ULTRASONIC CLEANING OF LATEX PARTICLE FOULED MEMBRANES

DISSEPTION

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By

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Membrane filtration has arguably been the most significant development in the area of water purification in the past 50 years. It has enabled many processes to become more reliable and to achieve purities that have not been achieved previously. One of the drawbacks of membrane use is fouling which is a decrease in the permeate flux with time. Fouling causes a decrease in production and requires some sort of treatment to remove or reverse its effects. In this research, the ultrasonic cleaning of particle-fouled membranes was investigated. Specifically, the mechanisms responsible for ultrasonic cleaning, the solution conditions and cake layer effects on ultrasonic cleaning and the implementation of ultrasound into an existing membrane cell were evaluated.

In initial studies, ceramic membranes were fouled by sulfate polystyrene latex particles in a dead-end filtration cell and subsequently subjected to ultrasound in a separate ultrasonic cleaning vessel at different frequencies, power intensities and durations of treatment. Results indicate that increased power intensity and lower frequency increase particle removal from a fouled membrane. These data along with SEM images suggest that cavitation mechanisms (i.e., microstreaming and microstreamers) are important in detaching particles from the membrane surface while
turbulence associated with ultrasound (i.e., acoustic streaming) plays a role in the transport of particles away from the surface following detachment.

In further studies, ceramic membranes were fouled in a dead-end filtration cell at different pH values and ionic strengths using polystyrene latex particles of differing sizes and subsequently subjected to ultrasonic cleaning in a separate ultrasonic cleaning vessel. Ultrasonic cleaning at high and low pH values was more effective than at neutral pH because of charge interactions among the particles. The particle-particle interactions at the lowest pH were strong and brought about large floc removal while the highest pH had the greatest repulsion among particles leading to rapid detachment of individual particles. Ultrasonic cleaning of fouling layers formed at higher ionic strength (> 0.3 M KCl) was less effective than cleaning at lower ionic strength (< 0.3 M KCl). High ionic strength caused particles to coagulate in solution and settle as flocs on the membrane surface forming a highly permeable fouling layer. This fouling layer was resistant to ultrasound at sub-optimal cleaning conditions used in this study due to the strong particle-particle interactions in the fouling layer. Membrane cleaning experiments performed with particles of varying size showed that particle size was less important than the surface charge characteristics of the particles. Particles that possessed the largest surface charge formed the thickest fouling layer and showed the greatest improvement in flux with ultrasonic cleaning. This research has shown that particle surface charge is the most important factor to consider when utilizing ultrasonic cleaning of particle-fouled membranes.

Finally, a transducer system was developed using a Navy Type I lead zirconate titanate piezoelectric material which was thin enough to require minimal modification for
incorporation in an existing, off-the-shelf cross-flow filtration cell. Hydrogen peroxide was detected in an external batch system that contained the transducer and water, which was an indicator of cavitation. Activity. Increases in hydrogen peroxide production rates were observed with increasing applied voltages. Chemiluminescence, formed through reactions with radical species created during cavitation, showed that increased voltages applied to the transducer resulted in larger zones of cavitation. For all voltages tested, chemiluminescence measurements indicated that the surface of the membrane was within the zone of cavitation. Membranes were then fouled in both a dead-end filtration cell and in a cross-flow filtration cell with polystyrene latex spheres. Using an external vessel to clean both ceramic and polymeric membranes fouled in the dead-end cell, showed that the thin transducer system was capable of effectively cleaning the fouled membranes and restoring flux. With increases in applied voltage there was an increase in flux recovery. Pulse operation was also successful in cleaning membranes, although the recovery was lower than for continuous treatment. In the cross-flow membrane cell, the transducer system was found to be effective at cleaning the polymeric membranes. Both pulse and continuous operation of the transducer improved flux with pulse being slightly lower than continuous operation. With operation at the highest voltages, some evidence of damage to the membrane was observed. At the lower applied voltages no damage of the membrane was found.

The results of this research elucidate the mechanisms and important factors influencing ultrasonic cleaning of particle-fouled membranes. A new laboratory-scale transducer flat sheet membrane system was developed which serves as a prototype for the
development of pilot and full-scale applications of this technology with flat sheet membranes. Ultimate utilization of this technology will lead to improved membrane performance.
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CHAPTER 1

INTRODUCTION AND BACKGROUND

1.1 Membrane Filtration

Membrane filtration is becoming the predominant fluid purification technique for industry and for many municipal treatment facilities. The world market for cross-flow membrane systems is nearly $6.3 billion and is expected to grow to $8.4 billion by 2007 [1]. The desalination market makes up the largest portion of the membrane market at around 20% of the total sales. Other areas, such as membrane bioreactors, are experiencing significant growth as well. With such a large market and a great potential for growth, improvements to membrane performance would greatly benefit end users of membranes.

Membranes are defined as structures which have a thickness much thinner than its lateral dimensions, through which mass transfer can occur under a variety of driving forces [2]. The most common membrane configuration is the asymmetric configuration comprising two layers 1) a semi-permeable layer which is very thin and is very selective and 2) a much more porous support material which is much less selective. The two layer system offers a high flux through the membrane while maintaining high purity in the end
product. Other membranes exist in different orientations, but this is the most common
membrane construction.

The most common membrane processes are reverse osmosis (RO), nanofiltration
(NF), electrodialysis (ED), ultrafiltration (UF) and microfiltration (MF). Reverse osmosis
is used mainly for the removal of salts from brackish or salty water. It is also capable of
rejecting synthetic organic compounds. Nanofiltration is slightly larger in pore size and is
used for water softening and for the removal of disinfection by-product precursors.
Electrodialysis is used for the removal of ions in solution and has seen extensive use in
demineralizing brackish water and in water softening of fresh water. Ultrafiltration and
microfiltration are primarily used for the removal of turbidity, pathogens and particles
from fresh waters [3]. The membrane types and the relative sizes of commonly occurring
materials are shown on Figure 1.1.

Membrane technology is used in many different configurations. The most
common configurations for reverse osmosis and nanofiltration are spiral wound or hollow
fiber. A spiral wound system has a flat sheet membrane laid over a permeate spacer that
is rolled into a cylindrical shape. The feed solution enters in one end of the cylinder and
permeate is collected through the center of the cartridge. Fluid which does not pass
through the membrane is allowed to pass through the length of the cylinder. A hollow
fiber system has many thin fibers placed into a cartridge. The feed for this system can be
either from the inside of the fiber out or from the outside in. Permeate is collected from
the inside or outside of the fiber at the outlet end of the cartridge depending on the
direction of permeate flow through the membrane. Hollow fiber and spiral wound
Figure 1.1 Membrane separation processes and the relative sizes of common materials from Koch membrane systems (http://www.kochmembranesystems.com/ps_exmem.html).
membranes are extremely popular because they offer a large surface area in a small volume. Microfiltration and ultrafiltration configurations are generally used with simple tubular orientations or with flat sheet cells [3].

Advantages of membrane filtration over other current treatment technologies are numerous. For example, membranes are able to produce a uniform product from feeds with widely varying starting compositions [3]. This capability is desirable for water and wastewater treatment facilities that need to ensure a consistent end product to meet regulatory requirements throughout the year. To meet these different needs, membranes are also able to be specifically designed for numerous types of feeds, such as extremely high ionic strength waste streams [4], particulate laden streams [5], metal contaminated streams [6] and many others. Membrane characteristics, such as charge and surface roughness can be altered by utilizing materials with different properties and making adjustments to the manufacturing process [17]. Membrane systems also require less space than conventional treatment systems [7]. The flexibility of the systems is one of the reasons that membranes are becoming more widely used.

1.2 Membrane Fouling

Although membrane systems are highly desirable, these systems have some disadvantages over conventional systems. Costs are relatively high for systems where a high degree of purification is necessary. In addition, with prolonged filtration of a solute, the membranes will experience fouling over time. Fouling is characterized by a decline in permeate flux over time. Fouling is usually a result of two separate factors, concentration polarization and membrane fouling which includes deposition, pore plugging and
deposition of fouling material in the pores [8]. As fluid is brought toward the membrane, fouling materials are drawn to the membrane surface. If they do not pass through the membrane, they begin to accumulate at the surface leading to the formation of additional layers of material through which the fluid must pass [3]. Particles form cake layers on the surface while macromolecules form gel layers. Concentration polarization occurs when there is a buildup of particle or fouling material near the membrane surface which creates a concentration gradient that causes counter-current flow against the feed solution [9]. Concentration polarization is the precursor to the formation of a cake layer. Concentration polarization is referred to as reversible fouling while membrane fouling by pore plugging and deposition is generally irreversible [95]. These two factors result in a decrease in permeate flux.

