higher frequency and the shielding effect of cavitation that restrict the propagation of ultrasound in water-filled vessels.

In addition to the vertical mapping, horizontal propagation of ultrasound waves in water was also illustrated as 3D and contour plotting in Figure 6.5. As shown in Figure 6.5, a decreasing intensity from center to edges was observed. Particularly at \( Z = 0 \text{ cm} \), it was obvious that the center area below the horn tip exhibited highest acoustic pressure level; at \( Z = +4 \text{ cm} \), the horn neck emitted ultrasound waves and created a large high acoustic pressure region; at \( Z = -4 \text{ cm} \), the acoustic pressure distribution was more dispersed without obvious intense spots. The observation of a larger scale of high
pressure region at $Z > 0$ cm and a more discrete distribution of acoustic pressures at $Z \leq 0$ cm were consistent to the simulation results in Figure 6.3. However, a standing wave pattern of propagation was not observed due to the following acoustic effects [261]: 1) cavitation shielding interferes with ultrasound transmission from center to edge; 2) collisions between emitted ultrasonic waves from horn neck and reflected waves from wall of water tank offset the applied acoustic pressure; and 3) agitation of water by acoustic streaming drifts vibrating molecules off their original positions resulting in the discrete and asymmetric distribution of acoustic pressure. Hodnett et al. (2007) [261] also showed an asymmetric but reproducible distribution of acoustic field in the characterization of a reference ultrasonic cavitation vessel. Mhetre and Gogate (2014) [302] in their most recent work presented a non-uniform cavitation activity distribution in traditional dosimetry tests using potassium iodide (KI) in a large scale sonochemical reactor (72 L in volume). It seems hydrophone measurements are capable to convey consistent results in the mapping of acoustic field to the traditional chemical method.

6.4.3 Cavitation Threshold and Reactive Region

After obtaining the acoustic field in the tested water tank, the next step was to evaluate the effective range of cavitation zones based on the threshold value of cavitation which was determined by the acoustic emission method. Figure 6.6 shows the acoustic waveforms acquired on the oscilloscope and the corresponding spectrum. The waveforms developed from sinusoidal to irregular shapes with increasing acoustic intensity ($< 0.04 – 1.16 \text{ W cm}^{-2}$). In an ideal system, the sinusoidal AC input is converted via a transducer
into sinusoidal vibration that is propagated through ultrasonic horn to the aqueous solution. Without dissipation, water movement, and cavitation bubbles, the hydrophone captures a sinusoidal sound signal that is displayed in the oscilloscope. With increasing power input, bubble oscillations depart from this linear nature producing convex in waveforms (Figure 6.6). The addition of shock waves, micro-jets, and micro-streaming after collapse of cavitation bubbles further increases the degree of irregularity of acoustic waveforms.

The frequency spectrum in Figure 6.6 exhibits consistent observations to the waveforms. In the spectrum, the driven frequency (f) and ultraharmonic frequency (2f) were observed first, followed by the appearance of subharmonic frequencies (≥ 0.04 W cm⁻²). The number of subharmonic and ultraharmonic frequencies increased significantly at 0.31 W cm⁻². At 0.74 W cm⁻², the baseline was elevated approximately to a magnitude of 10, showing a feature of broadband signal. This change of state was an indicator of transient cavitation. It can be concluded that transient cavitation occurs at approximately 0.74 W cm⁻², which was similar to the previous observation of 0.70 W cm⁻² by Ashokkumar et al. (2007) [180]. In this paper, we defined the acoustic intensity of 0.74 W cm⁻² as the “threshold” for transient cavitation, which corresponds to a hydrophone reading of 0.63 Volt. Even though it might underestimate the threshold of cavitation, the defined threshold could explicitly determine the scale of cavitation zones for a sono-reactor configuration without concerns on an insufficient design.

