ULTRASONIC CONTROL OF CERAMIC MEMBRANE FOULING CAUSED BY SILICA PARTICLES AND DISSOLVED ORGANIC MATTER

DISSERTATION

Presented in Partial Fulfillment of the Requirements for the Degree Doctor of Philosophy in the Graduate School of The Ohio State University

By

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This study systematically investigated the mechanism and efficiency of the ultrasonic control of ceramic membrane fouling caused by silica particles and dissolved organic matter (DOM). Ultrasound at 20 kHz was applied to a cross-flow filtration system with γ-alumina membranes in the presence of colloidal silica particles and/or DOM.

First, ultrasonic cleaning was explored with filtration of silica particles to investigate influence of both particle characteristics and ultrasonic factors on cleaning. Experimental results indicated that particle concentration affected the ability of ultrasound to control membrane fouling, with less effective control of fouling occurring at higher particle concentrations. Measurements of sound wave intensity and images of the cavitation region indicated that particles induced cavitation bubbles near the ultrasonic source, which resulted in less turbulence reaching the membrane surface and subsequently less effective control of fouling. When modified to be hydrophobic, silica particles induced more cavitation near the ultrasonic source compared to unmodified particles also resulting in less effective control of fouling. Particle size influenced the ability of ultrasound to clean; better permeate recovery was observed with larger particles.
Particle size did not affect sound wave intensity, suggesting that the more effective control of fouling by large particles was due to greater lift and cross-flow drag forces on larger particles compared to smaller particles. Based on the range of particle sizes and concentrations examined in this study, our results imply that ultrasound will be effective in controlling cake-layer membrane fouling caused by particles found in typical lake or ground water.

In addition to the effect of particle characteristics, ultrasonic factors affecting membrane cleaning were explored. Based on imaging of the ultrasonic cavitation region, optimal cleaning occurred when the membrane was outside but close to the cavitation region. However, damage in the form of pits and cracks were found when the membrane was within the cavitation region. An increase in the filtration pressure increased the compressive forces driving cavitation collapse and resulted in fewer cavitation bubbles absorbing and scattering sound waves and increasing sound wave penetration. Nevertheless, the increased filtration pressure also resulted in greater permeation drag, and subsequently less improvement in permeate flux. Furthermore, pulsed ultrasound with short pulse intervals resulted in a relative permeate flux improvement close to that of continuous sonication.

Second, besides sonophysical cleaning of particle fouled membranes, membrane cleaning was also explored by studying sonochemical reactions of DOM. Property changes of Aldrich and Pahokee peat DOM at different ultrasonic frequencies and energy densities were systematically investigated. Exposure of DOM to ultrasound resulted in decreases in total organic carbon (TOC), Color$_{465}$, specific UV absorbance (SUVA), aromaticity, and molecular weight, while DOM acidity increased. Compared to 20 kHz
ultrasound, greater sonochemical transformation of DOM occurred at 354 kHz and at higher energy density, due to greater hydroxyl radical (•OH) production. The changes to DOM properties suggest that ultrasound may enhance charge repulsion between DOM and a negatively charged membrane, decrease the fouling potential of hydrophobic membranes, and decrease the rejection rate of DOM by the membrane. To avoid the decrease in DOM rejection rate caused by sonochemical reactions of DOM, low ultrasonic frequency and low energy density would be favored.

Finally, the effect of solution chemistry on ultrasonic control of membrane fouling caused by DOM and silica particles was examined in this study. Experimental results indicated that solution chemistry affected the ability of ultrasound to control membrane fouling. More effective control of membrane fouling occurred at high pH, low ionic strength, and in the absence of divalent cations, due to stronger electrostatic repulsion among DOM macromolecules, silica particles, and the membrane. The decrease of the DOM rejection rate by ultrasound may be explained by the decreased steric exclusion effect, because ultrasound partially released membrane pore blocking and/or partially removed the foulant layer from the membrane surface. The ultrasonic energy density used in these filtration experiments was two orders of magnitude less than the energy density used to investigate sonochemical reactions of DOM; thus the chemical effects of ultrasound on membrane cleaning were likely insignificant.
Dedicated to my parents
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CHAPTER 1

INTRODUCTION AND BACKGROUND

1.1 Membrane Filtration and Membrane Fouling

A membrane is a thin layer of material that is capable of separating materials as a function of their physical and chemical properties when a driving force (e.g., pressure) is applied across the membrane [1]. Based on the pore sizes, membranes are classified into reverse osmosis (RO), nanofiltration (NF), ultrafiltration (UF), and microfiltration (MF) membranes [2,3].

An RO membrane has a pore diameter smaller than 1 nm. It retains virtually all ions but passes water. RO membranes are primarily used to remove salts from brackish water or seawater.

NF membranes have pore diameters smaller than 5 nm. NF membranes operate generally in a higher molecular weight cut-off (MWCO) range than the classic RO membrane. Generally, NF membranes exhibit much lower rejection of monovalent ions than RO membranes.
An UF membrane has a pore diameter ranging from 0.005 to 0.4 µm. An MF membrane has a pore diameter between 0.07 and 2 µm. Both UF and MF membranes are used to remove turbidity, high-molecular-weight materials, pathogens, and particles from waters.

Membrane technology is widely used for water and wastewater treatment, and in food, chemical, nuclear, and pharmaceutical industries because of the technology’s high removal capacity and ability to meet multiple treatment objectives. In water and wastewater treatment, membrane processes provide an alternative approach to conventional systems for desalination, ultra-pure water production, pathogen removal from water, and solid-liquid separation. With membranes having high removal thresholds, conventional coagulation/flocculation, and sedimentation operations can be replaced by a single process. Currently, the development of membranes is driven by a scarcity of water resources, increasingly stringent regulations, and a demand from consumers for higher water quality [4]. Among various membrane materials, ceramic membranes, such as γ-Al₂O₃, ZrO₂, TiO₂, and TiN are of increasing interest because of their higher chemical, thermal and mechanical stability compared to organic membranes [5].

However, one of the main barriers to greater use of membrane technology is membrane fouling. Generally, membrane fouling is caused by the accumulation of water impurities (i.e., membrane foulants), such as colloidal particles, sparingly soluble salts (scale formation), organic matter, and microorganisms on the membrane surface and/or within the membrane pores. This fouling affects both the quantity (permeate flux) and
quality (solute concentration) of the product water [6]. As a result, membrane fouling causes an increase in membrane resistance resulting in a decline of the permeate flux with filtration time. The characteristics and location of membrane foulants may play an important role in determining the extent and reversibility of permeate flux decline [7]. Irreversible fouling may require replacement of the membrane, and thus shortens membrane life [8]. Detrimental effects of fouling on membrane performance ultimately result in an increase in operation and maintenance costs. It is reported that membrane replacement due to fouling is the single largest operating cost when membranes are used in water treatment applications [9].

1.2 Mechanisms of Membrane Fouling

Among various types of membrane foulants, colloids are of particular concern [10,11], because they are small enough to pass through most pretreatment systems, and consequently block membrane pores and/or form a compact cake layer or gel layer on the membrane surface. A wide range of colloids in natural waters may lead to fouling during water treatment, including natural organic matter (NOM), silicate, iron oxides, calcite, and clays.

When colloids are present in the feed water, concentration polarization, cake formation, pore blocking, and adsorptive fouling appear to be the predominant causes of decreased permeate flux over time in low-pressure membrane systems, such as ultra- and micro-filtration [7].
**Concentration polarization**

As permeate water moves across the membrane, it draws solutes and particles toward the membrane. If these materials are rejected by the membrane, they may begin to accumulate on or near the membrane surface, leading to the formation of additional layers of material through which permeate water must pass. These materials achieve higher concentrations near the membrane surface in a flowing concentration boundary layer referred to as the concentration polarization layer. Concentration-polarization is often a precursor to cake or gel formation [2].

**Cake formation**

When the colloidal particle size is much bigger than the membrane pore size, colloidal particles are retained due to a sieving mechanism and a cake layer is formed by particles consequently depositing at the membrane surface. The resistance of the cake, $R_c$, can be expressed as the product of the specific resistance of the cake, $R'_c$, and the cake thickness, $\delta_c$. By the Carman-Kozeny equation, the specific resistance of an incompressible cake composed of uniform particles can be calculated as [2]:

$$R'_c = \frac{180(1-\varepsilon_c)^2}{\varepsilon_c^3 d_p^2}$$  \hspace{1cm} (1)

where $\varepsilon_c$ is the porosity of the cake layer, and $d_p$ is the diameter of particles deposited. From this equation, a cake layer composed of small particles causes greater specific resistance than a cake layer formed by larger particles. Wiesner and Aptel [7] indicate that gel layers of macromolecular materials may produce greater resistance in comparison with cakes of deposited colloidal materials. The cake or gel layer deposited on a
membrane surface essentially acts as a second membrane, through which the permeate water must pass, and therefore, increases the rejection rate of ultra- and micro-filtration membranes [7].

Membrane pore blocking

In addition to cake layer formation, another important type of membrane fouling is membrane pore blocking. Bowen et al. [12] summarized pore blocking mechanisms in relation to filtration performance. The decline in permeate flux is related to the type of membrane pore blocking, which may be classified into the following three categories [12,13]:

1) Complete blocking. Complete blocking occurs when each particle arriving at the membrane participates in sealing pores with no superposition of particles. The particle size is close to the membrane pore size \((d_{\text{particle}} \approx d_{\text{pore}})\). The relationship between the total filtrate volume \((V)\) and time \((t)\) is,

\[
V = \frac{J_0}{k_{CB}} (1 - e^{-k_{CB}t})
\]

where, \(J_0\) is the initial permeate velocity of the filtrate, and \(k_{CB}\) is the complete blocking filtration constant.

2) Standard blocking. In this case, the membrane is envisioned to consist of a set of equal cylindrical pores. Each particle arriving at the membrane deposits onto the internal pore walls, thus leading to a decrease of the pore diameter. The particle size is much smaller than the membrane pore size \((d_{\text{particle}} \ll d_{\text{pore}})\). The relationship between the total filtrate volume \((V)\) and time \((t)\) is,
\[
\frac{t}{V} = \frac{1}{J_0} + \frac{k_{SB}}{J_0} t
\]  

(3)

where, \(k_{SB}\) is the standard blocking filtration constant.

3) \textit{Intermediate blocking}. In this type of pore blocking, particles accumulate within the cylindrical pores, and subsequently seal the membrane pores. The particle size is close to the membrane pore size \(d_{\text{particle}} \approx d_{\text{pore}}\). The relationship between the total filtrate volume \((V)\) and time \((t)\) is,

\[
V = \frac{J_0}{k_{IB}} \ln(1 + k_{IB} t)
\]  

(4)

where, \(k_{IB}\) is the intermediate blocking filtration constant.

\textit{Adsorptive fouling}

Adsorption of water impurities on the membrane surface and/or within the membrane pores may increase the membrane resistance. The adsorption of organic materials onto the membrane surface is often a controlling factor in determining membrane performance [7]. NOM is comprised of a wide range of compounds, which include cell wall residues of microorganisms, microbial exudates, polysaccharides and proteins, as well as humic substances [14, 15]. The chemical structure of NOM is ill-defined [16], varies depending on the source, but typically includes aromatic, aliphatic, carboxylic, and phenolic functional groups [17,18]. Carboxylic functional groups account for 60–90\% of all functional groups [19]. As a result, humic substances are negatively charged in the pH range of natural waters.
NOM and other naturally occurring organic materials can have a much greater effect on permeate flux than inorganic colloids, even at low mass concentrations [7,20]. Previous research indicates that NOM adsorbs both inside pores and on the membrane surface [21,22] and forms a gel layer [23]. NOM may adsorb on membranes via several mechanisms including electrostatic interactions, affinity to specific chemical functional groups, and hydrophobic interactions [24]. Hence, the chemical composition of the membrane, the solution chemistry, and NOM properties play important roles in the adsorption and fouling process.

Generally, cake formation, in combination with membrane pore blocking and adsorptive fouling, results in significant resistance to permeate flux [7]. In most cases encountered in water and wastewater treatment, it appears that the concentration-polarization layer, if it is formed, contributes negligible resistance to permeate flux compared to cake layer resistance ($R_c$) [7]. NOM and colloidal particles are major membrane foulants when membrane filtration is used for natural water treatment [10,25,26]. In addition to the direct effect on membrane fouling, NOM also influences the deposition of colloids in membrane systems. Previous work demonstrated that polyphenolic compounds, proteins, and polysaccharides bind together as colloids that deposit on the membrane and act to cement the cake to the membrane surface [27]. Evidence for at least three membrane fouling mechanisms in the presence of NOM exist: NOM may adsorb in the membrane pores and narrow or block the passageways available to the water; NOM may form a separate gel layer on the membrane surface; or in cases where both NOM and particles are present, NOM may bind particles together to form a low permeability particle/NOM layer on the membrane surface [28].
1.3 Factors Affecting Membrane Fouling

Solution chemistry

Electrostatic interactions among NOM macromolecules, colloidal particles, and the membrane depend on the surface charge and the solution conditions. Because of the presence of numerous carboxylic and phenolic functional groups, humic substances are usually negatively charged in aqueous solution at neutral to high pH [29]. If the membrane is also negatively charged at the filtration pH level, electrostatic repulsion causes less NOM adsorption onto the membrane surface and thus reduces membrane fouling [8, 30]. On the contrary, if the membrane is positively charged during filtration, more NOM adsorption occurs and results in severe membrane fouling. Hence, for filtration of NOM, a negatively charged membrane is preferred. Similarly, inorganic colloidal particles in the natural environment commonly have a negative surface charge due to adsorption of NOM [31].

Solution conditions, such as pH, ionic strength, and the presence of multivalent cations also affect electrostatic interactions [8,30]. NOM, colloidal particles, and the membrane are more negatively charged with increasing pH. Therefore, electrostatic repulsion is strengthened at high pH values. An increase in ionic strength causes a charge screening effect, leading to a decrease in electrostatic repulsion among NOM, colloidal particles, and the membrane. Furthermore, due to reduced inter-chain electrostatic repulsion at high ionic strength, humic macromolecules become coiled and spherical in shape [32], forming a more compact fouling layer [30]. Multivalent cations (such as Ca$^{2+}$ or Mg$^{2+}$) may bind specifically through complex formation with the acidic functional groups (predominantly carboxylic) of NOM [33]. Thus, in the presence of multivalent
cations, the charge of the NOM is reduced significantly not only due to effective charge screening but also due to complex formation [34]. In addition, bridging between NOM macromolecules and the membrane surface mediated by multivalent cation complexation may also contribute to the formation of a dense fouling layer [30].

**Hydrophobic interactions**

Hydrophobic interactions may increase the accumulation of NOM on membranes, leading to adsorptive fouling [7]. Aquatic NOM represents a wide range of structurally complex compounds derived from the chemical and biological degradation of plants and animals [35]. There is some experimental evidence that lower pH values may increase the hydrophobicity of humic materials as measured by the octanol-water partition coefficient [36]. The hydrophobic fraction of NOM gives the largest C/H, C/O, and C/N ratios and aromatic carbon content among the different isolated fractions. The transphilic acid fraction is found to be of intermediate polarity and to incorporate the highest proportion of polysaccharides, whereas the transphilic neutral fraction is almost entirely proteinaceous. The hydrophilic fraction of NOM gives the lowest C/H, C/O, and C/N ratios and aromatic carbon content [37]. It was reported that greater membrane fouling generally occurred with hydrophobic membranes, and the high molecular weight fraction of NOM (>30 kDa) was responsible for the major flux decline [38]. It was also reported that for both the hydrophilic and hydrophobic polyvinylidene difluoride (PVDF) membranes, the order of the fouling potential of the fractionated NOM is hydrophilic neutral > hydrophobic acids > transphilic acids > hydrophilic acids [38,39].
Using negatively charged hydrophilic ultrafiltration membranes, it was found that the major membrane foulants were the larger-sized neutral and/or basic NOM components, and not the humic substances that were efficiently rejected by the membrane [40]. Amy and Cho [41] reported that hydrophilic NOM (polysaccharides) is the dominant foulant of hydrophilic and negatively charged nanofiltration and ultrafiltration membranes. Source waters with a high hydrophilic fraction content of NOM resulted in significant flux decline [42].

**Operating conditions**

Membrane fouling also depends on the operating conditions of the filtration process. From the viewpoint of particle transport, the deposition of particles onto a crossflow membrane surface is governed by two competitive processes: fouling caused by sedimentation of particles transported by permeate flux from the bulk solution onto the membrane surface, and cleaning caused by back transport/removal of particles from the membrane surface to bulk solution by the crossflow. At steady-state, a mass balance of particle transport is achieved by these two competitive processes [43]. Based on this theory, the steady-state permeate flux increases with higher crossflow velocity and lower feed colloid concentrations [10,44].

In addition, the initial permeate flux of the membrane also affects the extent of membrane fouling. Rapid membrane fouling occurs at high initial permeate fluxes [30]. For crossflow filtration, there exists a critical permeate flux, below which there is no detectable membrane fouling [45].
According to Zhu’s report [6], it was shown that permeation drag, which was determined by the membrane permeate flux, played a paramount role in controlling the rate of colloid deposition onto membrane surfaces and subsequently the extent of membrane fouling.

1.4 Conventional Methods for Membrane Fouling Control

A number of approaches are available to reduce membrane fouling, the most common are backflushing/backwashing and chemical membrane cleaning [46]. Backflushing/backwashing is carried out by placing the membrane permeate under a pressure greater than the feed pressure. Usually a backwash pump is employed to reverse the permeate flow from the permeate side to the feed side of the membrane. The change in direction of the flow through the membrane makes it possible to detach the cake of particles deposited on the membrane surface. The backflush/backwash water is then wasted [47,48].

For chemical cleaning of fouled membranes, five categories of cleaning agents are commonly used: alkalines, acids, metal chelating agents, surfactants, and enzymes [49,50,51]. Commercial cleaning products are usually mixtures of these compounds [51]. The cleaning efficiency depends on the type of the cleaning agent and its concentration [52]. Chemical cleaning of fouled membranes is realized through chemical reactions between the cleaning agents and the foulants. A cleaning agent cleans the membrane by removing the foulants, changing the morphology of the foulants, or altering the surface chemistry of the fouling layer [51,53,54,55].
Although backflushing/backwashing and chemical cleaning are commonly used for membrane fouling control, these methods are not ideal. Backflushing/backwashing does not generally remove strongly adherent films or material trapped within the porous substructure of the membrane. In addition, degradation in flux typically occurs after repeated backwashes [46]. For effective operation of a membrane treatment plant, the filtration process must be shut down regularly for membrane cleaning or backflushing/backwashing to regain membrane permeability. Frequent cleaning by these means increases the labor and complexity of the membrane filtration process. For chemical membrane cleaning, restoring the flux may require some powerful cleansing agents, which may damage the membrane. Furthermore, chemical cleaning of membranes also results in increased cost and disposal of waste chemicals.

1.5 Ultrasonic Control of Membrane Fouling

Ultrasound provides an attractive approach for membrane fouling control. Ultrasound has significant advantages over traditional methods to control membrane fouling. For example, no chemicals are used in the membrane cleaning process. In addition, filtration is not interrupted to perform cleaning. The ability to maintain overall higher permeate fluxes through continuous or pulsed use of ultrasound during filtration reduces filtration driving pressure and total membrane area.

Ultrasound is a longitudinal wave greater than 18 kHz [56]. When ultrasound is introduced into water, water is subjected to alternating extension and compression cycles. Cavitation bubbles are formed during the rarefaction of sound waves when the pressure amplitude exceeds the tensile strength of water. Usually, cavitation bubbles are formed at
weak points in the liquid, such as particles and dissolved gases. Acoustic cavitation can be considered to involve at least three discrete stages: nucleation, bubble growth, and under proper conditions, implosive collapse [57].