The fouling of membranes is affected by changes in hydrodynamic and physicochemical operating conditions such as transmembrane pressure, particle size, crossflow velocity, ionic strength and pH [90]. For this study only solution conditions and particle size are considered. Two important solution variables are pH and ionic strength. Variation in pH changes the charge density of the particles and membranes and thus their interparticle repulsive interactions [10,90]. Ionic strength affects the thickness of the double layer, particle-particle and particle-membrane interactions, and subsequently the structure of the fouling layer [10,90]. Finally, particle size can affect the permeability [90], the deposition probability [11] and the packing structure of the fouling layer [12].

A significant amount of research has been done in the area of membrane fouling and ways to prevent membrane fouling. Many of the strategies have focused on the
prevention of fouling using techniques such as the use of cross flow configurations [13,14,15,16], alterations in membrane surface properties [17], backpulsing [18], vibratory shear techniques [19,20,21], among many others.

Cleaning techniques include hydraulic techniques such as back washing [22], chemical treatment [23], or a combination of these techniques. Problems with these techniques are that they require time, energy, equipment and in some cases chemicals. Often times the membrane system is shut down while cleaning is performed. This leads to increased operating costs and a reduction in output from the membranes.

1.3 Ultrasound

Ultrasound is longitudinal wave with a frequency above 20 kHz [24]. This frequency is above the sonic range (20 Hz to 20 kHz) at which humans can hear and below the megasonic region (>600 kHz) [37]. For waves of infinite length which propagate in a single dimension, the relationship between the speed of the wave (c), wavelength (\(\lambda\)) and frequency (f) is:

\[
c = f\lambda \quad (1)
\]

For waves which propagate from one medium to another, the acoustic impedance can determine how well the wave is transmitted into the other medium. The acoustic impedance is a function of the density of the material and the speed of sound in the medium (c) and calculated using:

\[
Z = \rho_0c \quad (2)
\]
If the acoustic impedance of one medium matches that of another, the transmission will be complete. Mismatched impedances can cause pressure or velocity changes in the sound wave or anti-phase reflections which result in standing waves [25].

Sound can be produced by creating a mechanical oscillation at a desired frequency and coupling this oscillation to a medium. The better the coupling (matching the acoustic impedances are of the different media) the more efficient the energy transfer [24]. For the purposes of ultrasonic cleaning the main method to generate ultrasound is through the use of piezoelectrics. Piezoelectric materials convert electrical energy into mechanical energy and vice versa. This behavior was discovered in 1880 by Jacques and Pierre Curie [26]. They demonstrated that several natural minerals are able to generate electrical signals as result of mechanical stresses. They later found that the reverse would also be possible to apply an electrical charge and get a mechanical response.

Transferring this mechanical response from one medium to another results in energy transfer. In membrane cleaning systems this would be transfer of energy from the piezoelectric material to a solution. One process of great interest for cleaning using ultrasound is in ultrasonically generated cavitation which occurs as a result of the negative pressure wave exceeding the tensile strength of the liquid creating a void in the fluid. Formation of this void is facilitated by dissolved gas, particles and other imperfections that are present in the solution. The bubble created can do one of 3 things: 1) dissolve back into solution, 2) grow and shrink with the acoustic wave, or 3) grow to a size at which the bubble can no longer maintain its structure and collapse. It is during this collapse that very high temperatures and high pressures are observed emanating from the bubble [24]. Depending on the size of the bubble, the nature of the solution and the sound
field, pressures and temperatures at collapse vary greatly. The growth and collapse of the bubbles are also associated with a great deal of turbulence.

The ultrasonic frequency gives the number of cycles per time. The higher the frequency, the smaller the maximum size that bubbles can attain [24] and the more collapses that occur per time. With increasing frequency there is also increased attenuation of acoustic energy, therefore, lower frequencies travel farther into the medium than higher frequencies [73]. With decreasing frequency, the size of the bubble created, the temperature and violence of the collapse increase [74,75].

1.4 Ultrasonic cleaning

Ultrasonic cleaning has become a commonly used laboratory technique in the past 20 years. Most ultrasonic cleaning devices work on the principle of cavitation. Cavitation creates micro turbulence and creates high shear velocities in its near vicinity and can also create shock waves that travel radially from cavitation collapses. These forces are able to dislodge particulate matter from surfaces and enhance the dissolution of substances due to the increased mass transfer of liquid to surfaces. Important variables of ultrasound are the frequency (the number of cycles per time) and the power intensity (the amount of power put into the system per unit area).

There have been many papers published on the area of ultrasonic cleaning of particles from surfaces. Farmer et al. [27,28] investigated the ultrasonic cleaning of silica particles and found that ultrasound was able to effectively clean coatings of clay and iron oxide from a silica surface. Other researchers have studied the ultrasonic pickling of steel
strip [29] and the cleaning of stainless steel surfaces [30]. All of these researchers have shown that ultrasound can effectively remove particles and other deposited material from surfaces.

Several different mechanisms have been proposed for particle release from a surface as a result of ultrasound. One mechanism is large scale movement of fluid as a result of absorption of acoustic energy called acoustic streaming [24]. Acoustic streaming increases in magnitude with increasing frequency and with increasing power intensity [65]. Increased fluid movement leads to increased mass transfer and dissolution and may be important in the detachment of loosely bound particles. Velocities on the order of 10 cm s$^{-1}$ have been observed with medical ultrasound with a frequency of 3 MHz [31].

Microstreaming is small-scale localized movement of fluid which occurs in the direct vicinity of bubbles. The growth and collapse of bubbles cause rapid changes in the magnitude and direction of the fluid movement around the bubbles resulting in significant shear forces [24,32]. The range of microstreaming is on the order of a bubble diameter [33], which varies with frequency.

Microstreamers are cavitation bubbles which form and travel towards pressure antinodes which are regions in the fluid experiencing the greatest negative pressure of the acoustic wave [24]. The bubbles take tortuous paths and coalesce as they travel forming larger bubbles. The migration is caused by Bjerknes forces existing between pulsating bubbles in a pressure field [34]. Microstreamers have an effective range on the order of millimeters [24].

Micro-jets are formed when cavitation bubbles collapse in the presence of a surface. This surface could be another bubble or a fixed surface. During bubble collapse,
the outer wall accelerates faster on the side opposite the solid surface or on the side closest to a neighboring bubble. This asymmetric collapse results in the formation of a jet with an estimated velocity of 100-200 m s\(^{-1}\) [24]. The effective range of micro-jets is on the order of the bubble diameter.

Shock waves are formed when the velocity of the collapsing wall of the bubble exceeds the speed of sound in the medium. This creates an uneven pressure wave in which the leading edge or high pressure region rapidly drops to the low pressure region [24]. This rapid change can cause other neighboring bubbles to collapse cause localized turbulence.

With megasonic cleaning, cleaning at frequencies higher than 600 kHz, the cavitation behavior is different from that seen at lower frequencies (20 kHz). The maximum size of bubbles is smaller than with the lower frequencies [24]. With smaller bubbles, the collapse associated with the bubbles is less intense. However, with the higher frequency there is increased absorption of the acoustic energy leading to increased acoustic streaming. Megasonic cleaning has been used extensively in the cleaning of silicon wafers. Deymier et al. [35,36,37] have looked at cleaning of silicon wafers using frequencies from 600 kHz to 1 MHz. This frequency range was chosen because typical ultrasonic cleaning systems operating from 17 to 100 kHz are known to damage the surfaces of the wafers. The researchers also calculated the forces necessary for particle detachment from silicon surfaces.
1.5 Ultrasonic Cleaning in Membrane Systems

Several studies have appeared in the past couple of decades which have investigated the use of ultrasound for the cleaning of membranes. These studies have seen that membrane processes can benefit from ultrasound and that there is great potential for this technology.