Using the determined cavitation threshold, a cavitation zone could be identified. As shown in Figure 6.4, the threshold for transient cavitation was plotted as a red dotted
line and the measurements beyond cavitation threshold mainly located from \( Z = 0 \) cm to \( Z = +15 \) cm. The cavitation region at \( Z > 0 \) cm extended to the distance of 10 cm while cavitation zones were within 5 cm at \( Z \leq 0 \) cm. In Figure 6.5, regions beyond the cavitation threshold (cyan color) were boarded with dotted red line. At \( Z = +4 \) cm, there was a large area with cyan to red colors surrounding the horn neck. In contrast, the cavitation spots were more spread at \( Z = 0 \) cm and \( Z = -4 \) cm. In order to quantitatively describe the cavitation regions in an X-Y plane, the ratio of data points beyond threshold value to total number of scanned points was calculated (Figure 6.7). At \( Z = +4 \) cm, the cavitation zone covered > 85.0% of a 10 cm \( \times \) 10 cm area. The percentage dropped to 73.2% and 49.5% when scales were extended to 12 cm and 20 cm, respectively. If > 85% were assigned as reasonable cavitation percentage, a cylindrical shaped reactor with a 10 cm radius could be designed to fit the multi-stepped horn. In the X-Y planes that were not crosscutting to the horn neck, the percentage of cavitation zones dropped dramatically. For example, at the 10 cm scale, the percentage of cavitation zones was 47.9% and 26.4% for \( Z = 0 \) cm and \( Z = -4 \) cm, respectively. Even though a relatively low percentage was observed at \( Z \leq 0 \) cm, both X-Y planes featured a high acoustic pressure center below the horn tip. Thus, a shrinking shaped bottom, such as a conical shape, could be introduced to the reactor design to increase the percentage of total cavitation volume and fit for the multi-stepped horn. In addition, the cone-shaped bottom was beneficial to the solution circulation inside the reactor, which was verified by our previous studies [15, 303].
With those conditions considered, we proposed a cylindrical shaped reactor with a 10 cm diameter and a conical bottom with 5 cm in depth (21 cm in total depth), as shown in frame 8 of Figure 6.8. Treatment volume for this design was approximately 5.0 L, which is nearly 100-fold greater than the reactor volume for a typical ultrasonic horn [15, 303]. We further verified the design in COMSOL software, in which we simulated the acoustic pressure distribution and animated the ultrasound propagation (frame 1-7 in Figure 6.8) in the reactor. As shown in Figure 6.8, the majority of the reactor was covered by high acoustic pressure regions in red (up to +1.59×10^5 Pa) or blue color (down to –1.59×10^5 Pa) suggesting multiple reactive zones and a large cavitation volume could be generated in the reactor if applying high intensity ultrasound. The animated pressure propagation starts from frame 1 and ends at frame 7. Frames 1 and 7 are identical indicating a complete cycle of propagation. Since the simulated propagation of acoustic pressures was also an indicative of water movement in the reactor, the cyclic movement could assure a more spread reactive zone and provide sufficient mixing for desired oxidation and mass transfer processes in the designed reactor.
6.5 Summary and Future Work

This study proposed and verified a coupling method of COMSOL simulations and hydrophone mapping for a sono-reactor design. The COMSOL simulations delivered comparable results to hydrophone mappings of acoustic pressure in a plexiglass tank suggesting the coupling method may be used as a reliable tool in the design and characterization of an ultrasonic system. In addition, the multi-stepped horn with a 10 cm radiation radius and 5.0 L treatment capacity shows a great potential for large-scale applications through an array of these horns. The next step is to build the sono-reactor with proposed configuration in this study and quantitatively evaluate its performance through traditional calorimetry, dosimetry, and sonochemical degradation of a model contaminant.