**Physical effects of ultrasound**

During the compression cycle, when the cavitation bubble collapses, localized hot spots are formed which reach temperatures and pressures in excess of 5000 K and 500 atm, respectively [58]. Associated with ultrasound propagation in water and cavitation bubbles, acoustic streaming [59], microstreaming [60, 61], microstreamers [59, 62], microjets [58, 59, 63], and shock waves [60, 64, 65] are generated. These processes result in fluid movement and may be capable of removing portions of the foulant layer from the membrane surface, and/or preventing the deposition of particles that lead to membrane fouling. The description of these mechanisms is listed below.

Acoustic streaming: As the acoustic wave travels through liquid, it may be absorbed. The momentum absorbed from the acoustic field manifests itself as a flow of the liquid in the direction of the sound field, termed acoustic streaming [59].

Microstreaming: When a bubble pulsates, it moves fluid back and forth. The fluid motion eventually manifests itself as a steady flow called cavitation microstreaming [60].

Microstreamers: A stably oscillating bubble experiences translational radiation forces in a traveling-wave field. A bubble travels from the nucleation site towards the pressure anti-node caused by Bjerknes forces. The translating microbubbles may follow a single pathway or stream, which is referred to as a “cavitation microstreamer” [59, 62].
Microjets: When a bubble is collapsing near a solid surface which is several orders of magnitude larger than the cavitation bubble, symmetric cavitation is hindered and collapse occurs asymmetrically [58,66]. As the bubble collapses, microjets of solvent are formed perpendicular to the solid surface. These microjets have an estimated speed of 100 m/s [63] and lead to pitting and erosion of the surface, in addition to the well-known cleaning effects associated with ultrasound [58].

Shock waves: Acoustic cavitation in liquids generates implosive bubble collapse and associated shock waves, which have pressure amplitudes as high as 10,000 atm [67,68]. Similar to acoustic streaming, shock waves are absorbed by liquid and as a result, liquid moves along the propagation direction of shock waves. Shock waves may also shear macromolecules in liquid [69,70].

**Chemical effects of ultrasound**

In addition to the physical effects of ultrasound, cavitation bubbles also have chemical effects. At the moment of cavitation bubble collapse, localized hot spots may result in the dissociation of chemical compounds including water [71], producing radical species including hydroxyl radicals (•OH). As a typical oxidant in advanced oxidation processes, •OH may oxidize various organics present in aqueous solution, including NOM. In addition, volatile organic compounds may enter the gas phase of cavitation bubbles and subsequently are subject to pyrolysis during cavitation collapse. As a result of sonochemical reactions, NOM properties may change and thus affect the physical-chemical interactions between NOM and the membrane during the filtration process.
1.6 Motivation of This Study

Although the effectiveness of ultrasound-assisted membrane filtration has been reported by several researchers using both polymeric and ceramic membranes [72,73,74,75,76,77,78,79,80,81,82], systematic investigations of the mechanism for ultrasonic control of membrane fouling are extremely scarce. Previous studies typically have shown an increase in permeate flux with ultrasound under different parameters. Few discussions exist on the cleaning mechanisms of ultrasound in a crossflow filtration system. In addition, in other studies membrane foulants such as dextran [73,74,77], peptone [75], baker’s yeast [76], dairy [78,79], Kraft paper mill effluent [80], and calcite particles [81] were subjected to sonochemical reactions during the filtration process. However, no systematic investigation was performed to study property changes of the membrane foulant as a result of sonication. Additionally, experiments performed in an ultrasonic bath [73,74,75,78,79] required sound to pass through the membrane housing. Obtaining reproducible results may be more difficult using a bath system because the amount of power reaching the membrane is highly dependent upon the placement of the membrane within the bath [58,83]. Furthermore, there is a discrepancy regarding the integrity of the membrane through sonication [72].

Due to the problems described above, it is necessary to systematically investigate ultrasonic effects for membrane fouling control. Of particular interest was the cleaning mechanism of ultrasound, the physical interactions between sound waves and colloidal particles (membrane foulant), the effect of ultrasonic factors for system optimization including how to maintain the integrity of the membrane during sonication, sonochemical reactions of NOM (which is a typical membrane foulant when membrane filtration is
used for drinking water treatment), and ultrasonic control of membrane fouling caused by NOM plus particles. Answering these questions is necessary for the fundamental understanding of ultrasonic control of membrane fouling.

The primary goal of this study was to investigate the mechanism of ultrasonic control of membrane fouling caused by colloidal particles and NOM. Based on the mechanistic understanding of ultrasonic cleaning, a series of experiments were performed to explore how to enhance the use of ultrasound to control membrane fouling, how to maintain the integrity of the membrane under harsh sonication conditions, and how to control membrane fouling caused by NOM and particles to simulate the application for drinking water treatment.

1.7 Overview of the Dissertation

This study systematically explored the mechanism and the efficiency of ultrasound to control membrane fouling caused by silica particles and NOM. The dissertation contains 6 chapters. In Chapter 2, silica particles were chosen as the model membrane foulant to study the physical cleaning effect of ultrasound, i.e., acoustic streaming and ultrasonically generated turbulence. In this study, the spatial distribution of ultrasonic cavitation region was determined by sonochemical-induced chemiluminescence (SCL). A physical mechanism for ultrasonic cleaning of membrane was proposed. In addition, the influence of particle characteristics including particle concentration, particle hydrophobicity, and particle size on ultrasonic control of membrane fouling was elucidated.
Chapter 3 studied the ultrasonic factors affecting the efficiency of ultrasound to control membrane fouling caused by silica particles, such as the distance between ultrasonic probe and the membrane surface, the filtration driving pressure, and the operational mode of ultrasound (continued or pulsed). The primary goal of this study was to enhance the ultrasonic efficiency (improve permeate flux and save energy) for membrane fouling control while maintaining the integrity of membrane throughout sonication. A mechanism of membrane damage by ultrasound was proposed in this study.

To fully understand the influence of ultrasound, it is necessary to study the chemical effect of ultrasound on membrane cleaning in addition to its physical effect. Sonochemically generated hydroxyl radicals may oxidize NOM. As a result of sonochemical reactions, the property of NOM may change, thus affecting the physical-chemical interactions between NOM and the membrane, Chapter 4 systematically investigated changes in the properties of NOM following sonication. Purified Aldrich and Pahokee Peat dissolved organic matter (DOM) were used as model NOM. Changes in properties of NOM were characterized by TOC, UV absorbance at 254, 280, and 465 nm, $^{13}$C NMR, acidity titration, and molecular weight before and after sonication. The mechanism of sonochemical reaction of DOM was proposed based on experiments performed at different ultrasonic frequencies and power densities. Based on the changes in DOM due to sonication, implications for the ultrasonic control of membrane fouling and the application of ultrasound in environmental remediation are discussed.

Chapter 5 investigated the effect of solution chemistry on ultrasonic control of membrane fouling caused by DOM and silica particles. Ultrasonic control of membrane
fouling was examined at different pH and ionic strengths, and in the presence of Ca$^{2+}$. A mechanistic explanation is given based on the analysis of foulant-foulant, and foulant-membrane interactions. Both the physical cleaning effect and the chemical effect of ultrasound are discussed.

Finally, the conclusions of this study and recommendations for future work are summarized in Chapter 6.
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2.1 Abstract

In this study, the effect of particle characteristics on the ultrasonic control of membrane fouling was investigated. Ultrasound at 20 kHz was applied to a cross-flow filtration system with γ-alumina membranes in the presence of colloidal silica particles. Experimental results indicated that particle concentration affected the ability of ultrasound to control membrane fouling, with less effective control of fouling at higher particle concentrations. Measurements of sound wave intensity and images of the cavitation region indicated that particles induced cavitation bubbles near the ultrasonic source, which resulted in less turbulence reaching the membrane surface and subsequently less effective control of fouling. When silica particles were modified to be hydrophobic, greater inducement of cavitation bubbles near the ultrasonic source occurred for a fixed concentration, also resulting in less effective control of fouling.
Particle size influenced the cleaning ability of ultrasound; with better permeate recovery observed with larger particles. Particle size did not affect sound wave intensity, suggesting that the more effective control of fouling by large particles was due to greater lift and cross-flow drag forces on larger particles compared to smaller particles. Based on the range of particle sizes and concentrations examined in this study, our results imply that ultrasound will be effective in controlling cake-layer membrane fouling caused by particles in typical lake or ground water.

Keywords: ultrasound, membrane cleaning, membrane fouling, luminol, cavitation

2.2 Introduction

Membrane technology is widely used for water and wastewater treatment, and in food, chemical, and pharmaceutical industries because of the technology’s high removal capacity and ability to meet multiple treatment objectives. Among various membrane materials, ceramic membranes are of increasing interest because of their higher chemical, thermal and mechanical stability compared to organic membranes [1].

Currently, one of the main barriers to greater use of membrane technology is membrane fouling. Membrane replacement due to fouling is the single largest operating cost when membranes are used in water treatment applications [2]. Membrane fouling affects both the quality and the quantity of product water [3] and ultimately shortens membrane life if the fouling is irreversible [4]. Among various types of membrane foulants, inorganic colloidal particles are of particular concern [3,5], because they are
small enough to pass through most pretreatment systems, and consequently block membrane pores or form a compact cake-layer on the membrane surface. A wide range of colloidal particles in natural waters may lead to fouling during water treatment including iron oxides, calcite, silicate, and clays.

A number of approaches are available to reduce membrane fouling, the most common are backflushing/backwashing and chemical membrane cleaning [6]. However, these methods are not ideal. Backflushing/backwashing does not generally remove strongly adherent films or material trapped within the porous substructure of the membrane. In addition, degradation in flux typically occurs after repeated backwashes [46]. For effective operation of a membrane treatment plant, the filtration process must be shutdown regularly for membrane cleaning or backflushing/backwashing to regain membrane permeability. Frequent cleaning by these means increases the labor and complexity of the membrane filtration process. Furthermore, chemical cleaning of membranes results in increased cost and disposal of waste chemicals.

Ultrasound provides an alternative technology for membrane fouling control. When ultrasound is introduced into water, cavitation bubbles are formed during the rarefaction of sound waves. During the compression cycle, when the cavitation bubble collapses, localized hot spots are formed which reach temperatures and pressures in excess of 5000 K and 500 atm, respectively [7]. Associated with ultrasound and cavitation bubbles, acoustic streaming, microstreaming, microstreamers, microjets, and shock waves are generated, which may be capable of removing portions of the fouling layer from the membrane surface, and/or preventing the deposition of particles that lead
to membrane fouling. Ultrasound has significant advantages over traditional methods to control membrane fouling. For example, there is no chemical use in the membrane cleaning process. In addition, filtration is not interrupted to perform cleaning. The ability to maintain overall higher permeate fluxes through continuous or pulsed use of ultrasound during filtration reduces filtration driving pressure and total membrane area.

The effectiveness of ultrasound-assisted membrane filtration has been reported by several researchers [8,9,10,11,12,13,14]. All these studies demonstrated the effectiveness of ultrasound in controlling membrane fouling and enhancing permeate flux using both polymeric and ceramic membranes. Also, these studies showed that the integrity of membranes was maintained under irradiation by ultrasound, except Masselin et al. [8] who observed damage to polyethersulfone membranes by ultrasound. However, the experiments performed in an ultrasonic bath [9,10] required sound to pass through the membrane housing. Furthermore, obtaining reproducible results may be more difficult using a bath system because the amount of power reaching the membrane is highly dependent upon the placement of the membrane within the bath [7,15].

Due to the problems described above, systematic studies on the role of ultrasound in controlling membrane fouling caused by colloidal particles are rather scarce, especially the physical interactions between sound waves and colloidal particles. The presence of colloidal particles leads to a number of physical phenomena, including attenuation of sound waves, nucleation of cavitation bubbles, and an increase in viscosity of the bulk solution. These interactions may affect membrane cleaning, and therefore, must be understood in order to determine relevant applications and optimize the efficiency of
ultrasound. Particle concentration, the hydrophobicity of the particles, and particle size, for example, are important factors influencing these physical interactions, and therefore, likely influence the ultrasonic cleaning process.

In the present work, experiments were performed with a crossflow ultrafiltration system coupled with an ultrasonic probe system to systematically investigate the role of particle characteristics on the ability of ultrasound to control ceramic membrane fouling. Experiments were carried out to determine the effectiveness of ultrasound for reducing membrane fouling. A mechanistic explanation is proposed by which particle concentration, hydrophobicity, and size affect the ultrasonic control of ceramic membrane fouling.

2.3 Materials and Methods

2.3.1 Membranes and Particles

Whatman (Clifton, NJ) Anodisc™ γ-Al₂O₃ ceramic membranes with a polypropylene support ring were used in all experiments. The diameter of the membranes was 47 mm. The membrane thickness was approximately 60 µm. The pore size of the membranes was 0.2 µm through most of the membrane cross-section, and narrowed to 0.02 µm for 2-3 µm at the membrane surface. Water used was from a MilliQ water purification system (R=18.2 MΩ cm). Colloidal silica particles from Sigma Aldrich (St. Louis, MO) were chosen as a model foulant because of their chemical stability with respect to oxidation/reduction. Before filtration experiments, silica particles were sonicated in an ultrasonic bath (Branson 2210, Danbury, CT) for 45 minutes to obtain a
consistent particle size as measured by a MasterSizer (Malvern Instruments Ltd.) or a 90plus Particle Size Analyzer (Brookhaven Instruments Corp.).

2.3.2 Ultrasonic System

A 20 kHz ultrasonic probe system with one inch diameter tip (550 Sonic Dismembrator) from Fisher Scientific (Pittsburgh, PA) was employed during filtration. Calorimetry [7] was performed to measure the power output of ultrasound, which was 19.0±0.5 W for all experiments. Before each experiment, the probe was polished with fine sand paper (220, 3M®) and tuned before sonication.

A K-type thermocouple embedded in the center of a silicone cylinder (4mm in diameter and 5mm in depth) was used to measure the local sound wave intensity at different locations in the membrane cell [16,17]. The K-type thermocouple (5SRTC-TT-K-20-36) with Teflon® insulation and a digital thermometer (HH11) with 0.1 °C resolution were from Omega (Stamford, CT). The temperature inside the silicone increased under the irradiation of ultrasound, thus increasing the temperature detected by the thermocouple embedded in silicone. The sound wave intensity was proportional to the initial rate of temperature increase inside the silicone [18,19] or to the difference between the equilibrium temperature of the thermocouple during sonication and the medium [16]. Measurements of sound wave intensity reflected by the equilibrium temperature difference between the thermocouple and the medium were performed in the membrane cell during crossflow of silica solutions. During measurements, the thermocouple was placed along the center line of the ultrasonic probe at fixed distances from the probe, while particle concentration, hydrophobicity, or size was changed. The initial dissolved
oxygen level of the solutions measured by Orion 810 DO meter (Beverly, MA) was 3.8 mg/L to maintain the same nucleation conditions between different experiments.

2.3.3 Membrane Filtration Experiments

All filtration experiments were performed at 34.5 kPa (5 psi) using a specifically designed crossflow filtration system containing an ultrasonic probe parallel to the membrane surface (see Figure 2.1). The membrane cell is made of plexiglass and is cylindrically shaped with 4.3 cm in diameter and 9.2 cm in depth. 1 mM KCl solution was used as a background electrolyte; the pH value was kept constant at 5.6±0.4. Pure water was run through the membrane before filtration tests with silica suspensions to remove any impurities and to allow the permeate flux to stabilize. The membrane permeate flux was determined by measuring the weight of water per time using an analytical balance (Mettler AJ100, Switzerland). Membrane permeate was returned to the feed tank during the filtration process. Permeate recovery, \( R \), was used to describe the ultrasonic effect as shown in eqn (1);

\[
R = \frac{J_{US} - J'}{J_{0,US} - J'} \times 100\%
\]  

(1)

where, \( J_{US} \) is the steady-state permeate flux with ultrasound, \( J' \) is the steady-state permeate flux without ultrasound, and \( J_{0,US} \) is the permeate flux of a clean membrane with ultrasound. Based on this expression, an \( R \) value of 0% indicates no improvement in permeate flux when using ultrasound; on the other hand, an \( R \) value of 100% indicates the permeate flux was completely restored to the pre-fouling value by using ultrasound.
Experiments were carried at distances between the membrane and the ultrasonic probe of 3.5 or 1.7 cm. At both distances, runs were carried out at the same crossflow velocity and temperature in the membrane cell. At 3.5 cm, the crossflow rate was 500 mL/min. At 1.7 cm, the free volume in the membrane cell was reduced, and therefore the crossflow rate decreased to maintain the same crossflow velocity as 3.5 cm.

2.3.4 Modification of Silica Particles

In select experiments, according to the method of Ducker et al. [20], the surface of silica particles was made hydrophobic by the chemical adsorption of a self-assembled monolayer of octadecyltrichlorosilane (OTS). OTS (≥90%) and dehydrated bicyclohexyl (≥99%) were supplied from Sigma Aldrich and Fluka, respectively. Following adsorption, total organic carbon measurement (by TOC-5000A analyzer, Shimadzu) was performed to test the possible release of OTS and other organics into the aqueous phase; no TOC signal was detected in the aqueous solution containing 0.3 g/L modified silica particles.

The hydrophobicity of silica particles was confirmed by contact angle measurements. The drop profile method (sessile drop) with a high performance CCD camera from Cohu (San Diego, CA) was used to measure the contact angle. The contact angle of the OTS-modified particle surface was 122°, showing high hydrophobicity of the modified silica particles. The contact angle of unmodified silica was less than 30°.

Due to the effect of hydrophobic flocculation, some of the hydrophobic silica particles remained on the water surface. Thus, the particle concentration of hydrophobic
silica in aqueous solution was determined by drawing 50 mL of the solution with a pipet followed by filtering through a pre-dried and weighed 0.45 µm membrane. The mass of hydrophobic silica on the membrane was examined gravimetrically.

2.3.5 Imaging of the Membrane and the Cavitation Region

A XL-30 FEG scanning electron microscope (SEM) (FEI Company, OR) was used to examine the foulant layer and the integrity of the membranes following exposure to ultrasound. Three samples of a given membrane were cut from the center and two other random locations on the membrane. The membrane samples were coated with carbon to enhance the conductivity of the surface. SEM images were taken from more than 5 random locations on each sample in order to obtain a representative image of the surface.

Sonochemical-induced chemiluminescence (SCL) was used to determine the spatial distribution of the cavitation zone in the membrane cell. Luminol (3-aminophthalhydrazide, 97%) and hydrogen peroxide (30% w/w) were acquired from Sigma Aldrich and Fisher Scientific, respectively. Determination of the hydrogen peroxide concentration was performed by the triiodide method [21] with a UV-VIS spectrophotometer (UV-2401PC, Shimadzu). Sodium hydroxide (pellets) and anhydrous sodium phosphate (Na$_2$HPO$_4$) were obtained from Mallinckrodt. The luminol solution was prepared according to the method described by McMurray et al. [22]. $10^{-3}$ M luminol was pH adjusted to 11.3 with sodium hydroxide. During the experiment, 1.5 L of the luminol solution was pumped from the feed tank into the cross-flow membrane cell and
subjected to sonication. A Nikon N90S camera equipped with an AF Micro-Nikkor
105mm f/2.8D lens and a tripod was used to image the cavitation region with an exposure
time of 20 sec. The color film was Fuji 1600. Scanned pictures were analyzed with
Image/J software and the intensity of cavitation was determined semi-quantitatively
based on the grey levels of the image.