The first significant work done in the area was done by Fairbanks and Chen [38] who investigated the use of ultrasound for the acceleration of liquid through porous media. They used sandstone and a stainless steel filter with crude oil and water and found that ultrasound was able to significantly increase the rate of liquid flow through both of the porous mediums tested. They also found that the maximum flowrate of oil was increased through the use of ultrasound. They did not, however, look at damage which may have been caused to the filters and did not give any information on the flowrates of oil through the media when ultrasound was stopped. The increase in flow rate may have been due to two different phenomena, acoustic streaming and damage to the filter media.

Fairbanks and Otsuka [39] continued work on ultrasound aided filtration, but Allen and Shippey [40] were the first researchers to investigate ultrasonic cleaning of membranes. They tested a number of different cleaning techniques and found that ultrasound was the most effective for cleaning reverse osmosis and ultrafiltration membranes.

In 1981, Thompson [41] patented a system to use ultrasound to scour off particles from reverse osmosis and ultrafiltration membranes. However, the system was to be operated below the cavitation threshold, possibly limiting mechanisms leading to the cleaning of fouled membranes.
Other systems appeared at the same time with membranes which were supposed to vibrate and prevent any fouling from occurring [42,43]. These membranes were made of materials or modified with materials which are similar to the piezoelectric materials that make up ultrasonic transducers, although they utilized polymeric piezoelectric materials. Both of them were unsuccessful in modifying the membrane material and causing the membrane material to vibrate within the membrane modules.

In the late 1980s Wakeman and Tarleton began working with electric fields to prevent the deposition of fouling material onto membranes [44,45]. This work showed promise with, but also led to experimentation with ultrasonic fields for the prevention of membrane fouling [46,47,48]. These experiments showed that it was possible to use ultrasound to maintain high fluxes with membrane systems that would otherwise foul.

These works by Tarleton and Wakeman increased interest in the ultrasonic cleaning of membranes and the next researchers to continue work in this area were Kobayashi and Chai et al. [49,50,51,52]. In these papers, they investigated fouled membrane cartridges submerged into an ultrasonic bath for treatment. They performed a number of experiments studying membrane type, frequency of the ultrasonic bath, and power intensity of the ultrasonic bath. They found that the ultrasound enhanced the filtration through the membrane. Lower frequencies and higher power intensities increased the membrane cleaning. They performed the first systematic experiments of ultrasound on membrane filtration. However, they lacked the ability to observe mechanistically how ultrasound affected membranes and whether or not there was any damage to the membrane.
Utilizing inorganic membranes, Kokugan et al. [53] found that ultrasound increased the mass transfer coefficient of water across membranes, but determined that ultrasound was not effective at removing fouling material inside pores. The rejection of fouling material was marginally decreased because of increased permeate flux. They utilized a probe system which irradiated approximately 1/8 of the membrane surface.

With a slightly different application of membranes and ultrasound, Zhu et al. [54] found that ultrasound enhanced membrane distillation up to 200%. They utilized a 20 kHz probe and subjected a small area of the membrane to ultrasonic treatment. They found similar trends as Kobayashi et al. [49,50,51,52] of increased enhancement with decreasing frequency and increased ultrasonic intensity.

Li et al. [55] used a probe ultrasonic system to clean membranes fouled with paper mill effluent. They found that they were able to increase permeate flux and restore the original structure of the membrane surface. SEM images did not reveal any damage to the membrane surface.

Juang and Lin [56] used a low frequency probe to clean ultrafiltration membranes. They studied regenerated cellulose membranes and suspensions of organic foulants in the system with a 20 kHz probe aimed at the membrane surface. They found that the membrane experienced increased fluxes and could maintain high fluxes with ultrasound. With control of the ultrasonic intensity (use of the transducer at lower power intensities), the degradation of the fouling organic compounds was prevented.

Masselin et al. [57] found significant damage to several types of polymeric membranes as a result of cleaning the membranes in an ultrasonic bath at 47 kHz. These
membranes were not in a membrane module during the experiment, rather they were placed in a beaker which was then put into an ultrasonic bath.

Most recently, Muthukumaran et al. looked at the use of ultrasound for cleaning ultrafiltration membranes in the dairy industry. The setup that they used was similar to that used by Kobayashi et al. [49,50,51,52] in that they had an enclosed membrane cell suspended in an ultrasonic bath. They found that the recovery in flux was independent of the sonication time and that there was an increase in flux with increases in ultrasonic power. They also used the membrane system in the ultrasonic bath for over a month and found that there was no change in the permeate flux, which indicated to them that there was no damage to the membrane.

The main problem with all of the ultrasonic cleaning systems which have been investigated is that they are very difficult to scale up to pilot or industrial scale systems. It is not practical to submerge membrane modules into large ultrasonic baths. Also, probe systems at low frequencies will require thick transducers that must be incorporated into membrane systems where space will be a premium. It may not be practical to incorporate large piezoelectric rods into membrane modules that might have the same thickness as the transducer.

Damage as a result of ultrasonic cleaning has also been largely ignored, which is a serious problem because most membrane systems utilize polymeric membranes. These membranes are quite fragile and when exposed to the harsh conditions of ultrasound, especially at low frequencies, some damage is likely to appear. Also, with membrane systems, the distances between the transducer and the membrane surface are likely to be very small. With short distances there lies the possibility of membrane damage.
1.6 Overview of the Dissertation

In this research, the first objective was to develop a mechanistic understanding of cleaning of particle-fouled membranes using ultrasound. To this end a fouled membrane was suspended away from a transducer surface, allowing the ultrasound to slowly clean the fouled surface. This technique allowed observation of the gradual ultrasonic cleaning of a particle fouled surface and mechanisms responsible for the cleaning were proposed based upon the cleaning results and images of the ultrasonically cleaned surfaces.

Solution conditions and particle size were also investigated using this system to determine whether they affect ultrasonic cleaning of membranes as much as they affect traditional cleaning techniques. It was hypothesized that changes in the charge of the particles and membrane would affect how well the ultrasound was able to clean the membranes and that the structure of the fouling layer would behave differently in the ultrasound as well.

Finally, a bench-scale ultrasonic membrane cleaning system was developed through the use of thin piezoelectric disks. The use of thin piezoelectric disks facilitated the incorporation of an ultrasonic transducer system within an off-the-shelf flat sheet membrane system. These disks were incorporated into the membrane cell and used to clean the fouled surface during filtration. It was thought that the high frequency was also capable of cleaning the membrane surface whereas other studies have looked only at low frequencies.
1.6.1 Mechanisms and factors influencing the ultrasonic cleaning of particle-fouled ceramic membranes

In chapter 2, the mechanisms and factors responsible for ultrasonic cleaning are presented. This work involves the use of an alumina membrane which is fouled in a dead-end filtration cell by sulfate latex particles. The membranes were removed from the cell after fouling and cleaned in an ultrasonic cleaning vessel, at a considerable distance from the transducer surface, using different power intensities and frequencies ranging from 70 kHz to 1062 kHz. The distance away from the transducer slows down the progression of cleaning and allows for observation of differences among the operating conditions. At short distances, cleaning is very rapid and no differences were observed among different operating conditions. Following treatment the cleaning efficiency of the ultrasound was evaluated in the dead-end cell. The membrane was dried and prepared for scanning electron microscopy (SEM). Every membrane was examined using SEM and all surface phenomena were recorded. Based upon the results of the cleaning results and the SEM images, mechanisms for removal were proposed.

1.6.2 Effect of Solution Conditions and Cake Layer Structure on the Ultrasonic Cleaning of Ceramic Membranes

In chapter 3, the effect of solution conditions and particle size on the ultrasonic cleaning of particle-fouled membranes was evaluated. This research investigated the effect of solution conditions such as pH and ionic strength on the fouling and ultrasonic cleaning of membranes. In these experiments, membranes were fouled with sulfate latex particles in a dead-end filtration cell as a function of pH and ionic strength, followed by
cleaning in an ultrasonic vessel at the corresponding pH and ionic strength. The cleaning was also performed at long range to slow down the progression of cleaning. The flux of water through the ultrasonically cleaned membranes were measured and the membranes was then prepared for imaging using SEM.