6.6 Acknowledgments

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Figure 6. Schematic diagram of experimental setup for hydrophone measurements in the plexiglass box (Dimension is 61 cm × 61 cm × 45 cm and volume is 167.5 L; the depth tangential to horn tip is defines Z = 0; 1 — Branson 902R Model transducer; 2 — serial stepped ultrasonic horn; 3 — Reson T4013 hydrophone; 4 — water; 5 — plexiglass box)
Figure 6.2 Simulation of acoustic pressure distribution in a X-Z plane (Units for color label and number are Pa and mm, respectively)
Figure 6.3 Simulation of acoustic pressure distribution in X-Y planes at different depths (1 — X-Y plane near water surface; 2 — X-Y plane in the middle of horn neck; 3 — X-Y at Z = 0 cm; 4-6 — X-Y planes at Z < 0 cm; units for color label and number are Pa and mm, respectively)
Figure 6. 4 Acoustic pressure distribution in Z-direction at different distances (2cm, 5cm and 10cm) and power levels (50%, 75% and 100%; red dotted line is the cavitation threshold value of 0.63 V)
Figure 6. 5 3D (left) and contour (right) mapping of hydrophone measurements in plexiglass tank (This scan was carried out at room temperature with 50% power input from power supplier to transducer; a — X–Y plane at $Z = +4$ cm; b — X–Y plane at $Z = 0$ cm; c — X–Y plane at $Z = -4$ cm; red dotted line is the cavitation threshold value of 0.63 V)
Figure 6.6 Ultrasonic waveforms and frequency spectrum observed in water at different power intensities (Convex feature in the waveform results from the sum of waveforms in different frequencies to the original waveform)
Figure 6. 7 Percentage of cavitation zones in different X-Y planes (% of cavitation zones = Measurements not less than 0.63 V in a X-Y plane / Total measurements in the X-Y plane × 100%; 0.63 V is measured cavitation threshold using acoustic emission method)
Figure 6. 8 Simulation of acoustic pressure propagation in proposed reactor (red — up to $+1.59 \times 10^5$ Pa; blue color — down to $-1.59 \times 10^5$ Pa)
CHAPTER 7

CONCLUSIONS
Mechanisms for ultrasonic remediation in previous studies, as discussed in Chapter 2, suggest that a logical extension of ultrasound technology from slurry systems to porous media is possible. In this thesis, different ultrasonic systems were developed to gain fundamental knowledge and mechanistic insights to the application of ultrasound in remediation of contaminated sediments. In Chapter 3, the column study revealed localized cavitation which was consistent with observations in water. However, reduced water viscosity due to cavitation heating, in conjunction with the presence of alternating ultrasound waves, increased flow velocity in the porous media. The system was modeled as Darcy flow in the acoustic field. Bromide breakthrough tests demonstrated enhanced tracer transport and dispersion in the presence of ultrasound. The localized cavitation and enhanced mass transfer suggest that ultrasound may be useful for compact treatments at a contamination site.

The combination of ultrasound and chemical oxidant, persulfate, was examined to understand its utility in remediation. EPR measurements showed that *OH was the predominant radical species in the US-PS system due to the much improved reaction between SO$_4^{2-}$ and water molecules in the interfacial region of cavitation bubbles. Kinetic reactions and modeling revealed a rapid dissociation rate of PS at the high temperature bubble-water interface. The much larger interfacial region for PS dissociation as compared to previous reports indicated the interface should be defined relative to the specific reactions occurring. In addition to thermal dissociation, *OH activation of PS was also verified using nitrobenzene to scavenge *OH.
Disadvantages of current ultrasonic systems led us to redesign the horn configuration for improved sonochemical performance in Chapter 5. The multi-stepped shape and a cone-shaped tip achieved higher energy efficiency, multiple reactive zones, increased cavitation volume, and faster sonolysis as compared to the typical horn which was restricted by localized cavitation below its small tip. Chapter 6 determined the treatment capacity for the designed horn in a large-scale application using a coupling method of COMSOL modeling and hydrophone mapping. The COMSOL simulation delivered comparable results to hydrophone mappings of acoustic pressure in a plexiglass tank suggesting that the coupling method could be used as a reliable tool in the design and characterization of a large-scale ultrasonic system.

In this thesis, improving ultrasonic remediation of contaminated sediments was accomplished through a broad range of efforts including mechanism exploration, chemical oxidant addition, and scale-up designs. More in-depth investigation for each strategy is still needed before seeing a wide application of ultrasound in remediation. For example, effective degradation of contaminants using the US-PS combination necessitates an optimization of operational conditions such as US power level, US frequency, and persulfate dosage; the potential effects of natural organic matter and inorganic ions (e.g., halide ion and carbonates) on persulfate activation and radical consumption at the contamination site are not clear. Likewise, novel ultrasonic system designs to improve electromechanical conversion and energy efficiency in the transducer are still needed. Previous results indicate a successful approach usually comes from a combination of existing processes together with the development of innovative
technologies. Therefore, the combination of ultrasound with other remediation methods may provide an environmentally friendly and economically feasible means to degrade toxic and persistent contaminants in sediments.
1. Supporting Information for Chapter 3