2.4 Results and Discussion

2.4.1 Ultrasonic Control of Membrane Fouling

Experimental results indicated that ultrasound significantly reduced cake-layer
fouling. In these experiments, the mean particle size was 1.56 µm (determined by low angle
laser light scattering) and the membrane pore size was 0.02 µm, which was much smaller
than the silica particles. Hence, the main mechanism of membrane fouling was cake-layer
formation. Figure 2.2 shows that the permeate flux with ultrasound (open symbols) was
significantly higher than that without ultrasound (filled symbols). During filtration without
ultrasound, the permeate flux decreased gradually due to membrane fouling. In the
presence of ultrasound, the permeate flux remained close to 0.68 g min⁻¹ cm⁻², which was
equivalent to the clean water flux.

It should be noted that during the filtration of clean water, the membrane permeate
flux with ultrasound was slightly higher than that without ultrasound (data not shown). It
was determined that the temperature was 2.4 °C higher in the membrane cell when
ultrasound was used. Temperature increase is one of the reasons leading to an increase of
the permeate flux with ultrasound. The enhancement of the permeate flux with temperature,
and in the absence of particles, is due to the viscosity change of the solution as determined by [23],

\[
\frac{J_T}{J_{25}} = 1.026^{T-25}
\]  

(2)

where \( T \) is temperature (°C), and \( J \) is the permeate flux at \( T \) or 25 °C. Eqn (2) predicts that the increased temperature in the membrane cell resulted in a 0.04 g min\(^{-1}\) cm\(^{-2}\) increase in the permeate flux, which corresponds closely to the experimental data with clean water solutions. In the presence of particles, the higher permeate flux observed with ultrasound was much higher, and therefore, not solely due to an increase in temperature.

### 2.4.2 Imaging the Cavitation Region

Acoustic cavitation is reported to be the most important mechanism responsible for the cleaning action of ultrasound [24]. When a cavitation bubble collapses, a localized hot spot is formed which reaches high temperatures and high pressures. Cavitation bubble collapse and sound wave propagation produce a number of phenomena that result in high velocity fluid movement in the membrane cell, including microjets [25, 26], microstreaming [27,28], shock waves [27,29,30], microstreamers [26,31], and acoustic streaming [26]. The velocity/pressure and the impact distance of these mechanisms are listed in Table 2.1. It should be noted that the effective distance of microjets, microstreaming, and shock waves are derived from a single cavitation bubble event. During the continuous operation of ultrasound, there are numerous cavitation bubbles collapsing at the same time. Although the effective distance of these mechanisms is in the
micron range, the turbulence generated by the transformation of microjets, microstreaming, and shock waves is considerable.

To determine whether the control of fouling in our experiments was due to the direct action of acoustic cavitation or indirectly by the turbulence generated, the cavitation region in the membrane cell was imaged. Figure 2.3(a) is a photograph of sonochemical-induced chemiluminescence (SCL) caused by the oxidation of luminol monoanion by hydroxyl radicals with emission of light at 430 nm [22]. The hydroxyl radical is a direct product of the collapse of cavitation bubbles. Therefore, SCL of luminol elucidates the spatial distribution of cavitation in solution [22,32]. Generally, the cavitation region was parabolic in shape and extended from the ultrasonic probe surface into solution. The brightest part of the image was below the center of the probe surface, and the brightness decreased with increasing distance away from the probe. It is also interesting to note that the horizontal distribution of the cavitation region was not symmetric. In the crossflow filtration cell, this asymmetry was likely caused by the influence of the crossflow. In Figure 2.3(a), the solution flowed from the inlet at the bottom left to the outlet at the top right above the ultrasonic probe surface.

The collapse of cavitation bubbles in the cavitation region was quantified based on the grey levels of the image. Higher grey levels correspond to a larger population and/or more violent collapse of cavitation bubbles. The profile of the cavitation region was obtained along the central axis of the ultrasonic probe. As shown in Figure 2.3(b), the grey level of the image declined sharply with distance between 0.5 and 1.5 cm from the probe surface into solution. This sharp decline leveled out at further distances corresponding to the grey level of the solution background, since no hydroxyl radical was
locally produced outside the cavitation region. Figure 2.3(b) indicates that the cavitation region extended 1.5 cm from the probe surface.

In this study, the membrane position was chosen to be 1.7 or 3.5 cm from the ultrasonic probe, which was outside the cavitation region. At these distances, therefore, the main mechanisms responsible for ultrasonic removal/prevention of the deposition of particles were acoustic streaming and ultrasonically generated turbulence.

2.4.3 Effect of Particle Concentration

Next, the effect of particle concentration on the ultrasonic control of membrane fouling was examined. Increasing the particle concentration may result in increased attenuation of acoustic energy, enhanced nucleation of cavitation bubbles, and increased viscosity of the solution. Therefore, it was hypothesized that ultrasound may be less effective with an increase in particle concentration. To test this hypothesis, the influence of ultrasound on permeate flux was investigated with different concentrations of silica particles.

Figure 2.4 shows the permeate recovery ($R$) at different particle concentrations during membrane filtration in the presence of ultrasound. In this figure, the particle concentration effect was examined at distances of 1.7 and 3.5 cm between the ultrasonic probe and the membrane surface. Higher permeate recovery occurred at lower particle concentrations for a given probe-membrane distance. At a distance of 3.5 cm, the permeate recovery decreased from 98% to 34% when the particle concentration increased from 0.1 to 1.8 g/L. While at a distance of 1.7 cm, the permeate recovery declined from 100% to 65% when the particle concentration increased from 0.5 to 1.8 g/L. At low particle
concentrations (0.1 g/L for the probe distance of 3.5 cm or 0.5 g/L for the probe distance of 1.7 cm), little membrane fouling was observed with ultrasound, resulting in a permeate flux close to that of clean water. However, at the same particle concentration without ultrasound, the permeate flux declined significantly showing membrane fouling.

Comparing the permeate recovery of ultrasound at different distances between the ultrasonic probe and the membrane surface, a significantly higher permeate recovery was observed at 1.7 cm than at 3.5 cm. At the closer distance, more ultrasonic energy and ultrasonically generated turbulence is focused on the membrane surface, and therefore, better permeate recovery was obtained. However, at low particle concentrations (<0.8 g/L), the decline of the permeate recovery with the increase in particle concentration is more apparent at 3.5 cm than at 1.7 cm. At the 3.5 cm distance, the permeate recovery decreased from 98% to 45% with an increase in particle concentration from 0.1 to 0.8 g/L. While, at this range of particle concentration, almost 100% permeate recovery was obtained at 1.7 cm. With a further increase in particle concentration (≥0.8 g/L), the effect of particle concentration was more apparent at 1.7 cm than at 3.5 cm. At 1.7 cm, the permeate recovery declined 28% from 93% to 65% with the increase in particle concentration from 0.8 to 1.8 g/L. However, at 3.5 cm and with the same increase in particle concentration, the permeate recovery decreased 11%, from 45% to 34%.

Similar experimental findings, namely that higher permeate flux with ultrasound occurred at lower particle concentrations, were reported by Kokugan et al. [12] and Tarleton and Wakeman [14]. Tarleton and Wakeman suggested the decrease of the ultrasonic efficiency under high solid concentrations was due to the attenuation of sound waves, but provided no experimental evidence.
To elucidate the underlying cause of the decrease in permeate recovery with increased solids, model calculations were used to quantify sound wave attenuation by particles. The attenuation of an acoustic wave through a particle suspension may be calculated by [33],

\[ I = I_0 \exp(-2\alpha d) \]  

(3)

where, \( I \) is the intensity of sound waves, \( \alpha \) is the attenuation coefficient, and \( d \) is the penetration distance of sound waves. The total attenuation can be considered as the sum of the different attenuation mechanisms, including intrinsic losses \( \alpha_{int} \), thermal losses \( \alpha_{th} \), visco inertial losses \( \alpha_{vis} \), and scattering losses \( \alpha_{sca} \) \[34,35,36\]. Table 2.2 lists the values of the physical properties of water and silica used for the calculation of sound wave attenuation. In Table 2.2, \( f \) is the frequency of sound wave, \( \rho \) is the density, \( C \) is the sound speed in fluid or particle, \( \gamma \) is the specific heat, \( \beta \) is thermal expansion coefficient, \( \beta_C \) is compressibility, \( \lambda \) is thermal conductivity, and \( \eta \) is the dynamic fluid viscosity.

Based on model predictions, the attenuation of ultrasound caused by particles was less than 0.5% at particle concentrations as high as 5 g/L with the propagation distance of 3.5 cm. Similar results were obtained from another model developed by Carlson et al. \[37\]. Therefore, the attenuation of sound waves by silica particles does not explain the better permeate recovery at lower particle concentrations.

It should be noted that the models described above quantify the physical attenuation of sound waves in the absence of cavitation bubbles (i.e. two-phase system: water and particles). To confirm the model calculations for a non-cavitating system, the sound wave intensity, as reflected by the equilibrium temperature difference between the
thermocouple during sonication and the medium, was measured in the membrane cell at
distances of 1.7 and 3.5 cm from the ultrasonic probe. During the measurements, the
sound wave intensity was set below the threshold of cavitation, as determined
photographically by SCL. The temperature difference between the thermocouple and the
medium was 0.8 and 0.3 °C at the distance of 1.7 and 3.5 cm from the ultrasonic probe,
respectively. No difference in the sound wave intensity as measured by the equilibrium
temperature difference was observed as a function of particle concentration (up to 1.8
g/L). The measurements verified that the effect of particle attenuation of sound waves
was not the controlling factor.

During membrane filtration with ultrasound, cavitation bubbles were present, and
therefore, we had a three-phase system consisting of water, particles, and cavitation
bubbles. Sound wave intensity is consumed by cavitation bubbles due to their scattering
and absorption of sound waves. To investigate the influence of particles on these
processes, the profile of sound wave intensity reflected by the equilibrium temperature
difference in the presence of different concentrations of silica particles was examined
(Figure 2.5). An exponential decrease in sound wave intensity up to 2.0 cm from the
ultrasonic probe was observed. In addition, sound wave intensity decreased with
increasing particle concentration at these short distances. When the distance increased
from 2.0 to 2.5 cm, however, reduction in sound wave intensity reflected by the
equilibrium temperature difference was minimal. When the distance was greater than 3.0
cm, there was no significant difference in sound wave intensity at different particle
concentrations. Since SCL images showed that the extension of the cavitation region was
1.5 cm. Figure 2.5 indicates that most of the ultrasonic energy was consumed in the zone of cavitation.

Based on these results, a likely explanation of the effect of particle concentration is that particles induce additional cavitation bubbles within the solution in the zone of cavitation close to the ultrasonic probe. Particles act as the nuclei within a liquid from which bubbles can grow [26,38,39]. A cavitation bubble attenuates the sound wave due to both scattering and absorption, and thus impedes the propagation of the sound wave, especially at its resonance size [40] (so-called bubble shielding [27]). This scattering and absorption results in a decrease of sound wave intensity compared to in the absence of bubbles (or compared to fewer bubbles at low particle concentrations). Thus, the sound wave intensity decreases more rapidly with distance from the source at high particle concentrations compared to low particle concentrations. As a result, the intensity of sound waves observed at the edge of the cavitation zone in the presence of a high particle concentration was lower compared to the case of a low particle concentration. The lower intensity of sound waves results in weaker collapse of cavitation (weaker microjets and weaker shock waves), weaker microstreaming, weaker microstreamers, and weaker acoustic streaming compared to higher intensity sound waves. As a result, lower velocity gradients \((dv/dy)\) were produced and less shearing stress \((\tau_{Wall}=\mu(dv/dy))\) occurred on the membrane surface. Therefore, the ability of ultrasound to remove particles from the membrane surface as measured by the lift force \(F_L\) of particles was reduced. \(F_L\) is expressed as [41,42],

\[
F_L = 0.761 \left(\frac{\tau_{Wall}}{\eta}\right)^{1.5} \alpha_p^3 \rho^{0.5} \eta
\]  

(4)
where, $\tau_{\text{wall}}$ is the shear stress at the membrane surface, $\mu$ is the kinetic fluid viscosity, $a_p$ is the particle radius, and $\rho$ is the density of the fluid. Thus, due to the lower shearing stress on the membrane surface, a reduction in permeate recovery was observed at higher particle concentrations. It should be noted also that the particles on the membrane surface experienced a smaller drag force, $F_Y$, due to a lower permeate flux at higher particle concentrations. Due to the low Reynolds number of the permeate flow, Stokes-equation is used to estimate the permeate drag force, $F_Y$ [41,42].

$$F_Y = 3\pi \eta a_p \nu$$  \hspace{1cm} (5)

where, $\nu$ is the velocity of the permeate flux. This latter effect reduces fouling but does not entirely explain the effect of particle concentration on permeate recovery in the presence of ultrasound.

Another effect that may influence the ultrasonic control of membrane fouling at high particle concentrations is increased viscosity. Increased viscosity affects both cavitation [43] and the membrane permeate flux. However, based on calculations of the change in viscosity caused by silica particles [44], the viscosity increase was only approximately 1% when the particle concentration was as high as 5.0 g/L. Thus, changes in viscosity were insignificant in this study.

The data in Figure 2.5 are also consistent with our previous findings that particle concentration ($\geq$0.8 g/L) had a more significant effect on membrane fouling control when the probe was placed 1.7 cm from the membrane compared to 3.5 cm. From Figure 2.5, the difference in sound wave intensity reflected by the equilibrium temperature difference
for different particle concentrations at distances of 2 cm or less was greater than the differences observed at 3.5 cm.

2.4.4 Effect of Particle Hydrophobicity

To verify further the hypothesis that particles induce additional cavitation bubbles and decrease the intensity of sound waves, silica particles were made hydrophobic to enhance their ability to induce cavitation bubbles [38,39]. The profile of sound wave intensity reflected by the equilibrium temperature difference was obtained with 0.3 g/L hydrophilic or hydrophobic silica particles. As shown in Figure 2.6(a), sound wave intensity in the presence of hydrophilic silica particles at distances less than 2 cm was significantly higher than that for hydrophobic silica particles. This trend verifies that sound wave intensity decreased more rapidly due to bubble shielding caused by hydrophobic particles inducing more cavitation bubbles near the ultrasonic source than hydrophilic particles. Although more cavitation bubbles appear near the ultrasonic source in the presence of hydrophobic particles, the turbulence generated by bubble collapse is less effective for membrane fouling control because of the larger distance between these cavitation bubbles and the membrane surface. As a result of reduced sound wave intensity, as well as greater particle-particle and particle-membrane interactions, these results suggest that ultrasonic control of membrane fouling will be less effective for hydrophobic colloidal particles. Membrane filtration results (not shown) of 0.3 g/L hydrophilic or hydrophobic silica suspensions indicated that ultrasound was more effective at controlling membrane fouling caused by hydrophilic particles than
hydrophobic particles. The permeate recovery was $75\pm7\%$ and $59\pm4\%$ for hydrophilic and hydrophobic silica particles, respectively.

To visually observe the change of the cavitation region with particles of different hydrophobicity, SCL photographs were taken. Figure 2.6(b) is the comparison of the cavitation region containing a 0.11 g/L hydrophilic or hydrophobic silica suspension. The figure shows that the cavitation region in the presence of hydrophobic particles was more intense than in the presence of hydrophilic particles up to 0.34 cm from the probe surface. This result confirms that additional cavitation bubbles were induced close to the ultrasonic source by hydrophobic particles. However, with a further increase in distance from 0.43 to 1.70 cm, the cavitation region in the presence of hydrophilic particles was more intense than in the presence of hydrophobic particles. Also the extension of the cavitation region was larger in the presence of hydrophilic particles as compared to hydrophobic particles. This result proves that hydrophobic particles reduced the cavitational effects (the bubble quantity and/or the violence of cavitation collapse) at a threshold distance away from the ultrasonic source (0.43 cm in this study). Due to the light scattering of particles, the cavitation region determined by SCL in the presence of particles is not comparable to that of solutions without particles. In addition, this scattering effect makes it impossible to directly examine the cavitation region by SCL at different particle concentrations.
2.4.5 Effect of Particle Size

In addition to particle concentration and hydrophobicity, the effect of particle size was also investigated in this study. Because the cake-layer is more compact with small particles, it was expected that ultrasound would be more effective for the removal/prevention of the deposition of large particles onto the membrane surface. As shown in Table 2.3, silica particles with a mean size of 1.56 \( \mu m \) resulted in 75\( \pm \)7% permeate recovery, which was higher than for a particle size of 0.22 \( \mu m \) (43\( \pm \)0.4%) or 0.16 \( \mu m \) (40\( \pm \)9%). All measurements were carried out at a particle concentration of 0.3 g/L.

Based on the measurement of sound wave intensity reflected by the equilibrium temperature difference (see Figure 2.7) and verified with model calculations [34,35,37], particle size did not significantly affect sound wave intensity. A more likely explanation is simply that the turbulence generated by ultrasound was more effective at removing the large particles. The forces acting on a single particle at a membrane surface, include the lift force \( F_L \) (see eqn (4)), the drag force due to permeate flux \( F_Y \) (see eqn (5)), and the drag force due to crossflow \( F_D \) as shown below [41,42],

\[
F_D = 3.16\pi \tau_{Wall} a_p^2
\]

(6)

where, \( \tau_{Wall} \) is the wall shear stress of the membrane, and \( v \) is the velocity of the permeate flux. The lift force \( F_L \) and the crossflow drag force \( F_D \) contribute to the removal of particles from the membrane surface; while the permeate drag force \( F_Y \) contributes to the deposition of particles onto the membrane surface. From these equations, the lift force \( F_L \) and the crossflow drag force \( F_D \) are more sensitive to an increase in particle size than the
drag force due to permeate flux $F_Y$. Therefore, it is concluded that large particles were more easily removed from the membrane surface by the ultrasonically generated turbulence due to greater drag and lift forces. It should also be noted that the particle size was compared before and after filtration with ultrasound. After sonicating for 280 minutes, no change in particle size was observed with 1.56, 0.22, or 0.16 μm silica.