Particle size effects on fouling and ultrasonic cleaning were also investigated. Alumina membranes were fouled in a dead end filtration cell using different sized sulfate latex particles and subsequently cleaned in the ultrasonic cleaning vessel. Membrane fluxes were measured and the membranes were then prepared for SEM imaging. Membrane cross-sections were also taken of the different membranes to observe any change in the membrane fouling layer thickness with changes in solution conditions and particle size.

1.6.3 Cleaning of particle-fouled polymeric membranes using ultrasound embedded in a cross-flow filtration cell

In chapter 4, a transducer system was developed that could be incorporated into an existing flat-sheet, cross-flow membrane cell. A transducer was developed from a piezoelectric material, lead zirconate titanate (PZT) and this was incorporated into both an external cleaning vessel and into a cross-flow membrane cell. The transducer was initially evaluated for its ability to produce cavitation by measuring chemiluminescence imaged using high sensitivity film in a dark room.

Polyvinylidene difluoride (PVDF) membranes and ceramic membranes were fouled in a dead end cell and subsequently cleaned in an external ultrasonic cleaning vessel with the transducer. The cleaned fluxes of the membranes were measured in the
dead end filtration cell and the membranes were prepared for SEM imaging. Different applied voltages were used for the transducer as well as comparing continuous mode to pulse mode.

The transducer was embedded into the cross-flow membrane cell and used for cleaning a modified membrane during filtration and after fouling. The modified membrane was manufactured to restricted fluid to the area opposite the transducer surface. The transducer was used in continuous mode as well as in pulse modes. The applied voltage input to the transducer was also varied during the experiments.
CHAPTER 2

MECHANISMS AND FACTORS INFLUENCING THE ULTRASONIC CLEANING OF PARTICLE-FOULED CERAMIC MEMBRANES


2.1 ABSTRACT

This paper investigates factors affecting ultrasonic cleaning of particle-fouled ceramic membranes and possible mechanisms responsible for cleaning. Homogeneous ceramic membranes were fouled by sulfate polystyrene latex particles in a dead-end filtration cell and subsequently subjected to ultrasound at different frequencies, power intensities and durations of treatment. Flux measurements indicate that increased power intensity and lower frequency increase particle removal from a fouled membrane. These data along with SEM images suggest that cavitational mechanisms (i.e., microstreaming and microstreamers) are important in detaching particles from the membrane surface while turbulence associated with ultrasound (i.e., acoustic streaming) plays a role in the transport of particles away from the surface following detachment. Micro-jets did not appear to cause significant removal compared to microstreamers, although evidence of micro-jet pitting was visible in SEM images of the fouled surface. In addition,
SEM images did not show any visible damage to the membrane surface, even for prolonged periods of ultrasound at high power intensity and low frequency (20 W cm$^{-2}$, 20 kHz).

2.2 INTRODUCTION

2.2.1 Background

The use of membranes is a widely employed, versatile, and effective separation process. Different membrane types, ranging from microfiltration (MF) to reverse osmosis (RO), are capable of removing suspended particles and microorganisms to rejecting virtually all ions in solution, respectively. The versatility of membranes lies in their ability to meet the objectives of a variety of other treatment systems, such as coagulation, sand filtration, carbon adsorption, or ion exchange [58]. To date, a major limitation of membranes has been the high cost of operation. A significant impediment to the efficient operation of a membrane system is membrane fouling. Reductions in the prices of membrane systems and operating costs have occurred, but fouling remains a significant problem.

The predominant fouling mechanisms observed with ultrafiltration and microfiltration membranes are classified into three categories: the build-up of a cake layer on the membrane surface, blocking of membrane pores, and adsorption of fouling material on the membrane surface or in the pore walls [59,60]. Current membrane cleaning technologies include hydraulic, chemical, and mechanical methods [61,62,63]. A common hydraulic cleaning technique, backwashing [22], is not ideal, in that it experiences degradation of flux between backwashes and requires a break in operation to
be performed. Problems with other cleaning techniques include chemical costs, waste disposal, and significant capital investments for equipment [3].

Ultrasound is an effective technique for cleaning a variety of surfaces, from the delicate removal of particles on semiconductor wafers [64] to the removal of scale and oxides from steel strip [29]. Ultrasound is a sound wave traveling through a medium at a frequency above 18 kHz [65]. As a result of the propagation of ultrasonic waves, the medium is subjected to alternating rarefaction and compression cycles. If during the rarefaction stage of the cycle, the tensile stress exceeds the tensile strength of the fluid (i.e., water), a bubble cavity is formed. This cavity may: 1) dissipate back into the liquid, 2) grow to a resonant size and fluctuate about this size, or 3) grow to a size at which the surface tension forces of the liquid cause it to collapse on itself. The latter is termed cavitational collapse. Cavitational collapse results in extreme conditions producing light emission, shock waves and localized high temperatures (up to ~5000 K) and pressures (up to ~1000 atm) [65]. These high temperatures and pressures dissociate water into hydrogen atoms (H•) and hydroxyl radicals (OH•). More importantly with respect to membrane cleaning, cavitational collapse also produces a number of phenomena that result in high velocity fluid movement.

Recently, a number of researchers have demonstrated the effective use of ultrasound for cleaning fouled membranes or for increasing permeate flux of water through membranes. In cross-flow filtration using polymeric polyacrylonitrile membranes, Kobayashi et al. [50] found that in the presence of particles, ultrasound increased water flux and decreased the solute concentration near the membrane surface. Also, results suggested that ultrasound did not damage the membrane surface or increase
the pore size of the membranes used [50,51,52]. Using ceramic membranes, Kokugan et al. found that ultrasound was able to increase the mass transfer coefficient of water across membranes, but determined that ultrasound was not effective at removing fouling material inside pores [53]. Zhu et al. found that ultrasound could enhance membrane distillation up to 200% [54].

Although it is clear that ultrasound effectively cleans membrane surfaces and maintains high water fluxes, the mechanisms involved in cleaning membrane surfaces by ultrasound are still largely unknown. Understanding the mechanisms by which ultrasound cleans fouled membrane surfaces will aid in future design of systems. The primary mechanisms by which ultrasound aids cleaning may be affected by a number of factors, such as orientation and position of the ultrasonic field, ultrasonic power intensity and frequency, membrane material, membrane housing, operating pressure, and fouling material. As a first step using a dead-end flow filtration cell and an ultrasonic system capable of operating at different frequencies, we investigated the role of ultrasonic factors in controlling the mechanisms of membrane cleaning. Using the results of these experiments, combined with scanning electron microscopy (SEM) images of the surfaces, mechanisms for particle removal by ultrasound are suggested.

2.2.2 Ultrasonic Cleaning Mechanisms

Several different mechanisms may lead to particle release from a particle fouled surface as a result of ultrasound. Proposed mechanisms illustrated in Fig. 2.1 include:

Acoustic streaming – Although several definitions of acoustic streaming exist [65,24,77], in this study, it is defined as the absorption of acoustic energy resulting in fluid flow [24]. Acoustic streaming does not require the collapse of cavitation bubbles.
The distance over which acoustic streaming occurs is on the order of centimeters to tens of centimeters [66] with velocities in the range of 10 cm s\(^{-1}\). This removal mechanism is expected to be important near surfaces with loosely attached particles or with readily dissolvable surfaces [74]. Higher frequency ultrasound tends to have higher energy absorption and thus greater acoustic streaming flowrates than lower frequencies for the same power intensity [65]. In addition, higher power intensities lead to greater acoustic streaming flowrates due to higher energy gradients in solution between acoustically and non-acoustically stimulated areas. This mechanism causes bulk water movement toward and away from the membrane cake layer, with velocity gradients near the cake layer that may scour particles from the surface.

**Microstreaming** – Microstreaming is a time-independent circulation of fluid occurring in the vicinity of bubbles set into motion by oscillating sound pressure. Oscillations in bubble size cause rapid fluctuations in the magnitude and direction of fluid movement, and as a result significant shear forces occur [16,32]. The effective range of this mechanism is on the order of a bubble diameter (depending on acoustic pressure amplitude and frequency \(\sim 1-100 \mu m\)) [33]. When a cavitation bubble is near a cake layer surface, microstreaming will result in a dynamic velocity profile that will exert drag forces on particles leading to removal.