Figure A. 1 Schematic diagram of longitudinal vibration in porous media packed column (a) and mechanical energy for the experimental setup (b; P — acoustic pressure; \( V_0 \) — micro-volume of media packed in the column; h — piezometric head = 63 cm; z — elevation head; p — pressure head; k — media permeability; datum plane is defined at \( h = 0 \) cm)
Figure A. 2 Propagation of ultrasound from source in column with small sand

(mean diameter of 0.316 ± 0.011 mm; color key in kPa; numbers indicate power intensity in W cm\(^{-2}\))
Figure A.3 Propagation of ultrasound from source in column with medium sand
(mean diameter of 0.547 ± 0.012 mm; color key in kPa; numbers indicate power intensity in W cm$^{-2}$)
Figure A. 4 Propagation of ultrasound from source in column with small glass beads (mean diameter of 0.500 mm; color key in kPa; numbers indicate power intensity in $W \text{ cm}^{-2}$)
Figure A. 5 Propagation of ultrasound from source in column with media glass beads (mean diameter of 1.000 mm; color key in kPa; numbers indicate power intensity in W cm\(^{-2}\))
Figure A. 6 Propagation of ultrasound from source in column with large glass beads
(mean diameter of 2.000 mm; color key in kPa; numbers indicate power intensity in W cm\(^{-2}\))
Figure A.7 Flow velocity under long sonication time for large sand (mean diameter of 0.760 ± 0.005 mm; power intensity of 6.26 W cm⁻²)
Figure A. 8 Ultrasound propagation in water and in large sand (mean diameter of 0.760 ± 0.005 mm; power intensity of 6.26 W cm$^{-2}$)
Figure A. 9 Temperature change in the column packed with tested particles
(measurement locations at 1.0, 4.0, 7.0, and 10.0 cm; power intensity of 6.26 W cm\(^{-2}\))
Figure A. 10 Breakthrough as a function of pore volume in different media (□ — no sonication; ■ — sonication at power intensity of 6.26 W cm\(^{-2}\))
Unit conversion from hydrophone reading (volt) to acoustic pressure (Pa)

Sound pressure level (SPL; dB), a logarithmic measure of the effective sound pressure of a sound relative to a reference value, can be calculated with root mean square value of hydrophone signal \( V_{\text{rms}} = \sqrt{\frac{\sum_{n=1}^{n} V_n^2}{N}} \); volt) and hydrophone sensitivity (OCV; – 211dB re V/μPa for TC 4013):

\[
\text{SPL} = 20 \log(V_{\text{rms}}) - \text{OCV} \quad (A.1)
\]

where \( \text{SPL} = 20 \log \left( \frac{P_{\text{rms}}}{P_{\text{ref}}} \right) \), \( P_{\text{rms}} \) is the root mean square sound pressure being measured and \( P_{\text{ref}} \) (20 μPa) is the reference sound pressure.

Therefore,

\[
20 \log \left( \frac{P_{\text{rms}}}{P_{\text{ref}}} \right) = 20 \log(V_{\text{rms}}) - \text{OCV} \quad (A.2)
\]

Or

\[
P_{\text{rms}} = 20 \times 10^{-6} \times 10^{\log(V_{\text{rms}}) - 0.05 \text{OCV}} \quad (A.3)
\]
2. Supporting Information for Chapter 4

Figure A. 11 DMPO•−SO₄⁻ adduct formation in the absence and presence of TBA (100 mM; PS = 1 mM; DMPO = 40 mM; PD = 1.5 W mL⁻¹; P-value = 0.50 suggests no significant difference)
1) Estimation of bubble number using acoustic emission method.