### 2.4.6 The Integrity of Membrane after Sonication

To verify that the improvement in permeate flux during ultrasound was not a result of damage to the membrane, the integrity of the membrane was examined after sonication at 1.7 or 3.5 cm distances between the ultrasonic probe and the membrane surface. Although there was a report of a damaged polymeric membrane by ultrasound [8], neither SEM images nor the aluminum concentration of the solution indicated any damage of the membrane by ultrasound in our study. The aluminum released into solution was less than 1 μg/L through sonication of 180 minutes. In addition, the permeate flux of a sonicated membrane was identical with that of an un-sonicated membrane during the filtration of clean water without ultrasound. A similar result was also reported by Lamminen et al. [45]. Two reasons are responsible for the integrity of the membrane. First, the membrane was outside the cavitation region during sonication. Second, ceramic membranes have high stability with respect to high temperature and high pressure.
2.4.7 Implications for Water/Wastewater Treatment

This study suggests that ultrasound is helpful to control membrane fouling caused by inorganic colloidal particles. Generally, ultrasound is most effective at controlling fouling of larger, hydrophilic particles at lower concentrations. More efficient control of cake-layer fouling by ultrasound occurred when the membrane was placed outside but close to the ultrasonic cavitation region. For natural waters, particle concentrations are lower than 0.1 g/L in lake water [46,47] or ground water [48,49], and the major distribution of particle size is between 0.6 to 3 µm [50]. Among natural inorganic colloidal particles, silica, calcite, hematite, and illites are hydrophilic [20,51,52,53]. Therefore, ultrasound-assisted membrane ultrafiltration is expected to be very effective to control cake-layer membrane fouling caused by these particles. However, when hydrophobic particles are present, such as kaolinites [53], talc [51], and surfactants or NOM adsorbed on hydrophilic particles [52,54], the efficiency of ultrasound will be reduced. For secondary effluent of municipal wastewater, the particle concentration is typically lower than 30 mg/L [55] and particle sizes range from several nanometers up to more than 100 micrometers [56]. Sewage-borne particles including microorganisms are rich in organic matter and are hydrophobic [57]. Thus, for secondary effluent, ultrasound will likely be effective for most particles, except perhaps very small hydrophobic particles. Further research of the ultrasonic effect on secondary effluent needs to be undertaken. For example, ultrasound may destroy the cell structure of the microorganisms [58] thus increasing the complexity of membrane fouling control by ultrasound.
2.5 Conclusions

The experimental results showed that ultrasound reduced ceramic membrane fouling of silica particles during crossflow filtration. At low particle concentrations, there was little membrane fouling in the presence of ultrasound. However, the permeate recovery of ultrasound declined with an increase in particle concentration. At low particle concentrations (<0.8 g/L), the particle concentration effect was more apparent when the membrane was far away from the cavitation region. However, at higher particle concentrations (≥0.8 g/L), the particle concentration effect was more pronounced when the membrane was close to the cavitation region. Model calculations indicated that the particles did not significantly attenuate sound waves or increase the viscosity of the solution. Instead, particles induce cavitation bubbles resulting in a decrease in sound wave intensity at the edge of the cavitation zone through bubble shielding. As a result of reduced intensity of ultrasound and stronger particle-particle and particle-membrane interactions, fouling of hydrophobic particles was more difficult to control. Particle size did not significantly affect sound wave intensity. Instead, greater lift forces and greater crossflow drag forces occurred with larger particles. Consequently, better permeate recovery in the presence of ultrasound was obtained with larger particles. Based on the typical particle characteristics of lake water and ground water, ultrasound will likely be effective to control cake-layer membrane fouling during the filtration process. However, more studies need to be undertaken with ultrasound assisted membrane filtration of secondary effluent.
2.6 Acknowledgements

This study was supported by funding from the Ohio Water Development Authority and US Geological Survey.
References


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Table 2.1 The list of possible mechanisms associated with ultrasonic cleaning.
<table>
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<th>$\alpha f^2$</th>
<th>$\rho$</th>
<th>$C$</th>
<th>$\gamma$</th>
<th>$\beta$</th>
<th>$\beta_c$</th>
<th>$\lambda$</th>
<th>$\eta$</th>
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<td>Np·s$^2$/m</td>
<td>kg/m$^3$</td>
<td>m/s</td>
<td>J/(kg·K)</td>
<td>K$^{-1}$</td>
<td>GPa$^{-1}$</td>
<td>W/(m·K)</td>
<td>Pa·s</td>
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<td>Water</td>
<td>25×10$^{-15}$</td>
<td>998.2</td>
<td>1482.36</td>
<td>4182</td>
<td>21×10$^{-5}$</td>
<td>1/2.05</td>
<td>0.561</td>
<td>0.001</td>
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<tr>
<td>Silica (glass)</td>
<td>3.4×10$^{-15}$a</td>
<td>2100</td>
<td>5968</td>
<td>700</td>
<td>0.49×10$^{-6}$</td>
<td>1/41.2</td>
<td>1.6</td>
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Note: Data from Ref. [59] unless otherwise noted.

a Data from Ref. [33].

**Table 2.2** The acoustic properties of water and silica.
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<th>Particle size (µm)</th>
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<th>0.22</th>
<th>1.56</th>
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<tr>
<td>The permeate recovery of ultrasound (%)</td>
<td>40±9</td>
<td>43±0.4</td>
<td>75±7</td>
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**Table 2.3** The particle size effect on permeate recovery.
Figure 2.1 Diagram of the crossflow membrane filtration system with ultrasonic probe.
Figure 2.2 The permeate flux of the membrane with or without ultrasound. (Particle concentration was 0.1 g/L. Particle size was 1.56 µm. The distance between the membrane surface and the ultrasonic probe was 3.5 cm. The crossflow rate was 500 mL/min.)
**Figure 2.3 (a)** Image of the ultrasonic cavitation region as determined by sonochemical-induced chemiluminescence (SCL). The membrane position was 3.5 cm below the ultrasonic probe. (The crossflow rate was 500 mL/min.) **(b)** Detection of ultrasonic cavitation region based on the grey levels of the SCL image.

(Continued)
Figure 2.3 Continued

![Graph showing the relationship between distance from the ultrasonic probe (cm) and grey level of luminol image.](image)
Figure 2.4 Ultrasonic control of membrane fouling under different particle concentrations. (The particle size was 1.56 µm. The distance between the membrane and the ultrasonic probe \(d\) was 1.7 or 3.5 cm.)
Figure 2.5 The profile of sound wave intensity under different silica particle concentrations. (The particle size was 1.56 µm.)
Figure 2.6 (a) The profile of sound wave intensity in the presence of 1.56 µm hydrophilic or hydrophobic silica particles. (The particle concentration was 0.3 g/L). (b) Comparison of the SCL images of hydrophilic or hydrophobic silica suspensions based on the grey levels of the cavitation regions. (The particle concentration was 0.11 g/L.)
Figure 2.6 Continued

Distance from the Ultrasonic Probe (cm)

Grey Level of Luminol Image

- Hydrophilic SiO$_2$
- Hydrophobic SiO$_2$
Figure 2.7 The profile of sound wave intensity with respect to different particle sizes.

(The particle concentration was 0.3 g/L.)
CHAPTER 3

ULTRASONIC CONTROL OF CERAMIC MEMBRANE FOULING BY PARTICLES: EFFECT OF ULTRASONIC FACTORS

(submitted to Ultrasonics Sonochemistry, February 2005)

3.1 Abstract

Ultrasound at 20 kHz was applied to a cross-flow ultrafiltration system with γ-alumina membranes in the presence of colloidal silica particles to systematically investigate how ultrasonic factors affect membrane cleaning. Based on imaging of the ultrasonic cavitation region, optimal cleaning occurred when the membrane was outside but close to the cavitation region. Increasing the filtration pressure increased the compressive forces driving cavitation collapse and resulted in fewer cavitation bubbles absorbing and scattering sound waves and increasing sound wave penetration. However, an increased filtration pressure also resulted in greater permeation drag, and subsequently less improvement in permeate flux compared to low filtration pressure. Finally, pulsed ultrasound with short pulse intervals resulted in a relative permeate flux improvement close to that of continuous sonication.
Keywords: ultrasound, membrane cleaning, membrane fouling, luminol, cavitation, pitting.

3.2 Introduction

Membrane processes are of increased interest in water and wastewater treatment, food processing, and in the biotechnological, chemical, and pharmaceutical industries, due to their versatility and effectiveness. However, a common problem encountered during the application of membrane filtration is membrane fouling. Membrane fouling results in increased operating costs due to the higher pressures needed to maintain permeate flux, the time and materials needed for membrane cleaning [1], and membrane replacement [2]. Among various types of membrane foulants, inorganic colloidal particles are of particular concern [3,4], because they are small enough to pass through most pretreatment systems, and subsequently block membrane pores or form a compact cake-layer on the membrane surface [5].

Although considerable progress has been made in understanding membrane fouling, techniques for controlling membrane fouling remain inadequate [6]. Currently, the most commonly used methods to reduce membrane fouling include backflushing/backwashing and chemical cleaning of the membrane [7]. However, these methods are not ideal. For example, membranes exposed to backflushing/backwashing cycles typically experience a degradation in maximum flux after repeated backwashes [7]. Chemical cleaning may damage the membrane and causes secondary pollution [6]. In addition, the membrane filtration process has to be shutdown regularly for backflushing/backwashing and chemical cleaning.
Ultrasonic techniques provide an alternative method for membrane fouling control and cleaning. In a liquid medium (i.e., water), ultrasound creates oscillating regions of high and low pressure. Cavitation bubbles are formed when the pressure amplitude exceeds the tensile strength of liquid during the rarefaction of sound waves. The cavitation bubble collapses during the compression cycle of sound waves. Localized hot spots are formed which reach temperatures and pressures in excess of 5000 K and 500 atm, respectively [8]. Acoustic streaming, microstreaming, microstreamers, microjets, and shock waves are generated as a result of ultrasound. These processes result in fluid movement and may be capable of removing portions of the foulant layer from the membrane surface, and/or preventing the deposition of particles that lead to membrane fouling. There are a number of advantages of ultrasound over traditional methods to control membrane fouling. For instance, there is no chemical use in the membrane cleaning process. In addition, filtration is not interrupted to perform cleaning [5].

The effectiveness of ultrasound-assisted membrane filtration has been reported by several researchers [5, 6, 9, 10, 11, 12, 13, 14, 15, 16]. All these studies demonstrated the effectiveness of ultrasound in controlling membrane fouling and enhancing permeate flux using both polymeric and ceramic membranes. However, little research has been done examining how ultrasonic factors influence the ultrasound-assisted membrane filtration system in the presence of colloidal particles. In the present work, experiments were performed with a crossflow ultrafiltration system coupled with an ultrasonic system to systematically investigate the role of ultrasonic factors in controlling ceramic membrane fouling. Key factors, such as the distance between the ultrasound source and the
membrane, the filtration pressure, and the operation mode (continued or pulsed) of ultrasound were investigated.

In addition, there is a discrepancy in the literature regarding the integrity of membranes following exposure to ultrasound. Masselin et al. [9] observed damage to polyethersulfone membranes by ultrasound, while other researchers [5,10,12,13] showed that the integrity of membranes was maintained throughout sonication. The integrity of the membrane during sonication is of critical importance for the practical application of this technology to control membrane fouling. Therefore, the mechanism of membrane damage by ultrasound must be understood.

### 3.3 Materials and methods

#### 3.3.1 Particles and Membranes

Colloidal silica particles from Sigma Aldrich (St. Louis, MO) were chosen as a model fouulant because of their chemical stability with respect to oxidative conditions potentially resulting from ultrasound [5]. In addition, colloidal silica is a common fouulant found in natural waters. Before filtration experiments, silica particles were sonicated in an ultrasonic bath (Branson 2210, Danbury, CT) for 45 minutes to obtain a consistent particle size as measured by a MasterSizer (Malvern Instruments Ltd., Southborough, MA) or a 90plus Particle Size Analyzer (Brookhaven Instruments Corp., Holtsville, NY). Whatman (Clifton, NJ) Anodisc\textsuperscript{TM} $\gamma$-Al$_2$O$_3$ ceramic membranes with a polypropylene support ring were used in all experiments. The diameter of the membranes was 47 mm. The membrane thickness was approximately 60 $\mu$m. The pore size of the membranes was 0.2 $\mu$m through most of the membrane cross-section, and narrowed to 0.02 $\mu$m for 2-3
μm at the membrane surface. Water used was from a MilliQ water purification system (R=18.2 MΩ cm).

### 3.3.2 Ultrasonic System

The ultrasonic device used during membrane filtration was a 20 kHz ultrasonic probe system with one inch diameter tip (550 Sonic Dismembrator: Fisher Scientific, Pittsburgh, PA). Calorimetry was performed to measure the power output of ultrasound [8]. The power intensity was 3.8±0.1 W/cm$^2$ for all experiments. Before each experiment, the probe was polished with fine sand paper (220, 3M®) and tuned before sonication.

### 3.3.3 Membrane Filtration Experiments

Details of the experimental system have been described previously [5]. The specially designed crossflow filtration system contains an ultrasonic probe parallel to the membrane surface (see Figure 3.1). The cylindrically shaped membrane cell is made of plexiglass with a diameter of 4.3 cm and depth of 9.2 cm. 1 mM KCl solution was used as a background electrolyte; the pH value was kept constant at 5.6±0.4. Pure water was run through the membrane before filtration with silica suspensions to remove any impurities and to allow the permeate flux to stabilize. The membrane permeate flux was determined by measuring the weight of water per time using an analytical balance (Mettler AJ100, Switzerland). Membrane permeate and concentrate were returned to the feed tank during the filtration process.
Relative permeate flux improvement at steady-state due to ultrasound, \( R \), was used to describe the ultrasonic effect as shown in eqn (1) [5];

\[
R = \frac{J_{\text{US}} - J'}{J_{0,\text{US}} - J'} \times 100\%
\]

where, \( J_{\text{US}} \) is the steady-state permeate flux with ultrasound; \( J' \) is the steady-state permeate flux without ultrasound; and \( J_{0,\text{US}} \) is the permeate flux of a clean membrane with ultrasound, which accounts for an increase in the permeate flux due to a slightly higher temperature of the feed solution caused by ultrasound [5]. Based on this expression, an \( R \) value of 0% indicates no improvement in permeate flux when using ultrasound compared to without ultrasound; on the other hand, an \( R \) value of 100% indicates the permeate flux was completely restored to the pre-fouling value by using ultrasound.

Experiments were performed at distances between the membrane and the ultrasonic probe of 3.5, 2.6, 1.7, or 1.3 cm. At these distances, runs were carried out at the same crossflow velocity and temperature in the membrane cell. At 3.5 cm, the crossflow rate was 500 mL/min. At 2.6, 1.7, or 1.3 cm, the free volume in the membrane cell was reduced, and therefore the crossflow rate was decreased to maintain the same crossflow velocity as the 3.5 cm distance. In addition to changing the distance, the pressure within the membrane system was varied from 1 to 8 psi.

### 3.3.4 Imaging of the Ultrasonic Cavitation Region

Sonochemically-induced chemiluminescence (SCL) was used to determine the spatial distribution of the cavitation zone in the membrane cell [5]. Luminol (3-
aminophthalhydrazide, 97%) and hydrogen peroxide (30% w/w) were acquired from Sigma Aldrich and Fisher Scientific, respectively. The hydrogen peroxide concentration was determined by the triiodide method [17] with a UV-VIS spectrophotometer (UV-2401PC, Shimadzu). Sodium hydroxide (pellets) and anhydrous sodium phosphate (Na₂HPO₄) were obtained from Mallinckrodt. The luminol solution was prepared according to the method described by McMurray et al. [18]. During the experiment, 1.5 L of the luminol solution was pumped from the feed tank into the cross-flow membrane cell and subjected to sonication. A Nikon N90S camera equipped with a AF Micro-Nikkor 105mm f/2.8D lens and a tripod was used to image the cavitation region with an exposure time of 20 sec. The color film was Fuji 1600. Scanned pictures were analyzed with Image/J software and the intensity of cavitation was determined semi-quantitatively based on the grey levels of the image.

3.3.5 Examination of Membrane Integrity

The integrity of the membranes was investigated after exposure to ultrasound under different conditions in the absence of particles to better visualize possible damage at the membrane surface. A XL30 ESEM-FEG scanning electron microscope (SEM) (FEI Company, OR) was used to examine the integrity of the membranes following exposure to ultrasound [5]. The membrane samples were coated with carbon to enhance the conductivity of the surface. In addition to visualization by SEM, XDS-2000 x-ray diffraction (Scintag Inc., CA) was employed to analyze possible crystal structure changes of the ceramic membrane following exposure to ultrasound. Furthermore, an Inductively Coupled Plasma Atomic Emission Spectrophotometer (ICP-AES) (Varian Inc., Australia)
was used to examine the possible release of the membrane material (i.e., aluminum) into the solution as a result of sonication. The ICP-AES was calibrated using 4 standard concentrations of aluminum and a blank sample. The samples were acidified by addition of nitric acid (Trace Metal Grade, Fisher Scientific) to 5% (v/v) to dissolve alumina if present for ICP-AES measurements. 0.22 \( \mu \text{m} \) MCE syringe filters (Fisher Scientific) were used to filter solutions prior to acidification of samples to determine if aluminum present was particulate or dissolved. Finally, if analytical methods showed no damage, the membrane permeate flux of clean water was measured to confirm the integrity of the membrane after sonication.

### 3.4 Results and Discussion

#### 3.4.1 Effect of Distance between Ultrasonic Source and Membrane

Initial experiments examined relative permeate flux improvement due to ultrasound as a function of the distance of the ultrasonic probe from the membrane surface. Our previous research indicated that the ultrasonic cavitation region extended 1.5 cm from the probe surface at a filtration pressure of 5 psi [5]. In this study the membrane position was chosen to be 3.5, 2.6, 1.7, and 1.3 cm from the ultrasonic probe. In these positions, the membrane was outside the cavitation region, except at the 1.3 cm distance from the ultrasonic probe. Two mean particle sizes of silica were examined: 1.56 and 0.22 \( \mu \text{m} \) with the same particle concentration of 0.5 g/L. The membrane pore size was 0.02 \( \mu \text{m} \), which was much smaller than the silica particles. Hence, the main mechanism of membrane fouling was cake-layer formation.
Figure 3.2 shows that more relative permeate flux improvement occurred at smaller distances between the membrane and the ultrasound source, regardless of particle size. For 1.56 µm particles, the relative permeate flux improvement increased from 60% to 75% to 97%, as the distance decreased from 3.5 to 2.6 to 1.7 cm. For 0.22 µm particles, the relative permeate flux improvement increased from 29% to 36% to 59% at distances of 3.5, 2.6, and 1.7 cm between the ultrasonic probe and the membrane surface, respectively.

Acoustic cavitation is reported to be the most important mechanism responsible for the cleaning action of ultrasound in a variety of applications [19]. When a cavitation bubble collapses, a localized hot spot is formed which reaches high temperatures and high pressures. Cavitation bubble collapse as well as sound wave propagation produce a number of phenomena that result in high velocity fluid movement in the membrane cell, including microjets [20,21], microstreaming [22,23], shock waves [22,24,25], microstreamers [21,26], and acoustic streaming [21]. Thus, when the membrane is within the cavitation region, all of the mechanisms mentioned above may directly contribute to the cleaning action of ultrasound. However, when the membrane is outside the cavitation region, the main mechanism of ultrasonic cleaning is acoustic streaming, and ultrasonically generated turbulence [5]. A major difference between the fluid movement within or outside the cavitation region is the energy density, which is extremely high within the cavitation region where the high velocity fluid movement occurs at the micron-scale [27].

For the pressure, intensity, and distances between the membrane and the probe shown in Figure 3.2, the membrane was outside the ultrasonic cavitation region, which
extended 1.5 cm from the probe surface [5]. The decrease in effectiveness with increasing distance can be attributed to the fact that the sound wave intensity decreases with the propagation distance from the ultrasonic source. Therefore, at close distances, more ultrasonic energy reaches the membrane surface, which results in stronger acoustic streaming and stronger ultrasonically generated turbulence. The greater turbulence facilitates cleaning by generating a greater lift force, $F_L$, is expressed as [28,29],

$$F_L = 0.761 \left[ \frac{\mu (dv/dy)}{\eta} \right]_{wall}^{1.5} \frac{a_p^3 \rho^{0.5}}{\eta}$$  \hspace{1cm} (2)$$

where, $dv/dy$ is the velocity gradient at the membrane surface (wall) resulting from the ultrasonically generated turbulence, $\mu$ is the kinetic fluid viscosity, $\eta$ is the dynamic fluid viscosity, $a_p$ is the particle radius, and $\rho$ is the density of the fluid. As a result, more relative permeate flux improvement was observed at shorter distances between the ultrasonic source and the membrane.

Figure 3.2 also shows that for a given distance, fouling by larger particles was controlled more effectively than when smaller particles were present. This result is consistent with previous results [5], showing that greater lift forces and greater crossflow drag forces occur with larger particles for a given amount of ultrasonically generated turbulence.

For experiments in which the membrane was outside the cavitation region, the integrity of the membrane following sonication was examined by SEM, x-ray diffraction, ICP-AES, and permeate flux measurements of clean water. All these data indicated no damage to the membrane. However, when the membrane was located just within the ultrasonic cavitation region (1.3 cm from the ultrasonic probe), membrane damage was
found. Figure 3.3 shows SEM images that indicate pitting on the membrane surface. There were about 20 discrete pits in the center of the membrane following 5 minutes of sonication. The diameters of the pits on the membrane surface were around 1.1±0.2 µm.

In Figure 3.3(a), pitting at the top surface of the membrane was observed, revealing the larger pore size of the matrix structure of the membrane subsurface. In Figure 3.3(b), a similarly sized pit was observed. However, the underlying matrix structure is not visible suggesting a deeper pit.