**Microstreamers** – Cavitation bubbles that form at nucleation sites within the liquid and are subsequently translated to a mutual location (antinodes) are called microstreamers. The bubbles travel in ribbon like structures along tortuous paths at velocities approximately an order of magnitude faster than the average velocity of the fluid [81], coalescing as they collide with other bubbles. The migration of the bubbles is
caused by the Bjerkness force existing between pulsating bubbles in a pressure field [34]. We propose that antinodes located on the fouled surface may result in bubbles scouring away particles while translating to these antinodes [24]. These streamers have an effective range on the order of millimeters [81].

Micro-jets – Micro-jets are formed when a cavitation bubble collapses in the presence of an asymmetry (i.e., a surface or another bubble). During collapse, the bubble wall accelerates more on the side opposite to a solid surface, resulting in the formation of a strong jet of water with an estimated velocity of 100-200 m s\(^{-1}\) [24]. The effective range of micro-jets is on the order of the bubble diameter. While the high estimated velocity of micro-jets could effectively scour particles from a membrane surface, the extent of this phenomena in membrane systems has not been thoroughly investigated.

Other possible ultrasonic mechanisms of membrane cleaning include: vibrations, chemical interactions with radicals, and shock waves resulting from the collapse of bubbles. Vibrations were not investigated because previous research in ultrasonic cleaning have not shown it to be a significant cleaning mechanism. Radical species may react with the fouling material or the membrane surface; however, due to the short treatment periods in this study, radicals were not expected to have an effect on the system. Shock waves were not investigated in this study but could contribute to the cleaning of membranes and have been studied in other cleaning applications [64].
2.3 EXPERIMENTAL

2.3.1 Materials

Anodisc™ γ-alumina (γ-Al₂O₃) ceramic membranes (25 mm diameter) manufactured by Whatman (NJ) were used in all experiments. This 60 µm thick homogeneous membrane has a 0.2 µm uniform pore size throughout the membrane. The surface was positively charged at the pH used in the experiments as stated by the manufacturer and confirmed in our laboratory by surface charge titrations. Ceramic membranes were selected due to their resistance to high temperatures, thus limiting the possibility of high temperature alteration from collapsing cavitation bubbles. In addition, these membranes are well characterized [16,67,68,69]. Moreover, alumina is a good sound reflecting material that offered the potential for facile cleaning by ultrasound [65]. Membrane pores were large enough to allow for clear imaging using SEM, and therefore, could be visually inspected for any defects or damage as a result of ultrasonic treatment.

Sulfate polystyrene latex particles from Interfacial Dynamics Corporation (Portland, OR) were chosen to foul membranes. The particles were negatively charged at the pH used for all experiments as stated by the manufacturer and confirmed by electrophoretic light scattering measurements in a ZetaPlus (Brookhaven Instruments Corp, Brookhaven, NY). The particles had an average diameter of 0.53 µm. All solutions were prepared using Milli-Q (Millipore Corporation, Bedford, MA) water with a resistivity of 18.2 MΩ-cm and a total organic carbon concentration of less than 5-10 µg L⁻¹.
2.3.2 Fouling Experiments

The filtration apparatus used for all experiments was an Amicon Ultra Filtration 10 mL stirred cell (Bedford, MA). This cell operated in dead-end mode forcing all of the solution though the membrane. This cell was fed from a Nalgene polypropylene 4 L mixing vessel. The driving force for the system was ultra high purity nitrogen gas pressurizing the mixing vessel to a pressure of 0.7 atm (10 psig).

Initially, a dry membrane was weighed using a Fisher Scientific (Springfield, NJ) balance (accuracy ± 0.1 mg). The membrane was then placed into the filtration cell and filled with 8 mL of Milli-Q water. The initial flux was measured over a period of 5 minutes using a 1 mM potassium chloride solution, pH adjusted to 7.0 with 0.1 N sodium hydroxide. Experiments were done using prolonged periods of filtration using this pH adjusted 1 mM potassium chloride solution to ensure that no fouling occurred from this solution. A constant flux was obtained during these runs.

After initial flux measurements, the membrane was removed, inspected visually, and placed back into the filtration cell. The latex particle solution was then passed through the membrane. The solution consisted of 10 mg L\(^{-1}\) sulfate polystyrene latex particles suspended in 1 mM potassium chloride, pH-adjusted to 7.0 with 0.1 N sodium hydroxide. The membrane was fouled until the flux was approximately 25% of the initial flux of pH-adjusted potassium chloride solution. Based on gravimetric analysis and assuming that the cake layer had a random packing structure, the cake layer height was determined to be approximately 100 µm. The pH did not change during the experiment.
2.3.3 Ultrasonic Cleaning Experiments

The water jacketed cleaning vessel, ultrasonic generator and transducer were manufactured by L3 Communications Elac Nautik (Kiel, Germany). An illustration of the cleaning vessel and the membrane support stand are shown in Fig. 2.2. After fouling, the fouled membrane was removed from the filtration cell, placed between several sheets of Mylar® (Surplus Sales, NE), and then clamped to a stainless-steel stand. One sheet acted as a barrier to water flow through the membrane; another sheet surrounded the outer edge of the membrane preventing lateral movement; and the final sheet had a 25 mm hole in the center to allow for particles to be released from the membrane surface to solution. Mylar® was used because it is highly transmissive to acoustic waves and thus allowed for acoustic energy to pass essentially unaltered [70]. The stand was then placed into the glass cleaning vessel that was open to the atmosphere and filled with 500 mL of Milli-Q water. The cleaning vessel was maintained at 15°C by circulating water through the water jacket with a Fisher Scientific Isotemp constant temperature bath (Pittsburgh, PA). The stainless-steel stand holding the membrane was suspended 10.5 cm away from the transducer. Orientations of the fouled membrane to the transducer surface, frequency and power intensity of the ultrasound and duration of treatment were varied using this system. Ultrasound was amplified at frequencies of 70 kHz, 205 kHz, 354 kHz, 620 kHz and 1062 kHz. Power intensity input into the solution was measured using calorimetry [71].

Control experiments were performed with the cleaning vessel on its side to eliminate gravity as a possible removal mechanism. In addition, the fouled membrane was placed in the cleaning vessel in the absence of ultrasound to verify that transfer to the vessel itself did not have an effect on cleaning efficiency.
2.3.4 Analysis

After the membrane had been treated with ultrasound, the flux was measured using the filtration cell with pH-adjusted 1mM potassium chloride solution without latex particles. The flux of the cleaned membrane was then compared to the initial flux measured without latex particles. The “cleaned flux ratio” was calculated as $J/J_o$ where $J$ is the flux of pH-adjusted 1mM potassium chloride through the membrane following ultrasonic treatment and $J_o$ is the flux of pH-adjusted 1mM potassium chloride through the membrane prior to fouling with particles.

Following ultrasonic cleaning, the membranes were air dried for two days and weighed. Using the mass difference before and after treatment, the amount of particles removed was estimated. The mass of the particles before ultrasound was determined by using an average mass of three fouled membranes that had been air-dried. To determine if trapped water falsely elevated the weight of the particles on the membrane, in select experiments, fouled and cleaned membranes were dried at 103°C for 3 days to eliminate any residual water. Results showed 0.5% change in mass compared to air drying which represents 3% of the total mass of the fouling layer. Based on the size and density of a particle, this analysis was used to determine the percentage of particles remaining on the membrane surface after cleaning.

Lastly, samples were prepared for imaging using SEM. The membranes were coated with a thin layer (several hundred angstroms) of gold to enhance the conductivity of the surface. SEM was performed using a XL-30 FEG scanning electron microscope (FEI Company, OR) at voltages of 1-5V. The entire membrane was visible under the lowest magnification using SEM. Any phenomena found during scanning were
documented. Higher magnification images from more than 5 random locations were taken in order to obtain a representative sample of morphology of the surface. Also, different magnifications were taken of each membrane in order to obtain images on the scale of removal.