The relationship between acoustic pressure (P) and pressure impulse (P_b) from oscillating bubbles is given as follows in Pandit et al. (1992) [232]:

\[
P_b = \frac{\sqrt{3\gamma P_0}}{\pi f_0 r}
\]

(A.4)

where \( \gamma = 1.66 \) is the specific heat ratio of argon, \( \rho \) is the water density, \( f_0 \) is the natural frequency of an oscillating bubble, and \( r \) is the distance from the center of oscillating bubble. In a ultrasonic system, bubbles oscillate simultaneously and their resultant pressure (P_res) is:

\[
P_{\text{res}} = N_t P_b^2
\]

where \( N_t \) is the total bubble number. Thus, using Eq. (4.S2) we can calculate the number of bubbles in the ultrasonic system. Specifically, \( P \) is measured using a hydrophone; \( f_0 \) and \( P_{\text{res}} \) were obtained from FFT and inverse FFT analysis of hydrophone signals using AutoSignal v1.7 software. Several assumptions are necessary for this calculation:

1) The small amplitude of pressure pulsation for each bubble is addable.

2) All bubbles are contained in the bubble cloud.

3) \( r = \) horn tip diameter (0.635 cm) is assigned as an approximation of effective distance to hydrophone for all bubbles in the cloud.

4) The acoustic pressure inside the bubble cloud is homogeneously distributed.

Under these assumptions, the bubble number at different oscillating frequencies is estimated at US power density = 1.5 W mL\(^{-1}\), as shown in Table 4.S1.
Table A. 1 Bubble number and distribution at different oscillating frequencies (PD $= 1.5 \text{ W mL}^{-1}$)

<table>
<thead>
<tr>
<th>$f_0$, Hz</th>
<th>$P_{\text{res}}$, Pa</th>
<th>$N \times 10^7 \text{s}^{-1}$</th>
<th>% of $N$ of bubbles</th>
</tr>
</thead>
<tbody>
<tr>
<td>10000</td>
<td>57174.49</td>
<td>0.004</td>
<td>0.088</td>
</tr>
<tr>
<td>20000</td>
<td>507199.3</td>
<td>1.270</td>
<td>27.78</td>
</tr>
<tr>
<td>30000</td>
<td>133000.2</td>
<td>0.196</td>
<td>4.298</td>
</tr>
<tr>
<td>40000</td>
<td>339863.8</td>
<td>2.281</td>
<td>49.89</td>
</tr>
<tr>
<td>50000</td>
<td>95109.83</td>
<td>0.279</td>
<td>6.105</td>
</tr>
<tr>
<td>60000</td>
<td>98591.91</td>
<td>0.432</td>
<td>9.447</td>
</tr>
<tr>
<td>Other freq.</td>
<td>53041.29</td>
<td>0.078</td>
<td>0.171</td>
</tr>
</tbody>
</table>

The final estimated bubble number, including both cavitation bubbles and “stable” bubbles, is $\sim 4.57 \times 10^7 \text{ s}^{-1}$ in our system. The corresponding void fraction, the ratio of volume of bubbles to volume of total solution, is $7.0 \times 10^{-4}$, which is in the same order of magnitude as previous reports [304, 305].
2) Estimation of cavitation bubble number.

According to Colussi et al. (1998) [229], the energy ($E_b$) of a single cavitation bubble can be estimated by:

$$ E_b = P_{\text{total}} \times \Delta V = (P + P_0) \frac{4\pi}{3} \left( R_{\text{max}}^3 - R_{\text{min}}^3 \right) \approx \frac{4\pi}{3} R_{\text{max}}^3 (P + P_0) \quad (A.6) $$

Under a given PD, the formation rate for cavitation bubble is:

$$ N = \frac{PD}{E_b} = \frac{3PD}{4\pi R_{\text{max}}^3 (P + P_0)} \quad (A.7) $$

Using Eq. (4.54), we calculate the formation rate for cavitation bubble is $\sim 1.27 \times 10^7$ mL$^{-1}$ s$^{-1}$. We also calculated the volume of bubble cloud is $\sim 1.23$ mL by converting area of sonochemiluminescence imaging to volume using ImageJ 1.48 software. Therefore, we obtained the cavitation bubble number of $1.56 \times 10^7$ s$^{-1}$ as reported in the content. Form this calculation, $\sim 34.2\%$ of the total bubbles in the cloud are cavitation bubbles.
3) Estimation of interface temperature.