Literature on cavitation-induced metal surface erosion [27, 30, 31] suggests microjets and/or shock waves are likely responsible for the surface damage of the membrane. The velocity of microjets can be greater than 100 ms⁻¹ [20] and the pressure amplitude of shock waves can be as high as 1 GPa [22]. Both microjets and shock waves have extremely high energy densities. The existence of both mechanisms has been established during cavitation collapse, but their relative importance is a matter of debate [20]. According to Crum’s report of erosion of metals by cavitation collapse [27], the pitting on metal surfaces is more likely caused by microjets. Philipp and Lauterborn observed cavitational erosion on a flat metal specimen when bubble collapse occurred at a distance less than twice its maximum radius from a solid boundary [31]. Therefore, when the membrane was located outside the ultrasonic cavitation region, the membrane surface was unlikely to be directly impacted by microjets and/or shock waves generated from the final collapse of cavitation bubbles. As a result, the membrane integrity was maintained.

In addition to pitting of the membrane surface, membrane cracking occurred (see Figure 3.4) along with the release of aluminum into solution (see Table 3.1), when the
membrane was within the cavitation region. However, x-ray diffraction data did not show a change in the crystal structure of the membrane material (data not shown). In Figure 3.4, cracking was observed at the center of the membrane. As shown in Table 3.1, consistent with damage to the membrane material, a significantly higher concentration of total aluminum (about 6 \( \mu \text{M} \)) was observed in the bulk solution. Filtration of the solution revealed no dissolved aluminum above blank levels indicating that the released aluminum from the membrane was in particulate form. Therefore, the damage caused by ultrasound was likely mechanical in nature (e.g. cracking) and not chemical (e.g. dissolution).

In addition to membrane surface pitting, microjets and shock waves may also induce discrete micro-fissures \[27\]. These fissures may then propagate throughout the bulk of the membrane material upon repeated stresses acting on the membrane such as filtration pressure, turbulent shearing, and vibration. This mechanism is likely responsible for the membrane cracking observed in Figure 3.4, when the cavitation region extended to the membrane surface.

Previous studies examining ultrasound-assisted membrane filtration \[5,6,9,10,11,12,13,14,15,16\] have reported conflicting data regarding the integrity of membranes during cleaning. The results presented here suggest that in previous studies in which membranes were damaged, the membranes were likely within the ultrasonic cavitation region.

### 3.4.2 The Effect of the Filtration Pressure

The filtration pressure is an important factor affecting the ultrasound-assisted membrane filtration system. In Figure 3.5, the relative permeate flux improvement due to
ultrasound declined from 100±2% to 59±5% when the filtration pressure increased from 1 to 8 psi (6.9 to 55.2 kPa), respectively.

Filtration pressure affects both particle deposition behavior on the membrane surface and cavitational properties of ultrasound. An increase in filtration pressure results in a higher permeate velocity (v) through the membrane, and thus causes a stronger permeation drag force (F_D) on the particles at the membrane surface, which leads to greater membrane fouling [3]. The permeation drag force is proportional to the velocity of the permeate flow through the membrane and is determined by [28,29]

\[ F_D = 3\pi \eta_d v \]  \hspace{1cm} (3).

Also, an increase in filtration pressure increases the compressive forces driving cavitation collapse [21,32,33] but decreases in the quantity of cavitation bubbles formed [34,35]. The increased compressive forces at higher pressures result in an increase of the velocity of the bubble wall during implosion [21]. Consistent with an expected increase in violence of cavitation collapse, Whillock et al. [36] observed a significant increase in the corrosion rate of stainless steel by ultrasound with increasing hydrostatic pressure. Therefore, more violent cavitation collapse results in stronger mechanical effects that may potentially enhance the cleaning effect of ultrasound. In addition, fewer bubbles present in solution at higher pressure may limit bubble shielding [22], in which bubbles attenuate sound waves due to both scattering and absorption, also resulting in improved cleaning.

To directly compare the ultrasonic cavitation intensity under different pressures, photographs of SCL were taken at filtration pressures of 1 and 8 psi, as shown in Figure 3.6. SCL is caused by the oxidation of luminol monoanion by hydroxyl radicals with
emission of light at 430 nm [18]. The hydroxyl radical is a direct product of the collapse of cavitation bubbles. Therefore, SCL of luminol elucidates the spatial distribution of ultrasonic cavitation in solution [5,18,37]. Generally, the brightest part of the cavitation region was below the center of the probe surface, and the brightness decreased with increasing distance away from the probe.

Figure 3.6 shows a greater extension of the cavitation region at 8 psi than 1 psi. The collapse of cavitation bubbles in the cavitation region was quantified based on the grey levels of the image. Higher grey levels correspond to a larger population and/or more violent collapse of cavitation bubbles. The profile of the cavitation region was obtained along the central axis of the ultrasonic probe as shown in Figure 3.7. At 8 psi a higher grey level of the SCL image was seen at the beginning (between 0 and 0.45 cm from the probe surface) and at the end (between 1.1 and 2.1 cm from the probe surface) of the cavitation region compared to 1 psi. The extension of the ultrasonic cavitation region was 1.4 and 2.1 cm at pressures of 1 and 8 psi, respectively.

Therefore, at higher filtration pressures fewer bubbles present may facilitate the propagation of sound waves and result in a higher sound wave intensity reaching the membrane surface. The higher intensity of sound waves results in stronger acoustic streaming and ultrasonically generated turbulence (from more violent collapse of cavitation and possibly more cavitation bubbles collapse close to the membrane surface). As a result, higher velocity gradients \( (dv/dy) \) were produced and more shearing stress \( (\tau_{wall}=\mu(dv/dy)) \) occurred on the membrane surface [5], which enhances the ultrasonic cleaning effect. However, given that a decrease in the relative permeate flux improvement of ultrasound was observed with increasing pressure, the experimental
results suggest the increase in the permeate drag force was more significant than increased turbulence due to ultrasound with elevation of the filtration pressure.

3.4.3 The effect of Continued/Pulsed Ultrasound

To reduce energy consumption, ultrasound may be operated in a pulsed mode instead of a continuous mode. No previous work, however, has examined this operational practice for membrane fouling control. In Figure 3.8, different pulse intervals were used between ultrasound pulses of 1.0 s in duration, corresponding to pulse ratios (defined by pulse time/pulse interval time) ranging from 10 to 0.5. As shown in Figure 3.8, the relative permeate flux improvement decreased from 75±7% to 27±4% when the pulse interval increased from 0 to 2.0 s, respectively. However, when the pulse interval was short (i.e., 0.1 s), the relative permeate flux improvement was 73±4%, which was similar to continued sonication (75±7%). Therefore, using pulsed ultrasound at short pulse intervals (1.0 s on/0.1 s off) results in roughly 9% energy savings compared to continuous sonication, while maintaining the cleaning effects of ultrasound.

The loss of relative permeate flux improvement with increasing pulse interval was likely due to periodic losses in ultrasonically generated turbulence and subsequent deposition of particles on the membrane surface due to permeate flow. However, pulsing also affects bubble dynamics. During sonication, some bubbles grow by rectified diffusion to sizes greater than their resonance size. Such bubbles greater than the resonance size are ineffective at producing cavitation and absorption of ultrasonic waves (i.e., bubble shielding) [22]. Therefore, in continuous ultrasound, some bubbles are ineffective [38] and some ultrasonic energy is
wasted. However, during pulse intervals with pulsed sonication, bubble sizes are reduced back to below resonance size by dissolution, and some bubbles coalescence and consequently float to the water surface during the pulse intervals [21,22,40]. As a result, bubble size and bubble quantity may decrease during the pulse intervals reducing the shielding of sound waves by bubbles. Suitable pulse times and pulse intervals may reduce bubble shielding as well as make use of surviving bubbles from previous pulse cycles to generate effective cavitation collapses for optimal membrane fouling control. From the literature, yields of sonochemical reactions such as sonoluminescence [39], generation of free iodine from KI solution [40], and DNA degradation [40] increase with pulsed sonication, due to more effective use of ultrasonic energy. Therefore, as shown in Figure 3.8, when the pulse interval is short (i.e., 0.1 s), the relative permeate flux improvement of pulsed sonication was close to that of continuous sonication.

3.5 Conclusions

The experimental results show that ultrasonic factors play an important role in membrane fouling control. The ideal location of the membrane is outside but close to the cavitation region. At this location, high relative permeate flux improvement of ultrasound was obtained and the integrity of the membrane was maintained. However, if the membrane was within the cavitation region, damage was evident. Pitting was found on the membrane surface, and membrane cracking and the release of particulate aluminum into solution occurred. Furthermore, an increase in the filtration pressure caused a stronger permeation drag force on the particles at the membrane surface. As a result, the relative permeate flux improvement with ultrasound declined, although more violent
collapse of cavitation bubbles and greater extension of cavitation region occurred at higher filtration pressures. Finally, the relative permeate flux improvement decreased with long pulse intervals of ultrasound. However, when the pulse interval was short (i.e., 1.0 s on/0.1 s off), the relative permeate flux improvement was close to that of continuous sonication.

3.6 Acknowledgements

This study was supported by funding from the Ohio Water Development Authority and US Geological Survey.
References


Table 3.1 The release of aluminum from the membrane into the solution when the membrane was within the ultrasonic cavitation region.

<table>
<thead>
<tr>
<th>Sonication Time (min)</th>
<th>0</th>
<th>30</th>
<th>60</th>
<th>120</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration of Al without the membrane (blank) (µM)</td>
<td>0.26</td>
<td>0.74</td>
<td>0.96</td>
<td>1.15</td>
</tr>
<tr>
<td>Concentration of Al in the presence of membrane (sample was not filtered) (µM)</td>
<td>0.33</td>
<td>5.93</td>
<td>5.81</td>
<td>6.04</td>
</tr>
<tr>
<td>Concentration of Al in the presence of membrane (sample was filtered by a 0.22 µm syringe filter) (µM)</td>
<td>0.22</td>
<td>0.26</td>
<td>0.41</td>
<td>0.63</td>
</tr>
</tbody>
</table>
Figure 3.1 Diagram of the crossflow membrane filtration system with ultrasonic probe.
**Figure 3.2** Ultrasonic control of membrane fouling under different distances between the ultrasonic probe and the membrane. The particle concentration was 0.5 g/L. The filtration pressure was 5 psi.
Figure 3.3 Pitting on the membrane surface caused by microjets and/or shock waves when the membrane was within the ultrasonic cavitation region. The distance between the ultrasonic probe and the membrane was 1.3 cm. The filtration pressure was 5 psi.
Figure 3.4 Cracking at the membrane surface caused by cavitation collapse when the membrane was within the ultrasonic cavitation region. The distance between the ultrasonic probe and the membrane was 1.3 cm. The filtration pressure was 5 psi.
Figure 3.5 Relative permeate flux improvement of ultrasound at different filtration pressures. The particle concentration was 0.2 g/L. The particle size was 1.56 µm. The distance between the ultrasonic probe and the membrane was 3.5 cm.
Figure 3.6 Imaging of the ultrasonic cavitation region as determined by SCL at the filtration pressure of 1 and 8 psi, respectively. The membrane position was 3.5 cm below the ultrasonic probe.
Figure 3.7 Comparison of the cavitation regions between the filtration pressures of 1 and 8 psi based on the grey levels of the SCL image.
Figure 3.8 Ultrasonic control of membrane fouling with different pulse intervals of ultrasound. The pulse time was 1.0 s. The particle concentration was 0.3 g/L. The particle size was 1.56 µm. The distance between the ultrasonic probe and the membrane was 3.5 cm. The filtration pressure was 5 psi.
CHAPTER 4

SONOCHEMICAL REACTIONS OF DISSOLVED ORGANIC MATTER

(Research on Chemical Intermediates, 2004, 30(7-8), 735-753)

4.1 Abstract

Property changes of Aldrich and Pahokee peat dissolved organic matter (DOM) at different ultrasonic frequencies and energy densities were systematically investigated. Exposure of DOM to ultrasound resulted in decreases in TOC, Color$_{465}$, specific UV absorbance (SUVA), aromaticity, and molecular weight, while DOM acidity increased. Compared to 20 kHz ultrasound, greater sonochemical transformation of DOM occurred at 354 kHz and at higher energy density, due to greater •OH radical production. The changes to DOM properties suggest that ultrasound may significantly affect DOM-pollutant interactions (e.g., facilitate desorption of hydrophobic organics from DOM or promote complexation between metallic cations and DOM).

Keywords: natural organic matter, dissolved organic matter, ultrasound, $^{13}$C NMR, oxidation, aromaticity, Aldrich, Pahokee
4.2 Introduction

Sonication has been explored as an oxidation technology for the treatment of refractory organic pollutants in water [1,2] and contaminated sediment [3,4], and for disinfection [5] and membrane cleaning [6,7] in drinking water applications. The presence of natural organic matter (NOM), however, may significantly influence the effectiveness of ultrasound in these systems. NOM is present in natural waters due to the degradation of plant and animal matter. The chemical structure of NOM is ill-defined [8], varies depending on the source, but typically includes aromatic, aliphatic, carboxylic, and phenolic functional groups [9]. NOM can undergo a variety of reactions in natural and engineered systems and often interferes with treatment processes by binding organic and inorganic contaminants and scavenging reactive species [3,10]. In addition, it plays an important role in particle coagulation, trace-metal cycling, and mobility of both inorganic and organic pollutants [11,12].

Sonochemical techniques involve the use of sonic or ultrasonic waves to produce a turbulent and/or oxidative environment via cavitation bubbles generated during the rarefaction phase of sound waves. During the compression cycle, when the cavitation bubble collapses, localized hot spots are formed which reach temperatures and pressures in excess of 5000 K and 1000 atm, respectively [13]. These high temperatures result in the dissociation of chemical compounds including water [14], producing radical species including •OH radicals.

When polymers or other macromolecules (e.g., NOM) exist in the vicinity of cavitation bubbles, the solvent flow fields produced around cavitation bubbles serve to stretch and open the macromolecular coils, placing the chains under stress. These
macromolecules are then broken by shock waves resulting from the final collapse of cavitation bubbles [15]. This is referred to as shear degradation of macromolecules by ultrasound. Breaking of these macromolecules (i.e., cleavage of a covalent bond) can occur in two ways: homolytically, resulting in one electron from the bond going to each fragment to produce radical species; or heterolytically, with both electrons associating with one fragment, leading to formation of an ion pair [16]. Both of these possibilities have been observed during polymer degradation by ultrasound [16,17,18,19]. In addition to shear degradation, macromolecules may be broken down by ultrasound due to the production of • OH radicals [20,21].

Studies of changes in NOM as a result of sonication are scarce [20,21,22]. Previous studies focused on reducing disinfection by-products, and therefore, a detailed understanding of the influence of sonication on the chemical structure of NOM was not obtained. In the present work, dissolved organic matter (DOM) was characterized before and after sonication using a variety of analytical techniques. Two types of DOM were investigated: Aldrich and Pahokee peat DOM. Both have been studied previously, and are commonly used as model humic substances [23,24]. The purpose of this study was to systematically characterize chemical changes to DOM with respect to different ultrasonic frequencies and energy densities, and to determine how DOM reactivity is altered by sonication.
4.3 Methodology

Preparation of DOM

Commercial Aldrich humic acid (sodium salt) was supplied by the Aldrich Chemical Company (Milwaukee, WI). Aldrich humic acid was purified according to procedures described by Chin et al. [25] followed by washing with 0.3 M HF and dialysis with 1000 Dalton (Da) molecular weight cut off (MWCO) membranes and freeze drying. DOM extracted from Pahokee peat purchased from the International Humic Substances Society (IHSS) was isolated using the IHSS standard method for soil [26], followed by dialysis with 1000 Da MWCO membranes and freeze drying. For both DOM, the dialysis was continued until the dialyzing water was free of chloride as determined with an AgNO₃ indicator.

Ultrasonic Units

Ultrasonic reactions of DOM were performed with two different ultrasonic reactors: a 20 kHz ultrasonic probe system (550 Sonic Dismembrator) from Fisher Scientific (Pittsburgh, PA) and a URS 1000 Ultrasonic Laboratory Reactor consisting of a USW 51-52 ultrasonic transducer operating at 354 kHz with an LVG 60 Radio Frequency Generator (L3 Communications ELAC Nautik). In both systems, experiments were run as batch reactors, and calorimetry was performed to measure the power output of ultrasound [27]. Both reactors contained a water jacket connected to a cooling bath (Fisher Scientific 1006S Isotemp) to keep the reacting solution at 25 °C.

For the 20 kHz ultrasonic probe system, a 50 mL glass rosette reactor was used. The probe with replaceable titanium tip was immersed into the solution to a depth of 3.5
cm. The area of the tip was 1.26 cm². Before sonication, the titanium tip was polished with fine sand paper (220, 3M®) and tuned.

For the 354 kHz sonication system, sound waves were emitted from the bottom of the reactor. The emission area of the transducer was 23.7 cm². 100 or 500 mL solutions were sonicated to obtain different energy densities in solution.

**Experimental Conditions**

Water used was from a MilliQ water purification system (R=18.2 MΩ·cm). For all experiments, the TOC concentration of both DOM was 22.5 mg/L. All degradation experiments were run at an initial pH of 4.0. pH was adjusted manually by addition of 0.10 M nitric acid (Trace Metal Grade, Fisher Scientific) or 0.10 M sodium hydroxide (certified ACS, Fisher Scientific) to maintain the pH at 4.0. Additions did not exceed 1% of the original sonicated volume.

At specific times during sonication, samples were withdrawn from the batch reactors using a 5-mL pipette with Teflon tips. The total volume withdrawn during a single run never exceeded 5% of the total volume. Due to tip erosion in the 20 kHz probe system, samples from the probe system were centrifuged (Beckman centrifuge, Model J2-21) at 3500 rpm for 10 minutes to remove particles. For H₂O₂ detection in the probe system, samples were filtered with a 0.45 µm PTFE syringe filters. For the 354 kHz sonication system, samples were analyzed without centrifugation or filtration.
Sample Analysis

Total organic carbon (TOC) and dissolved organic carbon (DOC) were measured by a Shimadzu TOC-5000A analyzer operating in the non-purgable organic carbon mode. Determination of hydrogen peroxide was performed by the triiodide method [28]. The UV absorbance of DOM at 254, 280, and 465 nm was measured by a UV-VIS spectrophotometer (UV-2401PC, Shimadzu). Potentiometric acidity titration of DOM was performed under a N₂ atmosphere following the procedures of Edwards et al. [12] using an Orion 960 Autochemistry System (Beverly, MA).

Molecular weight distributions of DOM before and after sonication were measured by high pressure size exclusion chromatography (HPSEC) (Waters Associates, Milford, MA) at 360 nm according to the method described by Chin et al. [23]. A wavelength of 360 nm was chosen to minimize the interference of nitrate in analysis. The HPSEC was calibrated using sodium polystyrene sulfonates (Polysciences) with molecular weight of 18K, 8K, 4.6K, and 1.8K, respectively and acetone.

Cross Polarization Magic Angle Spinning (CPMAS) ¹³C nuclear magnetic resonance (NMR) spectra were obtained using a Bruker DPX 300 MHZ NMR-spectrometer (Bruker Analytic GmbH, Germany). About 80 mg freeze-dried DOM samples before and after sonication were analyzed according to the details described by Dria et al. [29]. The ¹³C NMR spectra were integrated according to the following regions: 0-45 ppm, paraffinic carbons; 45-60 ppm, methoxyl; 60-90 ppm, carbohydrate carbons; 90-112 ppm, carbohydrate and proton-substituted aromatic carbons; 112-140 ppm, carbon-substituted aromatic carbons; 140-160 ppm, oxygen substituted aromatic carbons; 160-190 ppm, carboxyl and aliphatic amide carbons; 190-220 ppm, aldehyde and ketone
carbons [29,30,31]. Total aromaticity was calculated by expressing aromatic C as a percentage of the aliphatic plus aromatic C [29,32].