SEM images were also used to examine the possibility of damage to the membranes as a result of ultrasound. Three non-fouled membranes were imaged before and after ultrasound at 20 randomly located sites. In addition, the solution in which the membrane was ultrasonically cleaned was analyzed for aluminum using a Varian inductively coupled plasma optical emission spectrophotometer (ICP-OES) (Varian Inc., Australia). Detection of aluminum is an indication of erosion of the alumina membrane material by ultrasonic mechanisms such as cavitation collapses on the membrane (micro-jets), shock waves, or solution effects. For ICP-OES analysis, a second-degree polynomial regression curve was developed using five calibration standards and a blank sample. A Varian fitted background correction was employed to eliminate background spectral interferences. Concentrations were measured at different wavelengths and the average concentration was compared to the background concentration.

2.4 RESULTS

2.4.1 Fouling Experiments

The reduction in flux due to fouling of the ceramic membrane by latex particles is shown in Fig. 2.3. Consistent and reproducible fouling was observed (relative standard deviation <5%) throughout all experiments. Experiments were performed with the fouled
membrane placed in a mixing vessel for 3 hours to ensure that the resulting fouling layer was not amenable to removal by rinsing or vigorous agitation.

2.4.2 Effect of Power Intensity and Frequency on Cleaning

The first series of ultrasonic cleaning experiments examined the relationship between the cleaned flux ratio on power intensity (Fig. 2.4) and frequency (Fig. 2.5). All membranes were fouled for 45 minutes using 10 mg L⁻¹ latex particles to a flux that was 25% of the original flux. To investigate the effect of power intensity, runs were performed with the fouled membrane surface facing away from the transducer at 620 kHz with a sonication time of 5 seconds. The orientation and treatment times were not optimal, in order to view the progression of cleaning on the particle fouled surface. As seen in Fig. 2.4, clearly there is an increase in the cleaned flux ratio (circles) with increasing power intensity and a corresponding decrease in the amount of latex particles remaining on the surface (triangles). This trend of increasing cleaned flux ratio with respect to increasing power intensity, using 5 seconds of sonication time, also held true with other frequencies (205 kHz and 354 kHz).

Kobayashi et al. [50] found that with increased power intensity into the system (2.5-3.4 W cm⁻²) there was an increase in the permeate flux of dextran solution in their cross-flow system for the two lower frequencies used (28 and 45 kHz), but there was no effect in the higher frequency, 100 kHz, system. They attributed this to fewer cavitation bubbles occurring with the higher frequency unit compared to the lower frequency units. Our results show a similar trend of increased flux with increasing power intensity, although improvement in flux was obtained for all frequencies tested. Differences in improvement between this study and that of Kobayashi et al. may be attributed to
operational differences between the two systems. For example, Kobayashi et al. used a pressurized membrane cell and subjected the membrane and housing to ultrasound in an ultrasonic bath. In addition, polymeric membranes were used in their study. Although several differences between the two systems were observed, generally, increasing power intensity results in greater cleaning of the membranes.

Increasing the power intensity to the system increases the number of cavitation bubbles formed [72] and increases the size of the cavitating zone [65]. These increases are attributed to the higher pressure amplitude of the sound wave with increased power intensity. Hydrodynamic turbulence also increases with increased power intensity resulting from increased intensity of the implosion of bubbles, increased numbers of bubbles that are able to collapse and increased absorption of acoustic energy by the medium [24]. Our results showing increasing cleaned flux ratios and fewer remaining particles on the surface with increasing power intensity suggest that with increasing power intensity, the greater number of cavitation bubbles, the increased turbulence and the larger zone of cavitation are able to better clean the membranes than the lower power intensities.

In Fig. 2.5, experiments at five different frequencies (at a constant power intensity of 0.21 W cm$^{-2}$ and a treatment time of 5 seconds) show a trend of increasing cleaned flux ratio with decreasing frequency. A full recovery in flux was observed for all frequencies (except 1062 kHz) when ultrasonic treatment times exceeded 30 seconds and power intensities were greater than 1.05 W cm$^{-2}$. The inset of Fig. 2.5 shows complete recovery after 60 seconds at 620 kHz with a power intensity of 0.42 W cm$^{-2}$. Flux
recoveries occurred on increasingly shorter time scales as the frequency decreased or power intensity increased.

Kobayashi et al. [50] also looked at the effect of frequency on the permeate flux of a dextran solution in a cross-flow membrane. They found that with decreasing frequency (100-28 kHz) there was an increase in permeate flux. Again, there was no effect on the permeate flux for the highest frequency used. This trend agrees with our findings although membranes were cleaned effectively using frequencies higher than those used by Kobayashi et al. [50].

Altering the frequency of ultrasound input to a medium changes both the wave interactions with the fluid and the characteristics of the cavitation bubbles formed. For example, at higher frequency, sound is attenuated more readily [73]. Therefore acoustic energy may not be available for cleaning throughout the system. Also, the maximum size bubbles attain is smaller than with lower frequencies. However, there are more collapses per time, although the bubbles tend to collapse less violently producing lower temperatures and pressures [74,75]. Because our results demonstrating better cleaned flux ratios for lower frequencies suggests that cleaning depends more on the characteristics of bubble collapse, the intense shear forces involved with bubble oscillations or some non-cavitation mechanism than on the number of cavitation bubbles collapsing per time. The violence of the collapses at lower frequencies and the turbulence accompanying it appear to be more important in cleaning than increased numbers of weaker collapses observed at higher frequencies.

Researchers have observed that at low frequency, mechanical forces (i.e., shear stresses due to cavitation) are predominant mechanisms for the breakdown of polyvinyl
alcohol, while at higher frequencies radical formation causes the break down of these polymeric compounds [76]. This observation is consistent with the theory that mechanical forces predominate at lower frequencies and contribute significantly to the cleaning of membrane surfaces.

2.4.3 Elucidation of Mechanism

The dependence of cleaning on power intensity and frequency shown in Fig. 2.4 and Fig. 2.5, provides insight into some of the possible removal mechanisms. As mentioned above, with increasing power intensity, there is an increase in the number of cavitation events and an increase in the zone where cavitation bubbles form. In Fig. 2.1, three of the four mechanisms (i.e., microstreamers, micro-jets, and microstreaming) depend directly on cavitation, while acoustic streaming depends on absorption of acoustic energy by the liquid medium. We expect both cavitating and non-cavitating mechanisms to increase their effects with increasing power intensity.

In control experiments, hydraulic turbulence generated from a propeller mixer, was introduced to the system in the absence of ultrasound. The fluid velocity as a result of mixing was visually observed (by tracking the distance particles traveled with respect to time) to be approximately 10 cm/sec. In the mixer system, no significant recovery in flux was observed after hydraulic cleaning. The surface of the hydraulically-cleaned membrane was completely coated with latex particles and no visible changes were observed compared to fouled membranes using SEM.

The hydraulic generated velocity was comparable to acoustic streaming observed by Starritt et al. [77]. Starritt et al. was using a higher frequency (3 MHz vs. 70-1062 kHz) and higher power intensity (122 W cm\(^{-2}\) vs. 0.21-2.1 W cm\(^{-2}\)) than the system used
here; therefore, the velocity in our study was expected to be lower due to the comparatively lower frequency and lower power intensity resulting in less acoustic streaming. However, Starritt et al. velocities are smaller than velocities used in most cross-flow membrane systems which are on the order of m s\(^{-1}\) [78,79]. This lower velocity would indicate that acoustic streaming may not be able to remove particles from the membrane surface in the same manner as a cross-flow membrane system. Because the velocity produced by the mixer was similar to or greater than that produced by acoustic streaming, we suspect that acoustic streaming is not an important factor in detaching particles from the surface.