At the boundary of gas phase and interface, the following equation is obtained based on continuity of heat flux [230]:

$$\kappa_g \frac{\partial T_g}{\partial T} = \kappa_w \frac{\partial T_w}{\partial T} \quad (A.8)$$

where $\kappa_g$ ($1.600 \times 10^{-2}$ W m$^{-1}$ K$^{-1}$ for argon) and $\kappa_w$ ($1.600 \times 10^{-2}$ W m$^{-1}$ K$^{-1}$ for water vapor) are the thermal conductivity for gas side and liquid side of interface, respectively; $T_g$ and $T_w$ are temperature on two sides. Due to the supercritical state of water in the interfacial region, parameters of water vapor were used other than water. Given the distance of heat diffusion, $d_g$ in the gas phase and $d_w$ in liquid phase, Eq. (4.5) becomes:

$$\frac{T_c - T_s}{d_g} = \frac{T_s - T_\infty}{d_w} \quad (A.9)$$

where $T_c$ (160000 K for argon bubble [215]), $T_s$, and $T_\infty$ are the temperature at bubble center, at interface, and in ambient solution, respectively. The diffusion distance can be estimated using $d = \sqrt{D \Delta t}$ ( $D = \frac{\kappa}{\rho C_p}$ is the thermal diffusivity, $2.200 \times 10^{-5}$ and $2.338 \times 10^{-5}$ m$^2$ s$^{-1}$ for argon and vapor, respectively; $\Delta t$ can be an acoustic cycle or 50 $\mu$s for 20 kHz waves). Thus, Eq. (4.6) converts to:

$$\frac{T_s - T_\infty}{T_c - T_s} = \frac{\kappa_g \sqrt{D_w}}{\kappa_w \sqrt{D_g}} = \frac{\kappa_g \rho_g C_{p,g}}{\kappa_w \rho_w C_{p,w}} \quad (A.10)$$
Substituting all values into Eq. (4.87), we get the interface temperature $T_s \approx 2260K$, which is close to the previous estimation of $\sim 1900K$ [215].
3. Supporting Information for Chapter 6

1) COMSOL Simulation.

Figure A. 12 Geometry of multi-stepped horn and sonicated water region in 2-D axisymmetric dimension in COMSOL setup (1—transducer; 2—multi-stepped horn; 3—water)
Table A. 2 Initial inputs for three domains in COMSOL simulation

<table>
<thead>
<tr>
<th>Domain</th>
<th>Material</th>
<th>Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid domain</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>ρ</td>
<td>1000 kg m⁻³</td>
</tr>
<tr>
<td></td>
<td>c</td>
<td>1418 m s⁻¹</td>
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<tr>
<td>Horn domain</td>
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<tr>
<td></td>
<td>ρₘ</td>
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</tr>
<tr>
<td></td>
<td>E (Young’s modulus)</td>
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<tr>
<td></td>
<td>ν (Poisson’s ratio)</td>
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<tr>
<td>Transducer domain</td>
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<tr>
<td></td>
<td>ρₘ</td>
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<td>cₑ (6×6 matrix)</td>
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</tr>
<tr>
<td></td>
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<td>8.47 8.47 11.7×10¹⁰ Pa</td>
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<tr>
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<td>dᵀ (6×3 matrix)</td>
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212
2) Numerical analysis of sub- and ultra-harmonic vibrations for bubble

The nonlinear oscillations of cavitation bubbles can be analyzed mathematically. The Rayleigh-Plesset-Noltingk-Neppiras-Poritsky (RPNNP) equation describes the bubble dynamics when the motion is spherically symmetric and surrounding liquid is incompressible and viscous [292, 306].