4.4 Results

Initial Characterization of Aldrich and Pahokee Peat DOM

The chemical nature or structure of NOM is determined by its source materials and by biogeochemical processes that take place at the site of their formation [33]. Aldrich humic acid is extracted from coal by base extraction by Aldrich Chemical Company [34]. Generally, Aldrich humic acid is more aromatic and has a higher molecular weight than humic materials isolated from natural waters [23]. Pahokee peat is a typical agricultural peat soil of the Florida Everglades. Pahokee series soils consist of very poorly drained soils that are 36 to 51 inches thick over limestone. Pahokee soils formed in organic deposits of freshwater marshes [35]. It has been shown that soil and peat humic acids are generally less aliphatic and more aromatic than aquatic humic acids [36].

The properties of humic substances are important in complexation of trace metals, the solubilization and transport of relatively insoluble organic compounds, and biogeochemistry [37]. Important characteristics of humic substances include concentration of organic carbon (measured by TOC), color (measured by Color_{465}, i.e., the UV-Vis absorbance at 465 nm), hydrophobicity (measured by specific UV absorbance (SUVA) at 254 nm), aromaticity (measured by SUVA at 280 nm and \textsuperscript{13}C NMR), molecular weight (measured by HPSEC), and acidity (measured by potentiometric titration) [37]. Of these parameters, color relates to chromophores in
DOM, including conjugated double bonds, aromatic rings, and phenolic functional groups. These groups serve as color centers in humic substances [38]. SUVA (m\(^{-1}\)L/mgC) expressed by the ratio of UV absorbance at 254 or 280 nm over dissolved organic carbon concentration, increases with an increase in hydrophobicity and aromaticity of DOM, because \(\pi-\pi^*\) electron transitions occur at these wavelengths [23, 39, 40]. Higher hydrophobicity, higher aromaticity, and greater molecular weight of humic substances results in stronger affinity to non-polar neutral organics [41], such as polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) [42]. Higher acidity of humic substances, on the other hand, facilitates increased complexation with metallic cations, mineral surfaces, and other positively charged species [43, 44].

The characteristics of Aldrich and Pahokee peat DOM prior to sonication are shown in Table 4.1. Aldrich DOM has higher aromaticity, color, SUVA, and total acidity than Pahokee peat DOM; while Pahokee peat DOM has a greater weight-averaged molecular weight (4200 Da) and number-averaged molecular weight (2500 Da) than Aldrich DOM (3200 and 2100 Da, respectively). Higher Color\(_{465}\) of Aldrich DOM likely reflects the greater aromaticity of Aldrich DOM compared to the Pahokee peat DOM, because aromatic rings and phenolic functional groups are common chromophores in DOM [38]. Higher SUVA values reflect the greater hydrophobicity and aromaticity of Aldrich DOM. Based on \(^{13}\)C NMR analysis, Aldrich DOM has a higher percentage of carbon-substituted aromatic carbons and oxygen substituted aromatic carbons; while Pahokee peat DOM has a higher percentage of methoxyl and carbohydrate carbons (data not shown). Greater average molecular weight of Pahokee peat DOM suggests that its carbohydrates are expected to be composed of significant amounts of long-chain carbons.
The differences in the initial characteristics of these two DOM suggest that Aldrich DOM has a stronger affinity to non-polar neutral organics and has more complexation sites with metallic cations.

**TOC Reduction of DOM**

As shown in Figure 4.1 and Figure 4.2, no TOC reductions were observed for either DOM through 4 hours of sonication at 20 kHz with an energy density of 450 W/L. At 354 kHz with an energy density of 120 W/L, the TOC of Aldrich DOM decreased from 22.5 to 20.4 mg/L after 4 hours, while no obvious TOC reduction was observed with Pahokee peat DOM. When the sonolytic energy density was increased to 450 W/L at 354 kHz, the TOC of both DOM decreased significantly. TOC decreased from 22.5 mg/L to 15.0 and 18.2 mg/L after 4 hours for Aldrich and Pahokee peat DOM, respectively. These data demonstrate that Aldrich DOM was more readily mineralized than Pahokee peat DOM.

**Changes in Color}_{465}**

Although no TOC reduction was observed after 4 hours of sonication at 20 kHz, it is possible that the molecular structure of DOM changed through sonication. Figure 4.3 and Figure 4.4 show that Color}_{465} (UV-Vis absorbance at 465 nm) of Aldrich and Pahokee peat DOM decreased with sonication at all frequencies and power densities. At 20 kHz after 4 hours, Color}_{465} decreased from 0.21 to 0.19 and from 0.17 to 0.14 for Aldrich and Pahokee peat DOM, respectively. Again, a significant decrease of Color}_{465} with increased sonication occurred at higher ultrasonic frequency and higher energy...
density. These results indicate that sonication caused the destruction of chromophores in DOM, such as conjugated double bonds, aromatic rings, and phenolic functional groups [38]. Figure 4.4 indicates that a greater decline of Color_{465} occurred with Pahokee peat DOM than Aldrich DOM at 20 kHz and at 354 kHz with 120 W/L. At 354 kHz and 450 W/L, similar reduction in Color_{465} was observed for both Aldrich and Pahokee peat DOM.

\textit{SUVA Changes to DOM}

Experimental results show that SUVA of Aldrich and Pahokee peat DOM decreased with sonication time at either 20 kHz or 354 kHz. For example, SUVA at 254 nm decreased from 6.65 to 5.99 and from 5.56 to 4.42 m^{-1}L/mgC for Aldrich and Pahokee peat DOM, respectively over 4 hours of sonication at 20 kHz (see Figure 4.5 and Figure 4.6). A more significant decrease of SUVA at 254 nm was observed at 354 kHz and at the higher energy density. A similar trend was found for SUVA at 280 nm (see Figure 4.7 and Figure 4.8), which shows an increased loss of SUVA with sonication at higher ultrasonic frequency and energy density. Further, greater decrease of SUVA at 254 nm and 280 nm occurred with Pahokee peat DOM compared to Aldrich DOM at 20 kHz and at 354 kHz with 120 W/L. At 354 kHz with 450 W/L, a similar reduction in SUVA was observed for both Aldrich and Pahokee peat DOM. The decrease in SUVA at 254 and 280 nm suggests that the hydrophobicity and the aromaticity of DOM reduced through sonication.
$^{13}$C NMR Changes to DOM

$^{13}$C NMR spectra (see Figure 4.9) were used to directly determine changes in molecular structure of DOM as a result of sonication. Generally, the aromatic peak area (determined from the spectra between 112~160 ppm) of Aldrich and Pahokee peat DOM decreased and the aliphatic peak area (determined from the spectra between 0~90 ppm) increased through sonication, particularly at 354 kHz. As shown in Table 4.2, for both Aldrich and Pahokee peat DOM, sonication generally caused a decrease in the percentage of aromatic carbon, and an increase in the percentage of aliphatic carbon of the DOM. As a result, the aromaticity of DOM declined through sonication. For Pahokee peat DOM, its aromatic carbon decreased from 33.2% to 31.6%, its aliphatic carbon increased from 51.0% to 53.5%, and its aromaticity decreased from 39.4% to 37.1% after 4 hours of sonication at 354 kHz. Changes to the $^{13}$C NMR spectra were not obvious with 20 kHz sonication. A more significant trend was observed with Aldrich DOM. The percentage of aromatic carbon declined from 43.4% to 40.3% and to 35.8%, and the aliphatic carbon increased from 40.5% to 44.1% and to 49.6% through 4 hours of sonication at 20 kHz and 354 kHz, respectively. As a result, the aromaticity of Aldrich DOM dropped from 51.7% to 47.8% through sonication at 20 kHz, and dropped to 41.9% through sonication at 354 kHz. With the decrease of aromaticity, the hydrophobicity of DOM is expected to decline with increased sonication. Therefore, $^{13}$C NMR spectral analysis is consistent with the SUVA results that show a decrease in hydrophobicity and aromaticity of DOM through sonication.
Molecular Weight Changes to DOM

In addition to the molecular structural changes to DOM, the molecular weight was expected to decrease through sonication. Figure 4.10 and Figure 4.11 show the spectra of HPSEC of DOM before and after sonication. Generally, the decline of the peak area suggests that sonication destroys the chromophores of both Aldrich and Pahokee peat DOM molecules centered around 3000 Da. Sonication at 354 kHz resulted in a greater decrease in peak area than 20 kHz sonication. At 354 kHz, sonication reduced the peak more at the higher energy density than at the lower energy density. Comparing sonication at 20 kHz with 450 W/L (spectrum (2)) to 354 kHz with 120 W/L (spectrum (3)), we observed a broadening of the peak of spectrum (3) and a shifting of the peak of spectrum (2) to longer retention times for both Aldrich and Pahokee peat DOM. This result suggests that 20 kHz ultrasound preferentially transformed large molecules (larger than 6400 Da based on a retention time of 8.5 min).

The weight-averaged and number-averaged molecular weight of DOM before and after 4 hours of sonication are shown in Table 4.3. For Aldrich DOM, the weight-averaged molecular weight decreased from 3200 to 2900 and to 2400, the number-averaged molecular weight decreased from 2100 to 2000 and to 1600 after sonication at 20 kHz and at 354 kHz with 450 W/L, respectively. A more apparent decrease in molecular weight occurred with Pahokee peat DOM. The weight-averaged molecular weight decreased from 4200 to 3400 and to 3100; the number-averaged molecular weight decreased from 2500 to 2100 and to 1800 after sonication at 20 kHz and at 354 kHz with 450 W/L, respectively. However, only a slight decrease in molecular weight was observed with Pahokee peat DOM, and no obvious decrease in molecular weight was
found with Aldrich DOM at 354 kHz with 120 W/L. Generally, lower molecular weight DOM have lower hydrophobicity and lower aromaticity than higher molecular weight DOM [45]. Thus, this result is contrary to the results of SUVA and $^{13}$C NMR, which show a more significant decrease in the aromaticity of DOM at 354 kHz and 120 W/L than at 20 kHz and 450 W/L. Nevertheless, the general trend shows a decrease in the average molecular weight of DOM, consistent with previous results indicating a decrease in aromaticity and hydrophobicity of DOM through sonication.

**Total Acidity Measurement of DOM**

Acidity is a fundamental characteristic of humic substances. It is believed that the acidity of humic substances is due primarily to the presence of carboxyl (strong acid) and phenolic (weak acid) functional groups [43]. $^{13}$C NMR spectra cannot conclusively distinguish these functional groups. Therefore, it is necessary to use potentiometric titration to determine the acidity of DOM upon exposure to sonication.

Previous studies have shown an increase in the total acidity of NOM compounds following ozonation [46,47]. As illustrated in Table 4.4, the result of acidity titrations indicates an increase in the total acidity of both Aldrich and Pahokee peat DOM after 4 hours of sonication, although no significant change was observed at 20 kHz ultrasound.

**4.5 Discussion**

**Ultrasonic Factors Affecting Sonochemical Reactions of DOM**

The experimental results of TOC, Color$_{465}$, SUVA, acidity titrations, $^{13}$C NMR, and molecular weight distribution suggest that more significant ultrasonic effects
occurred at 354 kHz than at 20 kHz ultrasound with the same energy density (450 W/L).

At 354 kHz, the effect of sonication was more apparent at the energy density of 450 W/L than 120 W/L. These results indicate that ultrasonic factors played an important role in the sonochemical reaction of these DOM.

Sonochemically generated •OH radical is important for the oxidation of chemical constituents by ultrasound [14]. The detection of H₂O₂ formation is used to estimate relative quantities of •OH radical generated during sonication [48,49]. •OH radical can self-recombine to form hydrogen peroxide:

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

(1)

The recombination rate constant measured in water under ambient conditions is \(5.5 \times 10^9\) L mol\(^{-1}\) s\(^{-1}\) [50]. Figure 4.12 shows the concentration of H₂O₂ formed with sonication in the absence of DOM. The highest concentration of H₂O₂ (0.4 mM after 4 hours) was produced at 354 kHz with an energy density of 450 W/L. The second highest H₂O₂ concentration (0.3 mM after 4 hours) was generated at 354 kHz with an energy density of 120 W/L. However, the lowest concentration of H₂O₂ was formed at 20 kHz (0.07 mM after 4 hours), even though the energy density was higher than 120 W/L at 354 kHz. Higher •OH radical production has been observed at 354 kHz in other studies [48,51]. As shown in Figure 4.12, the trend of increasing H₂O₂ concentration is consistent with changes observed to DOM. Ultrasonic factors that produced more •OH radical also resulted in more significant changes in DOM properties, suggesting that •OH radical plays a dominant role in the sonochemical alteration of dissolved organic matter.

It is well known that •OH radical may cleave aromatic rings [52,53,54]. The decrease in aromaticity determined from \(^{13}\)C NMR spectra and SUVA correlates well
with an increase in \( \text{H}_2\text{O}_2 \). Thus, the higher •OH radical concentrations at 354 kHz result in more cleavage of aromatic rings than at 20 kHz. Considering the relatively non-selective nature of oxidation by •OH radicals [40], the aliphatic functional groups of DOM are also subject to degradation and consequently lead to partial mineralization of DOM. Therefore, a more obvious reduction in TOC and molecular weight occurred with higher •OH radical concentrations. It is reported that ozonation of NOM leads to the destruction of carbon-carbon double bonds and production of organic acid and aldehyde groups [55]. Similarly, sonication of DOM is expected to produce organic acids through oxidation by •OH radicals, increasing the total acidity of DOM. Insignificant changes in the acidity of DOM at 20 kHz may be due to lower •OH radical production at this frequency.

In addition to •OH radical oxidation, dynamic shearing caused by cavitation bubbles may also play a role in breaking covalent bonds of macromolecules [15, 56]. Table 4.3 indicates that 20 kHz ultrasound had a more significant effect on the decrease in the molecular weight of DOM than 354 kHz with 120 W/L. Moreover, Figure 4.10 and Figure 4.11 show that 20 kHz ultrasound effectively transformed DOM molecules greater than 6400 Da for both Aldrich and Pahokee peat DOM. Cavitation bubbles at 20 kHz ultrasound are thought to undergo more violent collapse and thus have stronger mechanical effects (for example, dynamic shearing) than at 354 kHz [57], although less •OH radicals were generated than at 354 kHz. Dynamic shearing is more effective in the degradation of polymers with higher molecular weight than lower molecular weight. In addition, there exists a limiting molecular weight of polymers, below which no further ultrasonic transformation occurs with time [16]. This phenomenon is observed because
when the molecule is small enough, the physical dimension of polymer will be too small to be impacted by shock waves. Based on these analyses, dynamic shearing of cavitation bubbles likely contributed to the breakdown of Aldrich and Pahokee peat DOM macromolecules, especially at 20 kHz. $\text{H}_2\text{O}_2$ produced at 354 kHz with 120 W/L was more than four times that at 20 kHz. Thus, if the degradation of DOM solely depended on •OH radical and dynamic shearing did not play a role, we would not observe the more significant decrease in molecular weight at 20 kHz than at 354 kHz with 120 W/L (see Table 4.3).

Finally, thermal pyrolysis cannot be ruled out as a transformation mechanism of DOM. When macromolecules composing DOM are degraded to smaller molecules, they may volatilize into the gaseous cavity of cavitation bubbles, and consequently are dissociated under high temperature during bubble collapse. These studies did not provide any evidence to support or refute this possibility.

**Alterations to DOM through Sonication**

For both Aldrich and Pahokee peat DOM, the experimental results indicated that Color$_{465}$, SUVA at 254 nm and 280 nm, aromaticity, and average molecular weight all decreased, while total acidity increased with sonication time. TOC reduction was observed at 354 kHz only. These results are consistent with previous studies which show a decrease in molecular weight [20], partial mineralization [21], and a decrease in UV absorbance at 254 nm [21,22] of NOM as a result of sonication.

In this study, the decrease of Color$_{465}$ suggests that sonication partially degraded chromophoric functional groups on DOM, which include conjugated double bonds,
aromatic rings, and phenolic functional groups [38]. As mentioned above, SUVA at 254 nm and 280 nm increase with higher hydrophobicity and higher aromaticity of DOM, because \( \pi-\pi^* \) electron transitions occur at these wavelengths [23,39,40]. The decrease of SUVA indicates that the DOM became less hydrophobic (i.e., more hydrophilic) and less aromatic as a result of sonication. The decrease of SUVA suggests that sonication changed the molecular structure of DOM, possibly by cleaving aromatic rings on the DOM. \(^{13}\)C NMR verified this hypothesis by showing a decrease in the percentage of aromatic carbon and an increase in the percentage of aliphatic carbon through sonication. Also, an increase in the total acidity of DOM as a result of sonication implies more organic acids were produced. The HPSEC data indicates a decrease in the molecular weight of DOM through sonication. All these characteristic measurements show that the DOM became less hydrophobic, less aromatic, smaller in size, and had higher total acidity as a result of sonication. These results suggest that sonication changed the characteristics of both Aldrich and Pahokee peat DOM. The differences in changes to Aldrich and Pahokee peat DOM indicate that the degree of change depends on the source of DOM as well as ultrasonic factors.

Although Pahokee peat DOM was less readily mineralized than Aldrich DOM, a greater decrease in Color\(_{465}\), SUVA at 254 and 280 nm, and molecular weight at 20 kHz and 354 kHz with 120 W/L was observed for the Pahokee peat DOM. This suggests that alterations to the molecular structure of Pahokee peat DOM were more pronounced than the changes for Aldrich DOM through sonication. Based on \(^{13}\)C NMR and HPSEC analysis, Pahokee peat DOM has a higher percentage of carbohydrate carbons that have higher molecular weight and presumably are long-chain carbons, although its aromaticity
is lower than Aldrich DOM. These carbohydrates are more difficult to mineralize but are readily modified. A reason for a greater decrease in the molecular weight of Pahokee peat DOM through sonication is that these long-chain carbons are more readily cleaved by dynamic shearing of cavitation bubbles, since dynamic shearing preferentially causes breaks in the middle of a polymer chain \[16,58\], until the limiting molecular weight of the polymer has been reached.

However, similar effects of sonication on Color$_{465}$ and SUVA at 254 and 280 nm were observed at 354 kHz and 450 W/L for both Aldrich and Pahokee peat DOM. This may be due to the greater $\cdot$OH radical production observed at 354 kHz and 450 W/L than at the other sonication conditions. The high $\cdot$OH radical concentration allows for extensive oxidation of both DOM resulting in significant changes to their molecular structures.

**Implications for Use of Sonolysis in Environmental Applications**

This study shows that the aromaticity, the hydrophobicity, and the molecular weight of both Aldrich and Pahokee peat DOM decreased, while the acidity increased with sonication time. These trends were more significant with 354 kHz at a higher energy density. These characteristic changes to DOM have a significant impact on the behavior of DOM in the environment. A decrease in aromaticity and hydrophobicity of DOM is expected to weaken hydrophobic interactions between DOM and hydrophobic organic compounds \[59\] (for example, non-polar neutral organics \[41\] and bacteria \[60\]), and thus decrease the adsorptive affinity between them. Because DOM is ubiquitous in soil, sediment, and natural waters, these effects suggest that sonochemical techniques may
reduce the interaction of hydrophobic organics with soil, sediment, or aqueous NOM. However, the affinity between DOM and bacteria is expected to be weaker. This effect may influence biodegradation of DOM and adsorbed organic contaminants. In addition, in the presence of DOM, the oxidation rate of organic contaminants is decreased due to scavenging of •OH radicals by DOM [3].