To evaluate whether turbulent flow generated by acoustic streaming could aid in the transport of particles from the surface, we compared the difference in cleaning fouled membrane surfaces facing toward the transducer (Panel B, Fig. 2.2) and facing away (Panel C, Fig 2.2) from the transducer. In both cases highly acoustically transmissive Mylar\textsuperscript{®} support [70] was placed directly beneath the membrane (i.e., on the side opposite to the fouled surface) eliminating flow through the membrane while allowing acoustic energy from the transducer to pass through the membrane (Panel C, Fig. 2.2). In both experiments, the fouled surface was the same distance away from the transducer. By using Mylar\textsuperscript{®} sheets as a barrier between the transducer and the fouled surface (Panel C, Fig. 2.2), acoustic streaming generated turbulence was minimized near the membrane surface, confining turbulence to the region between the Mylar\textsuperscript{®} sheet and the transducer. Hence, cavitation mechanisms remained in both cases but acoustic streaming generated turbulence was minimized with the fouled membrane surface facing away from the source of the ultrasound.
Fig. 2.6 shows that cleaning was more effective when the fouled surface was facing the transducer, and the power intensity was high, or the treatment times were longer. Under condition (A) in Fig. 2.6, with the membrane facing away from the transducer, the system had a cleaned flux ratio of 0.78. When the fouled surface faced the transducer, the cleaned flux ratio increased to 0.94 for the same power intensity. The difference in the cleaned flux ratio with membrane orientation decreased with increasing power intensity and decreasing frequency of the system. This result indicates that acoustic streaming is an aid to cleaning the membranes (at least at low power intensity and short treatment times), but is likely not an important detachment mechanism. Acoustic streaming may remove detached particles from the vicinity of the membrane surface that attenuate acoustic energy and inhibit cavitation related detachment mechanisms.

As further evidence of effects of acoustic streaming on particle removal, SEM was performed on the fouled surface of the membrane after ultrasonic cleaning. From Fig. 2.7, SEM images of the fouled surfaces after cleaning showed that when the fouled surface was facing away from the transducer, the membrane surface remained heavily coated with particles (panel A). Panel B is an image of the same membrane using a lower magnification showing that there are still clusters of particles on the membrane. When the fouled surface was facing the transducer, there were exposed membrane surfaces with few particles (panel C). Panel D is an image of the same membrane showing that there are still clusters of particles on the surface but more removal occurred on the adjacent exposed areas. At higher power intensities (> 1.05 W cm\(^{-2}\)), and lower frequencies (<205 kHz) images of fouled membrane surfaces facing toward and away from the transducer
showed no differences in the number of particles still attached to the surface by SEM and gravimetric analysis with only a few particles still remaining on each membrane surface. Thus SEM images and gravimetric analyses support cleaned flux ratio observations suggesting that acoustic streaming aids in removal of detached particles from the membrane surface. The depressions that appear on the left edge of the SEM images (Fig. 2.7, panels B and D) are bare membrane surfaces that were covered by a seal during filtration and are not a result of ultrasonic cleaning.

2.4.4 Surface Formations as a Result of Ultrasound

Longer ultrasonic cleaning treatment times (greater than 5 seconds) cleaned the membrane surface significantly, as observed by flux measurements and by SEM, under a variety of frequencies and power intensities; thus, experiments to investigate the mechanisms of removal were done under sub-optimal conditions for particle removal (i.e., irradiation times of five seconds with the fouled surface facing away from the transducer). The cavitation mechanisms affecting cleaning are expected to remain the same although there will be less acoustic streaming because of the Mylar® barrier. These conditions allowed for visualization of the initial stages of particle removal from the surface to be observed using SEM.

SEM images were taken of all of the samples tested; several similarities among the membranes were discovered. Three major types of formations appeared on all but a few membranes regardless of frequency, power intensity, or time of treatment. The first type of formation was an indentation, appearing as a round deep impression on the surface of the cake layer (Fig. 2.8). The indentations did not appear to disturb the latex particles directly adjacent to the formation. The average diameter of these cavities was 18
± 6 µm and was independent of frequency and power intensity. The number of indentations varied from sample to sample and no trend was established among different frequencies and power intensities. The indentations were similar in shape and size to damage caused by micro-jets on metal surfaces [80].

The second type of formation commonly observed was a circular patch of removal with an average diameter of 2.30 ± 0.7 mm at 620 kHz (see panels A and C, Fig. 2.9). From visual examination of the cleaning vessel during treatment, this patch appeared rapidly as ultrasound began with the number of patches increasing with time until finally, the entire surface was void of latex particle cake formations. This type of formation appeared to be the main source of particle removal based on the area of the formations.

On the edges of these circular patches of removed particles were channels as long as a millimeter in length, but only several micrometers wide, where particles appear to have been scoured. These channels are seen on panels B and D, Fig. 2.9. All circular patches of removal had channels on the perimeter, although channels also were found in isolated regions. These formations may be due to microstreaming caused by localized high fluid velocities near the fouled surface-cavitation bubble interface as the bubbles oscillate. Another possibility, however, is that these channels were formed as bubbles traveled along the surface scouring particles while they moved towards an antinode. These microstreamers have been observed by researchers investigating bubble dynamics in an ultrasonic field viewed with a high speed camera [24,81]. They found that bubbles moved in paths similar to the channels we observed on the particle-fouled membranes, and the bubbles tended to merge with one another and ended up at an antinode. If these
channels were coupled with the general turbulence associated with an ultrasonic field (acoustic streaming, micro-jets and microstreaming) this may lead to further erosion of the fouling layer.

The SEM images taken of membranes used to generate Figs. 2.4 and 2.5 support the concept that power intensity and frequency affect particle removal. With increasing power intensity and decreasing frequency, there was increased removal of millimeter-scale patches of particles from the membrane. For example, at 620 kHz, 0.21 W cm\(^{-2}\), and 5 seconds of treatment the cleaned flux ratio was 0.63. This ratio resulted in approximately 48 patches of removal (on the entire membrane surface) with an average patch diameter of 1.94 mm. However at 205 kHz, 0.21 W cm\(^{-2}\), and 5 seconds of treatment the cleaned flux ratio was 0.87, with approximately 15 patches of removal (on the entire membrane) with an average size of 4.02 mm. The ratio of total area of particle removal at the two frequencies (area of removal at 620 kHz / area of removal at 205 kHz = 0.74), correlates well with the ratio of the cleaned flux ratios (J at 620 kHz / J at 205 kHz = 0.73). The SEM images, along with the inset in Fig. 2.5, also support that removal occurs in stages. With increasing time, increased numbers of cavitation events take place that further erode particles from the surface and expose more membrane surface. This effect is observed with increased J/J\(_o\) with longer treatment times and correspondingly more patches of removal as imaged with SEM.

The SEM images, along with power intensity and frequency experiments, allow general conclusions to be made about what mechanisms play a role in ultrasonic cleaning of membranes. Microstreamers are likely to be the major mechanism for detaching particles from the membrane surface based on SEM images revealing circular patches of
removal with channeling. Microstreaming may play a role in the cleaning or work in conjunction with other mechanisms such as microstreamers to clean the membrane surface. Micro-jets, although present, appear at isolated sites and do not greatly enhance the removal of particles from the membrane surface. Acoustic streaming enhances ultrasonic cleaning, but is not capable of cleaning without other cavitation-based mechanisms present. The contribution of vibrations to the surface cleaning was discounted because with vibrations, we would expect evenly distributed removal instead of the patch and channel removal that was observed. It is possible that shock waves play a role in the removal of particles from a membrane surface, but they would be the subject of a future study.

2.4.5 Membrane Integrity upon Exposure to Ultrasound

Although Masselin et al. found significant damage to polymeric membranes as a result of ultrasound [57], our studies found no evidence of damage to the membranes using extensive SEM images of membrane surfaces and measurements of aluminum concentrations in the cavitating solutions. Also, there were no increases in flux of unfouled membranes as a result of ultrasound. SEM images taken throughout the trials never showed evidence of any damage to the membrane surface. Aluminum concentrations in the sonication solution were measured for each sample. The level never exceeded blank concentrations. Resistance of the membrane material to high temperatures and pressures or the short treatment times used for cleaning are potential reasons for the lack of damage in our study. For example, ultrasound-damaged membranes observed in other studies were less temperature resistant polymeric membranes [57]. In addition, the frequency used in those studies was lower than that used
in these experiments, thus more prone to cause surface damage. To determine if lower frequencies or longer treatment times result in damage to the membranes, clean membranes were subjected to lower frequency ultrasound (20 kHz) for periods of over an hour. No damage to the membrane was found by quantifiable aluminum in solution (< 1 µg L⁻¹) or surface damage investigated by SEM.