\[
\rho \dddot{R} + \frac{3}{2} \rho \ddot{R} = \left( P_{\text{stat}} - P_{\text{vapor}} + \frac{2\sigma}{R_0} \left( \frac{R_0}{R} \right)^3 \right) - \left( P_{\text{stat}} - P_{\text{vapor}} + \frac{2\sigma}{R} \right) - \frac{4\mu}{R} \dot{R} + P(t) \quad (A.11)
\]

where \( \rho \) is liquid density (kg \( \text{m}^{-3} \)), \( R \) is bubble radius (m) at time \( t \) (s), \( \dot{R} \) (m \( \text{s}^{-1} \)) and \( \ddot{R} \) (m \( \text{s}^{-2} \)) are bubble oscillating velocity and acceleration, respectively, \( P_{\text{stat}} \) is hydrostatic pressure (Pa), \( P_{\text{vapor}} \) is vapor pressure (Pa), \( \sigma \) is surface tension (N \( \text{m}^{-1} \)), \( R_0 \) is equilibrium radius (m), \( \gamma \) is ratio of specific heats, \( \mu \) is liquid viscosity (Pa s), and \( P(t) = P_A \cos(\omega t) \) is applied acoustic pressure (\( P_A \) is maximum acoustic pressure).

Assume bubble radius grows exponentially, we can perform power series in \( x \) and write [292, 307]:

\[
R \approx R_0 (1 + x) \quad (A.12)
\]

where \( x \ll 1.0 \) and its higher powers are negligible. Substitute Eq. (6.S2) into Eq. (6.S1), and resulting equation is [292]:

\[
\rho R_0^2 (1 + x)^2 \dddot{x} + \frac{3}{2} \rho R_0^2 \ddot{x} = \left( P_{\text{stat}} - P_{\text{vapor}} + \frac{2\sigma}{R_0} \left( \frac{R_0}{R} \right)^3 \right) \left[ 1 - 3\gamma x + \frac{3\gamma(3\gamma + 1)}{2} x^2 \right] - \left[ P_{\text{stat}} - P_{\text{vapor}} + \frac{2\sigma}{R_0} \left( 1 - x + x^2 \right) \right] - 4\mu \left( \ddot{x} - \dot{x} x \right) + P_A \cos(\omega t) \quad (A.13)
\]
The steady-state solution of Eq.(6.3) is given as [192, 292]:

\[ x = A_0 + A_1 \cos(\omega t + \varphi_1) + A_2 \cos(2\omega t + \varphi_2) + \cdots \]  

(A.14)

where \( A_0 \) is change in average radius, \( A_1 \) is first-harmonic amplitude (linear), \( A_2 \) is second-harmonic amplitude (nonlinear), \( A_i \) \((i=3, 4, 5, \ldots)\) are amplitudes for multiple harmonics, and \( \varphi_i \) \((i=1, 2, 3, \ldots)\) is the phase difference for \( i^{\text{th}} \) harmonics.

When applied acoustic pressure is above the cavitation threshold, the solution becomes unstable, corresponding to the appearance of subharmonics [192]. In this situation, a function of \( y(t) \) including both periodic \( x(t) \) and perturbation components is introduced to replace \( x(t) \) in Eq. (6.3) and the approximated solution is [192]:

\[ y = e^{\alpha \omega t^2} \sin \left( \frac{1}{2} \omega t + \varphi \right) \]  

(A.15)

where \( \alpha \) is characteristic exponent and \( \varphi \) is phase difference.

Eq. (6.5) indicates an exponential change for subharmonics with time, which explains the dominance of one-half subharmonic component in some frequency spectrum.

In summary, the oscillation period \((1/f_h)\) of a bubble in water could be an integral multiple of the excitation period \((1/f)\) of driven sound [306, 308]:

\[ f = mf_h, m = 1,2,3,\ldots \]  

(A.16)

In contrast, the oscillation period \((1/f_h)\) could also be an integral multiple of the excitation period \((1/f_R)\) at resonance [306, 308]:

\[ f_R = nf_h, n = 1,2,3,\ldots \]  

(A.17)

Therefore, the ratio \((\beta)\) of bubble oscillation resonant frequency to driving frequency is:
\[ \beta = \frac{f_R}{f} = \frac{n}{m} \]  

When \( n=2, 3, 4, \ldots \) and \( m=1 \), it corresponds to ultraharmonics; when \( m=2, 3, 4, \ldots \) and \( n=1 \), the oscillation is in subharmonic.
BIBLIOGRAPHY


[65] Z. He, Sonochemical remediation of mercury from contaminated sediments, PhD Dissertation, The Ohio State University, Columbus, OH (2006).


241