Furthermore, an increase in acidity means an increase in the sum of carboxylic and phenolic functional groups on DOM. These functional groups are responsible for the negative charge of DOM [61]; thus, DOM is expected to become more negatively charged through sonication. The charge of DOM affects the adsorption of metallic cations through outer-sphere complexation, colloid/particle coagulation, electrostatic interactions between colloids and DOM, and interactions between drinking water membranes and DOM [44,62,63]. When both DOM and environmental components are negatively charged, sonication is expected to enhance charge repulsion between the components and reduce interaction. Conversely, if the component interacting with DOM is positively charged, the interaction will be increased upon sonication.

This study was performed with sonication at high intensity. In practice, the degree of the property change to DOM depends on the energy density of ultrasound as well as sonication time. For practical applications, if property changes to DOM are desired, higher frequency (354 kHz vs. 20 kHz), higher energy density, and longer contact times with ultrasound would be preferred. Otherwise, lower frequency, lower energy density, and limited contact time with ultrasound would be favored.
4.6 Acknowledgments

This project was funded by the Ohio Water Development Authority, National Oceanic and Atmospheric Administration through the Ohio Sea Grant College Program, and the NSF Environmental Molecular Science Institute at The Ohio State University. The authors gratefully acknowledge William C. Hockaday for help with $^{13}$C NMR analysis. The authors also thank Jerry M. Bigham and Sandy Jones for their help with freeze drying.
References


<table>
<thead>
<tr>
<th></th>
<th>Aromaticity (%)</th>
<th>Color\textsubscript{465} (m\textsuperscript{3}/L/mgC)</th>
<th>SUVA (at 254 nm) (m\textsuperscript{3}/L/mgC)</th>
<th>SUVA (at 280 nm) (m\textsuperscript{3}/L/mgC)</th>
<th>Total acidity (meq/g TOC)</th>
<th>Weight-averaged molecular weight (Da)</th>
<th>Number-averaged molecular weight (Da)</th>
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</thead>
<tbody>
<tr>
<td>Aldrich DOM</td>
<td>51.7</td>
<td>0.21</td>
<td>6.46</td>
<td>6.19</td>
<td>12.7</td>
<td>3200</td>
<td>2100</td>
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<tr>
<td>Pahokee peat DOM</td>
<td>39.4</td>
<td>0.17</td>
<td>5.56</td>
<td>5.03</td>
<td>10.6</td>
<td>4200</td>
<td>2500</td>
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</tbody>
</table>

*Table 4.1* Comparison of the initial characteristics of Aldrich and Pahokee peat DOM.
<table>
<thead>
<tr>
<th>Before sonication</th>
<th>20 kHz 450 W, 4 h</th>
<th>20 kHz 20 W, 4 h</th>
<th>35 kHz 20 W, 4 h</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>aliphatic carbon</td>
<td>aromatic carbon</td>
<td>aliphatic carbon</td>
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<tr>
<td></td>
<td>(%)</td>
<td>(%)</td>
<td>(%)</td>
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<tr>
<td>Alrich DOM</td>
<td>40.5</td>
<td>43.4</td>
<td>41.7</td>
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<tr>
<td>Panke DOM</td>
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<td>33.2</td>
<td>59.4</td>
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<tr>
<td>pearl DOM</td>
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<td></td>
</tr>
</tbody>
</table>

**Table 4.2** Comparison of the aromaticity of DOM as a result of sonication.
|                   | Molecular weight (Da) | Before sonication | 20 kHz  
450 W/L | 354 kHz  
120 W/L | 354 kHz  
450 W/L |
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Aldrich DOM</td>
<td>Number-averaged</td>
<td>2100</td>
<td>2000</td>
<td>2100</td>
<td>1600</td>
</tr>
<tr>
<td></td>
<td>Weight-averaged</td>
<td>3200</td>
<td>2900</td>
<td>3150</td>
<td>2400</td>
</tr>
<tr>
<td>Pahokee peat DOM</td>
<td>Number-averaged</td>
<td>2500</td>
<td>2100</td>
<td>2300</td>
<td>1800</td>
</tr>
<tr>
<td></td>
<td>Weight-averaged</td>
<td>4200</td>
<td>3400</td>
<td>4100</td>
<td>3100</td>
</tr>
</tbody>
</table>

**Table 4.3** Molecular weight of DOM before and after 4 hours of sonication.
### Table 4.4 Acidity of DOM before and after 4 hours of sonication.

<table>
<thead>
<tr>
<th>Total acidity (meq/g TOC)</th>
<th>Before sonication</th>
<th>20 kHz (450 W/L)</th>
<th>354 kHz (120 W/L)</th>
<th>354 kHz (450 W/L)</th>
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<tr>
<td>Aldrich DOM</td>
<td>12.7</td>
<td>11.0</td>
<td>17.5</td>
<td>61.5</td>
</tr>
<tr>
<td>Pahokee peat DOM</td>
<td>10.6</td>
<td>9.2</td>
<td>19.2</td>
<td>16.3</td>
</tr>
</tbody>
</table>
Figure 4.1 TOC reduction of Aldrich DOM with sonication under different ultrasonic frequencies and energy densities.
Figure 4.2 TOC reduction of Pahokee peat DOM with sonication under different ultrasonic frequencies and energy densities.
Figure 4.3 Color_{465} loss of Aldrich DOM with sonication under different ultrasonic frequencies and energy densities.
Figure 4.4 $\text{Color}_{465}$ loss of Pahokee peat DOM with sonication under different ultrasonic frequencies and energy densities.
Figure 4.5 SUVA at 254 nm of Aldrich DOM decrease with sonication under different ultrasonic frequencies and energy densities.
Figure 4.6 SUVA at 254 nm of Pahokee peat DOM decrease with sonication under different ultrasonic frequencies and energy densities.
Figure 4.7 SUVA at 280 nm of Aldrich DOM decrease with sonication under different ultrasonic frequencies and energy densities.
Figure 4.8 SUVA at 280 nm of Pahokee peat DOM decrease with sonication under different ultrasonic frequencies and energy densities.
Figure 4.9 ¹³C NMR spectra of DOM before and after 4 hours of sonication. Y-axis represents relatively intensity. (a) Aldrich DOM. (b) Pahokee peat DOM.

(Continued)
Figure 4.9 Continued

354 kHz 120 W/L 4 hrs

20 kHz 450 W/L 4 hrs

without sonication
Figure 4.10 HPSEC spectra of Aldrich DOM before and after 4 hours of sonication.
Figure 4.11 HPSEC spectra of Pahokee peat DOM before and after 4 hours of sonication.
Figure 4.12 The formation of \( \text{H}_2\text{O}_2 \) with sonication under different ultrasonic frequencies and energy densities.
CHAPTER 5

ULTRASONIC CONTROL OF CERAMIC MEMBRANE FOULING CAUSED BY DISSOLVED ORGANIC MATTER AND SILICA PARTICLES: EFFECT OF SOLUTION CHEMISTRY

5.1 Abstract

The effect of solution chemistry on the ultrasonic control of membrane fouling caused by dissolved organic matter (DOM) and silica particles was investigated in this study. 20 kHz ultrasound was applied to a cross-flow ultrafiltration system with γ-alumina membranes. Experimental results indicated that solution chemistry affected the ability of ultrasound to control membrane fouling. More effective control of membrane fouling occurred at high pH, low ionic strength, and in the absence of divalent cations, due to stronger electrostatic repulsion between foulant-foulant and foulant-membrane components. A decrease in the DOM rejection rate during ultrasound was observed. This occurred due to decreased steric exclusion of DOM through the fouled membrane, as scanning electron microscope (SEM) images indicated that ultrasound partially removed
the foulant layer from the membrane surface allowing larger DOM to pass through the membrane.

**Keywords**: ultrasound, membrane cleaning, membrane fouling, natural organic matter, dissolved organic matter, ultrafiltration

### 5.2 Introduction

Ultrafiltration membranes are used in drinking water treatment for the removal or partial removal of microbiological contaminants, high-molecular-mass soluble species (e.g., natural organic matter), and particles [1]. Wider application of this technology is driven by increasingly more stringent regulations for finished water quality. However, problems caused by membrane fouling deteriorate the performance of ultrafiltration. A wide range of colloids in natural waters may lead to membrane fouling including natural organic matter (NOM), silicate, iron oxides, calcite, and clays [2].

For treatment of natural waters, NOM is often implicated as a major foulant controlling the rate and extent of fouling [3,4,5]. NOM may block membrane pores, form a gel layer, or bind particles together to form a low permeability NOM/particle cake layer on the membrane surface [4]. Solution chemistry directly affects electrostatic interactions among NOM, particles, and the membrane, as well as the solution conformation of NOM, and the steric packing of NOM at the membrane surface and/or within the membrane pores. Generally, more severe membrane fouling occurs at low pH, at high ionic strength, and in the presence of divalent cations [6,7,8,9,10,11,12].

Although considerable progress has been made in understanding membrane fouling, more effective techniques for membrane fouling control are still needed [13].
The conventional methods to reduce membrane fouling include backflushing/backwashing and chemical cleaning of the membrane [14]. However, these methods are not ideal. For example, membranes exposed to backflushing/backwashing cycles typically experience degradation in maximum flux after repeated backwashes [14]. Chemical cleaning may damage the membrane and cause secondary pollution [13]. In addition, the filtration process has to be shutdown regularly for backflushing/backwashing and chemical cleaning [2], which reduces permeate production capacity.

Ultrasonic techniques provide an alternative and attractive method for membrane fouling control. Ultrasound generates acoustic streaming and cavitation bubbles in a liquid medium (e.g., water). Cavitation bubbles and the collapse of cavitation bubbles cause microstreaming, microstreamers, microjets, and shock waves [15]. When the membrane is outside the cavitation region, acoustic streaming and ultrasonically generated turbulence resulting from microstreaming, microstreamers, microjets, and shock waves may shear the membrane surface to dislodge foulants from the membrane and/or prevent the deposition of foulants that cause membrane fouling [2]. The advantages of ultrasound over traditional methods to control membrane fouling are significant. For instance, there is no chemical use in the membrane cleaning process. In addition, filtration is not interrupted to perform cleaning. The clean water permeate flux of the membrane can be maintained with the assistance of ultrasound throughout the duration of the filtration process [2].

The effectiveness of ultrasound-assisted membrane filtration has been reported by several researchers [2,13,16,17,18,19,20,21,22,23,24]. All these studies demonstrated the
effectiveness of ultrasound in controlling membrane fouling and enhancing permeate flux using both polymeric and ceramic membranes. However, little research has been done on ultrasonic control of membrane fouling caused by NOM and inorganic colloidal particles, which is of practical importance for drinking water treatment. In this study, the control of membrane fouling in the presence of dissolved organic matter (DOM) and inorganic silica particles was explored. Experiments were performed with a crossflow ultrafiltration system coupled to an ultrasonic probe to systematically investigate the effectiveness of ultrasonic membrane cleaning with respect to solution chemistry; specifically pH, ionic strength, and the presence of divalent cations. The underlying hypothesis is that ultrasound is more effective at controlling membrane fouling as surface chemical interactions between the membrane and foulants, or between foulants becomes less attractive or more repulsive.

5.3 Materials and methods

5.3.1 Membranes, Particles, and DOM

Anodisc™ γ-Al₂O₃ ceramic membranes with a polypropylene support ring from Whatman (Clifton, NJ) were used in all experiments. The diameter and the thickness of the membranes was 47 mm and 60 µm, respectively. The pore size of the membranes was 0.2 µm through most of the membrane cross-section, and narrowed to 0.02 µm for 2-3 µm at the membrane surface. The contact angle of the membrane was less than 30° measured by the drop profile method (sessile drop) with a high performance CCD camera from Cohu (San Diego, CA), indicating the membrane was hydrophilic.
Zeta potential values of the membrane were determined by a commercial streaming potential analyzer (EKA, Brookhaven Instruments Corp., Holtsville, NY) with an asymmetric clamping cell (measuring cell) following the procedures described by Walker et al. [25]. The measured isoelectric point of the membrane was pH 7.3±0.4.

Silica particles from Sigma Aldrich (St. Louis, MO) were chosen because silica is a common membrane foulant found in natural waters. Before filtration experiments, silica particles were sonicated in an ultrasonic bath (Branson 2210, Danbury, CT) for 45 minutes to obtain a consistent particle size (mean diameter was 1.56 µm) as measured by a MasterSizer (Malvern Instruments Ltd., Southborough, MA). The Zeta potential of silica particles was determined by an electrophoretic light scattering instrument (ZetaPlus, Brookhaven Instruments Corp., Holtsville, NY). The isoelectric point of silica particles was pH 2.0±0.2. All solutions in this study were prepared with MilliQ water (R=18.2 MΩ·cm). Chemicals including KCl, CaCl₂·2H₂O, NaOH, and HCl solution (35~38% w/w, trace-metal grade) were from Fisher Scientific.

Commercial Aldrich humic acid (sodium salt) was supplied by the Aldrich Chemical Company (Milwaukee, WI). Aldrich humic acid purified according to the methods described by Chin et al. [26] was followed by washing with 0.3 M HF and dialysis with 1000 Dalton (Da) molecular weight cut off membranes [27]. The dialysis was continued until the dialyzing water was free of chloride as determined with an AgNO₃ indicator. The stock solution of DOM was stored in the dark at 4°C. The weight-averaged molecular weight of purified DOM was 3200 Da as determined by a high pressure size exclusion chromatography (HPSEC), its aromaticity was 51.7% [27]. The acidity of DOM was determined by potentiometric titration under a N₂ atmosphere.
following the procedures of Edwards et al. [28] using an Orion 960 Autochemistry System (Beverly, MA). The carboxylic acidity was determined to be 5.2 meq\(/(g \text{ TOC})^{-1}\) and the phenolic acidity was 7.5 meq\(/(g \text{ TOC})^{-1}\).

5.3.2 Ultrasonic System

A 20 kHz ultrasonic probe system with one inch diameter tip (550 Sonic Dismembrator) from Fisher Scientific (Pittsburgh, PA) was employed during filtration. Calorimetry [29] was performed to measure the power output of ultrasound, which was 9.2±0.4 W for all experiments. Before sonication, the ultrasonic probe was polished with fine sand paper (220, 3M®) and properly tuned. Experiments were performed at a distance between the membrane and the ultrasonic probe of 3.5 cm. At this distance, the membrane was outside the ultrasonic cavitation region [2].

5.3.3 Membrane Filtration Experiments

Details of the experimental system have been described previously [2]. Briefly, all filtration experiments were performed at 34.5 kPa (5 psi) using a crossflow filtration system containing an ultrasonic probe parallel to the membrane surface (see Figure 5.1). The membrane cell is made of plexiglass and is cylindrically shaped, 4.3 cm in diameter and 9.2 cm in depth. MilliQ water was run through the membrane before filtration tests with DOM and particles to remove any impurities and to allow the permeate flux to stabilize. The crossflow rate was 500 mL/min. The initial DOM concentration was 8 mg/L TOC for all of the experiments. When added to the system, the silica particle concentration was 0.3 g/L. For the filtration of DOM plus silica particles, 8 mg/L DOM
was mixed with a 0.3 g/L pre-sonicated silica particle solution followed by pH adjustment. The solution was stirred for 24 hrs before commencing filtration experiments. Experiments indicated that the adsorption of DOM on silica particles reached equilibrium within 24 hrs.

Solution pH was maintained at 4.0±0.1 or 9.2±0.1 during the filtration tests. A constant ionic strength of 3 mM was maintained unless otherwise noticed. The volume of the bulk solution was 2.0 L. A Fisher Scientific 1006S cooling system was used to keep the filtration bulk solution at a constant temperature of 20°C. The membrane permeate flux was determined by measuring the weight of water per time using an analytical balance (Mettler AJ100, Switzerland). Membrane retentate and permeate were returned to the feed tank during the filtration process.

Relative permeate flux improvement at steady-state due to ultrasound, $R$, was used to describe the ultrasonic effect as shown in eqn (1) [2]:

$$
R = \frac{J_{US} - J'}{J_{0,US} - J'} \times 100\%
$$

where $J_{US}$ is the steady-state permeate flux with ultrasound; $J'$ is the steady-state permeate flux without ultrasound; and $J_{0,US}$ is the permeate flux of a clean membrane with ultrasound, which accounts for the enhancement of the permeate flux due to an increase in temperature (~0.3 °C) of the feed solution caused by ultrasound. Based on this expression, an $R$ value of 0% indicates no improvement in permeate flux by ultrasound; on the other hand, an $R$ value of 100% indicates the permeate flux was completely restored to the pre-fouling value by ultrasound.
5.3.4 Analytical Methods

The DOM concentration was determined by total organic carbon (TOC) analysis, measured by a Shimadzu TOC-5000A analyzer operating in the non-purgable organic carbon mode. The DOM rejection rate of the membrane was determined by measuring the feed and permeate TOC concentrations during the filtration process. The UV absorbance of DOM was measured by a UV-VIS spectrophotometer (UV-2401PC, Shimadzu). Turbidity of the membrane permeate was determined by a Turbidimeter from Hach (Loveland, Co).

A JSM-820 scanning electron microscope (SEM) (JEOL, Japan) was used to examine the foulant layer at the membrane surface with and without ultrasound. Three samples of a given membrane were cut from the center and two other random locations on the membrane. The membrane samples were coated with gold to enhance the conductivity of the surface. More than 8 random locations on each sample were examined with SEM in order to obtain a representative image of the surface.

5.4 Results and discussion

Initial membrane filtration tests investigated the fouling potential of silica particles, DOM, and solutions containing both DOM and silica particles, respectively. As shown in Figure 5.2, silica particles alone caused greater fouling than DOM alone at short filtration times (<100 minutes). However, with the extension of filtration time (>190 minutes), DOM alone caused slightly greater membrane fouling than silica particles. Nevertheless, the most severe membrane fouling occurred during the filtration of the solution containing both
DOM and silica particles. Adsorption measurements revealed that less than 4% of the DOM in solution adsorbed on silica particles at pH 4.0. At pH 9.2, less than 2% of the DOM adsorbed. The adsorption densities of DOM on silica particles at pH 4.0 and 9.2 were 0.53 and 0.26 (mg TOC)/m², respectively. These results are consistent with the literature [4], indicating very little complexation between DOM and silica particles during the filtration process. Due to lack of complexation between DOM and silica particles, their effect on fouling was additive when both were added to solution. As a result, greater membrane fouling occurred when both DOM and silica particles were present in the filtration system, compared to when DOM and silica particles were added separately.

5.4.1 pH effect

Subsequent experiments examined how pH affected foulant-foulant and foulant-membrane interactions, and the resulting effect on the control of fouling by ultrasound. Experimental results indicated that pH significantly affected membrane fouling caused by DOM and DOM plus silica particles. Figure 5.3 shows that in the presence of DOM alone, greater membrane fouling occurred at pH 4.0 compared to pH 9.2 with and without ultrasound. The permeate flux without ultrasound dropped to 0.25 and 0.10 g/(min⋅cm²) after 240 minutes filtration at pH 9.2 and pH 4.0, respectively. A similar result was found with filtration of DOM with silica particles. As shown in Figure 5.4, the permeate flux without ultrasound after 240 minutes was 0.10 and 0.05 g/(min⋅cm²) at pH 9.2 and pH 4.0, respectively.

The use of ultrasound reduced membrane fouling, and a significant increase in permeate flux was observed. In Figure 5.3, the permeate flux with ultrasound was 0.48 and
0.36 g/(min⋅cm²) at pH 9.2 and pH 4.0, respectively. Higher relative permeate flux improvement was obtained at pH 9.2 (88%) than pH 4.0 (63%). In Figure 5.4, for the filtration of DOM plus silica particles, ultrasound improved the permeate flux to 0.39 and 0.17 g/(min⋅cm²) at pH 9.2 and pH 4.0, respectively. Again, higher relative permeate flux improvement was found at 9.2 (71%) than pH 4.0 (26%).

The effect of pH on membrane fouling may be explained by considering the electrostatic interactions between DOM, silica particles, and the membrane. The isoelectric points of the membrane and silica particles were at pH 7.3±0.4 and pH 2.0±0.2, respectively. Therefore, at pH 9.2 the membrane was negatively charged (+14.2±3.1 mV) due to ≡AlO− functional groups, while silica particles were negatively charged due to ≡SiO− functional groups. DOM acidity results from 5.2 meq (g TOC)−1 carboxylic acids (3 ≤pKa ≤6 [28]) and 7.5 meq (g TOC)−1 phenolic acids (8 ≤pKa ≤12 [28]); thus, DOM renders negatively charged at the solution conditions examined here. Therefore, an electrostatic repulsion existed between the membrane, DOM, and silica particles. Thus, less membrane fouling was observed at pH 9.2, and such fouling was more readily controlled by ultrasound.

However, at pH 4.0 the membrane was positively charged (43.3±2.2 mV) due to ≡AlO−H₂+ functional groups, DOM and silica particles were negatively charged. As a result, an electrostatic attraction exists between DOM and the membrane, as well as between silica particles and the membrane, which causes a higher affinity between these foulants and the membrane. Therefore, severe membrane fouling occurred at pH 4.0. In addition, DOM is less negatively charged at low pH than high pH. This reduced electrostatic repulsion
between DOM macromolecules leads to greater inter-molecular interactions. Furthermore, at low pH, reduced inter-molecular electrostatic repulsion causes DOM macromolecules to become coiled [6,30], forming a denser foulant layer within the membrane pores and/or at the membrane surface. As a result, ultrasound was less effective in controlling membrane fouling at low pH due to strong attractive interactions between DOM and the membrane, between silica particles and the membrane, as well as less repulsive interactions between DOM and other DOM macromolecules.

5.4.2 The effect of ionic strength

To further investigate the role that electrostatic interactions play in the ultrasonic cleaning of DOM fouled membranes, filtration experiments were carried out at different ionic strengths at pH 9.2. We suspect that high ionic strength will decrease electrostatic repulsion among DOM macromolecules, silica particles, and the membrane [31].

Figure 5.5 indicates that at pH 9.2 more significant fouling occurred at higher ionic strength, which is consistent with previous studies of membrane fouling [6,7,10,12]. The membrane permeate flux without ultrasound was 0.25, 0.12, and 0.09 g/(min-cm²) after 240 minutes of filtration at ionic strengths of 0.003, 0.02, and 0.25 M KCl, respectively. However, with ultrasound the corresponding permeate flux increased to 0.48, 0.38, 0.32 g/(min-cm²). The relative permeate flux improvement due to ultrasound was 88%, 67%, and 55% at pH 9.2 and ionic strengths of 0.003, 0.02, and 0.25 M KCl, respectively. Higher relative permeate flux improvement was observed at lower ionic strength at this pH. These results demonstrated that at high pH ultrasound was less
effective at high ionic strength, suggesting that stronger foulant-foulant and foulant-
membrane interactions made membrane cleaning more difficult.

It should be noted that ionic strength also affects cavitation bubble dynamics
because the surface tension of the solution increases with ionic strength. Iwai and Li [32]
observed more erosion of steel at higher surface tension due to more intense collapse of
cavitation bubbles. However, our results indicate that changes in bubble dynamics with
ionic strength are insignificant compared to the effect of charge screening, as severe
membrane fouling and decreased relative permeate flux improvement were found at high
ionic strength.

5.4.3 The effect of Ca$^{2+}$

The presence of divalent cations, such as Ca$^{2+}$ greatly affects the rate and the extent
of membrane fouling by DOM [6,8]. The effect of Ca$^{2+}$ on the ultrasonic control of
membrane fouling was investigated at pH 9.2, in which the membrane, DOM, and silica
particles were all negatively charged. A constant ionic strength of 3 mM was maintained by
either 1 mM CaCl$_2$ or 3 mM KCl.

Adsorption experiments indicated that approximately 10% of DOM adsorbed on 0.3
g/L silica particles (1.32 (mg TOC)/m$^2$) in the presence of 1 mM Ca$^{2+}$ at pH 9.2 after
reaching equilibrium, compared to only 2% without Ca$^{2+}$. As shown in Figure 5.6, the
presence of 1 mM Ca$^{2+}$ caused greater membrane fouling than 3 mM KCl. In the presence
of 1 mM Ca$^{2+}$ (see Figure 5.6(a)), the permeate flux after 240 minutes declined to 0.28 and
0.09 g/(min⋅cm$^2$) with and without ultrasound, respectively. However, in the presence of 3
mM KCl, the permeate flux was 0.48 and 0.25 g/(min⋅cm$^2$) with and without ultrasound,
respectively. The presence of 1 mM Ca\(^{2+}\) decreased the relative permeate flux improvement due to ultrasound from 88% to 45%. Similarly, for the filtration of DOM and silica particles, Figure 5.6(b) shows that the presence of 1 mM Ca\(^{2+}\) decreased the permeate flux with and without ultrasound. Higher relative permeate flux improvement was found in the presence of 3 mM KCl, which was 71% compared to 34% with 1 mM Ca\(^{2+}\).

Divalent cations, such as Ca\(^{2+}\) enhance membrane fouling by 1) charge neutralization of NOM through complexation with acidic functional groups of NOM; and 2) bridging among deposited NOM macromolecules, silica particles, and the membrane [6,7,36,33]. In the presence of Ca\(^{2+}\), a more compact foulant layer within the membrane pores and/or at the membrane surface is formed [6], thus leading to a greater decline of the permeate flux. Subsequently, ultrasound was less effective at removing this compact foulant layer from the membrane surface and/or from the membrane pores.

5.4.4 The rejection rate of NOM

In addition to membrane fouling, another concern during membrane filtration is maintaining a stable rejection rate. In this study, silica particles (1.56 \(\mu\)m) were much bigger than the membrane pore size (0.02 \(\mu\)m). Therefore, silica particles were totally retained by the membrane with no quantifiable turbidity in the permeate was observed. DOM, however, partially passed through the membrane into the permeate. Figure 5.7(a) shows that without ultrasound, higher DOM rejection rates (measured by TOC) occurred at pH 9.2 (86%) than pH 4.0 (76%). However, ultrasound decreased the rejection rate to 28% at pH 9.2, and to 71% at pH 4.0, respectively. The initial rejection rate of the clean membrane was approximately 30%, as can be seen at time zero in Figure 5.7(a). Therefore,
ultrasound restored the rejection rate of the clean membrane and did not degrade the performance of the designed system.

Figure 5.7(b) compares the DOM rejection rate at different pH values, in the presence of Ca\(^{2+}\) or KCl, with or without ultrasound. From this figure, without ultrasound or Ca\(^{2+}\), higher rejection rates of DOM were obtained at pH 9.2 than pH 4.0 for filtration of both DOM and DOM plus silica particles. The presence of 1 mM Ca\(^{2+}\) decreased the rejection rate of DOM at pH 9.2. However, when ultrasound was on, the rejection rate of DOM generally decreased. The most significant decrease in the rejection rate was found at pH 9.2 in the absence of Ca\(^{2+}\): ultrasound decreased the rejection rate from 75% to 31% and from 86% to 28% for filtration of DOM and DOM plus silica particles, respectively. The rejection rate declined slightly with ultrasound with filtration of DOM plus silica particles at pH 4.0 or in the presence of 1 mM Ca\(^{2+}\) at pH 9.2.

Rejection of DOM depends on electrostatic interactions, hydrophobic interactions, and steric exclusion [34]. At pH 9.2, charge repulsion between DOM and the membrane causes greater rejection of DOM macromolecules in the absence of ultrasound. At pH 4.0, charge attraction between DOM and the membrane may be responsible for the lower rejection rate than pH 9.2. In addition, DOM macromolecules become coiled at low pH [6,30]. Coiled DOM has a smaller hydrodynamic diameter than stretched shape of DOM at high pH [6,35]. Coiled DOM may be more easily passing through the membrane and therefore, the rejection rate decreased. Figure 5.7(a) shows that the rejection rate of DOM increased with filtration time, except at pH 9.2 with ultrasound in which the rejection rate was relatively constant. This result is consistent with the literature [3,36,37], because DOM may gradually block or close membrane pores, and/or form a gel layer at the
membrane surface causing the rejection rate of DOM to increase with filtration time. At pH 9.2 with ultrasound, the relatively constant rejection rate is likely due to more significant cleaning by ultrasound than at pH 4.0. In all cases, lower rejection rates were observed with ultrasound compared to filtration without ultrasound.

SEM images were used to directly observe the foulant layer at the membrane surface with and without ultrasound. Figure 5.8(a) shows that without ultrasound the membrane surface was greatly covered by a foulant layer composed of silica particles and DOM. However, during filtration with ultrasound, as shown in Figure 5.8(b), the foulant layer at the membrane surface was significantly reduced, revealing the membrane surface clearly. Braghetta et al. [10] reported that an increase in crossflow velocity reduced membrane fouling but caused a decrease in the NOM rejection rate of the membrane. In our study, increased turbulence at the membrane surface in the presence of ultrasound similarly reduced membrane fouling and decreased the DOM rejection rate.

5.4.5 Mechanism of ultrasound for membrane fouling control

In this study, the extent of membrane fouling is controlled by two competitive processes: fouling caused by deposition of DOM and silica particles onto the membrane surface, and cleaning caused by back transport/removal of DOM and particles from the membrane surface to the bulk solution by crossflow, acoustic streaming, and ultrasonically generated turbulence. At steady-state, a balance between these two competitive processes is achieved [38]. The introduction of ultrasound enhances back transport processes of the foulant from the membrane surface to the bulk solution by increased shearing, because acoustic streaming and ultrasonically generated turbulence
increase the velocity gradient at the membrane surface and thus cause a shearing stress on membrane foulant. When the affinity among DOM, particles, and the membrane is weak, ultrasound is more efficient at membrane fouling control.

Besides physical effects of ultrasound, such as acoustic streaming and ultrasonically generated turbulence, ultrasound also has chemical effects due to sonochemically generated hydroxyl radicals [29]. In our study, silica particles were stable with respect to the oxidative environment created by ultrasound. Changes in DOM properties as a result of sonochemical reactions, however, have been systematically investigated [27]. Generally, sonochemical reactions caused a decrease in molecular weight, hydrophobicity and aromaticity, and an increase in total acidity. However, these changes were less than 10% following sonication at 20 kHz for 4 hrs with a power density of 450 W/L. In this study, the power density of ultrasound was 4.6 W/L, two orders of magnitude lower than the previous study. Therefore, it is unlikely that chemical effects of ultrasound are significant under the conditions used in this study. Comparing UV absorbance from 200 to 600 nm of DOM solutions before and after sonication, there was little change. Consequently, the decline in the rejection rate with ultrasound was due to decreased steric exclusion by the foulant layer within the membrane pores and/or at the membrane surface, instead of due to changes in DOM properties by sonochemical reactions.

5.5 Conclusions

This study indicated that ultrasound significantly reduced membrane fouling caused by DOM and silica particles. The solution chemistry affected the ultrasonic efficiency to control membrane fouling. Better relative permeate flux improvement due to ultrasound
occurred at pH 9.2 compared to pH 4.0, because electrostatic repulsion among DOM, silica particles, and the membrane at high pH caused the membrane foulant to be readily removed. In addition, at high ionic strength, the relative permeate flux improvement decreased because of charge screening among DOM macromolecules, silica particles, and the membrane. As a result, strong interactions between foulant-foulant and foulant-membrane occurred. The presence of Ca$^{2+}$ at pH 9.2 enhanced membrane fouling due to charge neutralization and bridging among DOM, silica particles, and the membrane, causing fouling which was more difficult to be released by ultrasound. The experimental results indicated that DOM rejection depended on the mechanism of electrostatic interactions and steric exclusion. Higher rejection rate of DOM occurred at pH 9.2 than pH 4.0 due to charge exclusion between the membrane and deposited DOM macromolecules. The decline of DOM rejection rate of the membrane with ultrasound may be explained by decreased steric exclusion, because ultrasound significantly removed the foulant layer from the membrane surface.

5.6 Acknowledgements

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References


Figure 5.1 Diagram of the crossflow membrane filtration system with ultrasonic probe.
Figure 5.2 The permeate flux of membrane filtration of 0.3 g/L silica particles, 8 mg/L DOM, and 8 mg/L DOM and 0.3 g/L silica particles at pH 4.0 without ultrasound.
Figure 5.3 The permeate flux of membrane filtration of 8 mg/L DOM at pH 4.0 and pH 9.2 with or without ultrasound, respectively.
Figure 5.4 The permeate flux of membrane filtration of 8 mg/L DOM and 0.3 g/L silica particles at pH 4.0 and pH 9.2 with or without ultrasound, respectively.
Figure 5.5 The permeate flux of membrane filtration of 8 mg/L DOM at different levels of ionic strength with or without ultrasound, respectively. The solution pH was 9.2.
Figure 5.6 (a) The permeate flux of membrane filtration of 8 mg/L DOM at pH 9.2 in the presence of 1mM CaCl₂ or 3mM KCl with or without ultrasound. (b) The permeate flux of membrane filtration of 8 mg/L DOM and 0.3 g/L silica particles at pH 9.2 in the presence of 1mM CaCl₂ with or without ultrasound.

(Continued)
Figure 5.6 Continued

![Graph showing filtration time (min) vs. permeate flux (g/min cm$^2$) for different conditions: no US (3mM KCl), US (3mM KCl), no US (1mM CaCl$_2$), US (1mM CaCl$_2$).]
Figure 5.7 (a) The TOC rejection rate of the membrane at pH 4.0 and pH 9.2 with or without ultrasound, respectively. Initial concentration was 8 mg/L DOM and 0.3 g/L silica particles. (b) The TOC rejection rate of the membrane after 240 minutes filtration at different pH and in the presence of either Ca$^{2+}$ or KCl with or without ultrasound, respectively. Initial DOM and silica particle concentration was 8 mg/L and 0.3 g/L, respectively.

(Continued)
Figure 5.7 Continued
Figure 5.8 SEM images of the membrane surface after 240 minutes filtration with 8 mg/L DOM and 0.3 g/L silica particles at pH 9.2. (a) without ultrasound. (b) with ultrasound.
CHAPTER 6

CONCLUSIONS AND FUTURE WORK

6.1 Conclusions

This study showed that ultrasound reduced ceramic membrane fouling caused by silica particles and/or dissolved organic matter (DOM) during crossflow filtration. First, particle characteristics affected ultrasonic cleaning. At low particle concentrations, there was little membrane fouling in the presence of ultrasound. However, the permeate recovery of ultrasound declined with an increase in particle concentration. At low particle concentrations (<0.8 g/L), particle concentration changes altered membrane cleaning substantially when the membrane was far away from the cavitation region. However, at higher particle concentrations (≥0.8 g/L), the particle concentration effect was more pronounced when the membrane was close to the cavitation region. Model calculations indicated that the particles did not significantly attenuate sound waves or increase the viscosity of the solution. Instead, particles induce cavitation bubbles resulting in a decrease in sound wave intensity at the edge of the cavitation zone due to increased scattering and absorption of sound waves by bubbles. As a result of reduced intensity of
ultrasound and stronger particle-particle and particle-membrane interactions, fouling of hydrophobic particles was more difficult to control. Particle size did not significantly affect sound wave intensity. Instead, greater lift forces and greater crossflow drag forces occurred with larger particles. Consequently, better permeate recovery in the presence of ultrasound was obtained with larger particles. Based on the typical particle characteristics of lake water and ground water, ultrasound will likely be effective to control cake-layer membrane fouling during the filtration process. However, more studies need to be undertaken with ultrasound assisted membrane filtration of secondary effluent.

Second, ultrasonic factors also played an important role in membrane fouling control. The ideal location of the membrane was outside but close to the cavitation region. At this location, high relative permeate flux improvement of ultrasound was obtained and the integrity of the membrane was maintained. However, if the membrane had been within the cavitation region, pitting was found on the membrane surface, in addition to membrane cracking and the release of particulate aluminum into solution. In addition, an increase in the filtration driving pressure caused a stronger permeation drag force on the particles at the membrane surface. As a result, the relative permeate flux improvement of ultrasound declined, although more violent collapse of cavitation bubbles and greater extension of the cavitation region occurred at higher filtration driving pressures. Furthermore, the relative permeate flux improvement decreased with long pulse intervals of ultrasound. However, when the pulse interval was short (i.e., 1.0 s on/0.1 s off), the relative permeate flux improvement was close to that of continuous sonication.
In addition to the physical effects of ultrasonic cleaning, the chemical effect on ultrasonic cleaning was explored with Aldrich and Pahokee peat DOM at different ultrasonic frequencies and energy densities. Exposure of DOM to ultrasound resulted in decreases in TOC, Color$_{465}$, SUVA, aromaticity, and molecular weight, while DOM acidity increased. Greater sonochemical transformation of DOM occurred at 354 kHz and at higher energy density, compared to 20 kHz ultrasound, due to greater \textbullet OH radical production. The changes of DOM properties throughout sonication suggest that ultrasound might enhance the electrostatic repulsion between DOM and the negatively charged membrane, decrease the fouling potential of hydrophobic membrane, and decrease the reject rate of DOM by the membrane.

Finally, the effect of solution chemistry on ultrasonic efficiency to control membrane fouling caused by DOM and silica particles was examined. Better ultrasonic defouling occurred at pH 9.2 compared to pH 4.0, because electrostatic repulsion among DOM, silica particles, and the membrane at high pH caused the membrane foulant to be easily removed. In addition, at pH 9.2 and at high ionic strength, ultrasonic efficiency decreased because of charge screening among DOM macromolecules, silica particles, and the membrane. As a result, strong connections among membrane and foulants, and a tight packing of membrane foulant was formed. The presence of Ca$^{2+}$ at pH 9.2 enhanced membrane fouling due to charge neutralization and bridging among DOM, silica particles, and the membrane, causing fouling which was more difficult to be released by ultrasound. Experimental results indicated that DOM rejection depended on the mechanism of electrostatic interactions and steric exclusion. Higher rejection rate of DOM occurred at pH 9.2 compared to pH 4.0 due to charge exclusion of the membrane and deposited DOM.
macromolecules. The decline of DOM rejection rate of the membrane with ultrasound may be explained by decreased the steric exclusion, because ultrasound partially released foulants causing membrane pore blocking and/or partially removed foulant layer from the membrane surface.

6.2 Future Work

(1) Extend the study of ultrasonic control of ceramic membrane fouling to organic membranes, especially polymer membranes, because organic membranes are much more popular in practical applications. Organic membranes with high redox and thermal stability properties are preferred.

(2) Extend the study of ultrasonic control of ultrafiltration membrane fouling to nanofiltration (NF) and reverse osmosis (RO) membranes, which require filtration pressure as high as 4 MPa [1]. The high filtration pressure of nanofiltration and reverse osmosis may increase the threshold of ultrasonic cavitation. It is reported that the intensity of sonoluminescence decreased to zero when pressure was higher than 1.5 MPa [2], which means possibly no significant cavitation exists during RO filtration process. Therefore, the main mechanism for ultrasonic control of membrane fouling might be acoustic streaming if no ultrasonic cavitation occurs. The big advantage of this condition is that there is no worry about the cavitation damage of the membrane, including both surface pitting and sonochemically generated •OH attack of membranes.

(3) Study the ultrasonic efficiency to control membrane fouling caused by scale formation at RO or NF membrane surfaces. The typical sparingly soluble salts such as CaSO₄, CaCO₃, BaSO₄, and SrSO₄ [3] may be selected for the filtration tests.

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(4) Investigate the ultrasonic efficiency for membrane fouling control with different configurations of the membrane cell. For example, the ultrasonic transducer may be modified as a container and holds hollow fiber membranes inside. Therefore, inner wall of the container may emit ultrasonic waves to the hollow fiber membranes during filtration process to reduce and prevent membrane fouling.
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