### 2.5 CONCLUSIONS

This research has shown that ceramic membranes may be effectively cleaned using ultrasound at frequencies from 70 kHz up to 620 kHz without damage to the membranes. Increases in power intensity of the system increased the cleaned flux ratio. This increase was attributed to an increase in the number of cavitation bubbles in the system and an increase in acoustic energy in the system. Lower frequencies had higher cleaning efficiencies than higher frequencies. Although higher frequencies may have more cavitation bubbles collapsing with time, they are smaller in size and collapse less energetically; thus, they may not be capable of detaching particles from the cake layer as readily as lower frequencies.

The mechanisms of removing a cake layer from the surface of a membrane are attributed to two factors: 1) detachment or loosening of any particles from the surface by cavitation mechanisms (i.e., microstreamers), and 2) transport away from the surface by acoustic streaming. Acoustic streaming alone did not have a significant affect on cleaning. Microstreaming may also play a role in cleaning membrane surfaces, however, no direct evidence for microstreaming was observed. Other cavitation mechanisms such as micro-jets did not appear to significantly remove particles from fouled membranes,
although evidence of micro-jets was visible in SEM images of the fouled surfaces. Shock waves were not investigated in detail but also may contribute to the detachment of particles from the surface.
Figure 2.1. Possible mechanisms for particle removal / detachment observed with ultrasonic cleaning.
Figure 2.2. A) Ultrasonic reactor chamber and transducer. The membrane support stand sits in the glass vessel surrounded by a cooling jacket. The support stand is a ring of stainless steel to hold the membrane and the Mylar® with three prongs holding it to the stand, allowing the Mylar® sheets and the membrane to be held without interfering with cleaning. B) and C) Membrane support stand with the membrane sandwiched between several sheets of Mylar® with the fouled surface of the membrane facing the transducer (B) or facing away from the transducer (C).
Figure 2.3. Flux of solution during fouling using sulfate latex particles at pH = 7.0, [KCl] = 1mM, and [latex particles] =10 mg L⁻¹.
Figure 2.4. Cleaned flux ratio of different power intensities using ultrasound at 620 kHz and 5 seconds of treatment (Δ). Latex particles remaining (%) on the surface of the membranes (○).
Figure 2.5. Cleaned flux ratio of ultrasound at different frequencies using a power intensity of 0.21 W cm$^{-2}$ and a treatment time of 5 seconds. Inset: Cleaned flux ratio of fouled membranes cleaned for different treatment times at 620 kHz, and 0.42 W cm$^{-2}$. 
Figure 2.6. Cleaned flux ratio of fouled membranes under various conditions. A) 620 kHz, 0.42 W cm\(^{-2}\), 5 sec treatment; B) 620 kHz, 2.1 W cm\(^{-2}\), 5 sec treatment; C) 620 kHz, 2.1 W cm\(^{-2}\), 30 sec treatment; and D) 205 kHz, 0.42 W cm\(^{-2}\), 30 sec treatment.
Figure 2.7. Effect of ultrasonically-induced turbulence on the removal of particles from the membrane surface; (A) and (B) are SEM images at different magnifications of the same membrane when treated with ultrasound at 620 kHz, with a power intensity of 0.21 W cm$^{-2}$ for 5 sec with the fouled surface facing away from the transducer; (C) and (D) are SEM images at different magnifications of the same membrane treated at 620 kHz, 0.21 W cm$^{-2}$ for 5 sec with fouled surface facing the transducer.
Figure 2.8. SEM images showing evidence of micro-jet impacts on the surface of the cake layer. Left: 1062 kHz for 5 sec, 0.21 W cm\(^{-2}\). Right: 620 kHz for 5 sec, 0.12 W cm\(^{-2}\).
Figure 2.9. SEM images of circular patches of cake layer removal and channel-like formations along the edges of the circular patches that is attributed to microstreaming / microstreamers; (A) 620 kHz for 5 sec, 0.21 W cm\(^2\); (B) 620 kHz for 5 sec, 0.12 W cm\(^2\); (C) 620 kHz for 5 sec, 0.42 W cm\(^2\); (D) 205 kHz for 5 sec, 0.21 W cm\(^2\).
CHAPTER 3

EFFECT OF SOLUTION CONDITIONS AND CAKE LAYER STRUCTURE ON THE ULTRASONIC CLEANING OF CERAMIC MEMBRANES

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3.1 Abstract

Homogeneous ceramic membranes fouled by polystyrene latex particles at different pH values and ionic strengths were subjected to ultrasonic cleaning. Cleaning was more effective at high and low pH than at neutral pH. At low pH values, less repulsive particle-particle interactions caused particle removal to occur as millimeter-scale aggregates resulting in highly effective cleaning. At near-neutral pH, more repulsive particle-particle interactions caused detachment to occur as individual particles from the cake layer rather than as flocs, which was a slightly less effective cleaning mechanism. Ultrasonic cleaning of fouling layers formed at high ionic strength (> 0.3 M KCl) was less effective than cleaning at lower ionic strength (< 0.3 M KCl). High ionic strength caused particles to coagulate in solution and settle as flocs on the membrane surface forming a highly permeable fouling layer. This fouling layer was resistant to
ultrasound at sub-optimal cleaning conditions used in this study, perhaps due to aggregation likely occurring within a primary energy minimum. Membrane cleaning experiments performed with particles of varying size showed that particle size was less important than the surface charge characteristics of the particles. Particles that possessed the largest surface charge formed the thickest fouling layer, irrespective of particle size, and showed the greatest improvement in flux with ultrasonic cleaning.

3.2 Introduction

The use of ultrasound for membrane cleaning has been investigated by a number of researchers. These studies have shown that ultrasound can effectively clean fouled membranes and increase permeate flux through membranes [49,50,51,52,53,54,55,82]. Most of these systems used polymeric membranes, fouled with small organic molecules in which the membranes were subjected to ultrasound via an ultrasonic bath or other ultrasonic device.

Our previous work investigated mechanisms and ultrasonic factors affecting ultrasonic cleaning of ceramic, particle-fouled membranes [83]. We determined that cavitation played a significant role in detaching particles from membranes and disrupting aggregates, while hydrodynamic turbulence accompanying ultrasound transported particles away from the membrane surface. Of particular importance were microstreamers, or millimeter-scale phenomena with bubbles that were formed by cavitation and migrated along the membrane surface towards pressure antinodes, thereby effectively scouring particles from the surface. One aspect that was not addressed was the effect of fouling solution conditions during fouling and cleaning and the subsequent
alteration of the fouling cake layer structure. We suspect that changes in solution conditions (e.g., pH and ionic strength) and cake structure affect ultrasonic membrane cleaning.

Membrane fouling and cleaning are affected by changes in pH and ionic strength [88,92]. Changes in pH result in changes to the viscosity of the solution and changes to the particle-particle and particle-membrane interactions. Decreasing pH lowers the viscosity of the solution, causing an increase in permeate flux [90]. The zeta potentials of both particles and membranes change with pH and ionic strength as well. Higher ionic strength decreases the range of repulsive forces between particles and particles and the membrane surfaces [90]. Also, surface tension of the solution is affected by ionic strength. Changes in pH alter the surface charge of membranes and particles and therefore also influence particle-particle and particle-membrane electrostatic interactions.

The attachment of particles onto membranes and the formation of a cake layer are governed by the chemical characteristics of the solid-solution interface [84]. Ultrasound is also affected by solution conditions. Increased surface tension results in fewer cavitation bubbles formed, but increased violence of collapse [85]. It has also been shown that bubble coalescence is decreased with increasing ionic strength [86], which may diminish some of the ultrasonic mechanisms leading to membrane cleaning such as microstreamers [83]. Understanding these different factors will aid in the future design of ultrasonic membrane cleaning systems.
3.3 Methodology

Surfactant-free polystyrene latex particles with sulfate functional groups from Interfacial Dynamics Corporation (Portland, OR) were chosen to foul membranes. The particles are spherical and monodisperse. Three particle sizes were used for the experiments: 1.0 µm, 0.53 µm and 0.3 µm. The membranes used in these experiments were Anodisc™ γ-alumina (γ-Al₂O₃) ceramic membranes (25 mm diameter) manufactured by Whatman (NJ). This 60 µm thick homogeneous membrane has a 0.2 µm uniform pore size throughout the membrane. Water used for all experiments was from a Milli-Q (Millipore Corporation, Bedford, MA) water system.

3.3.1 Fouling Experiments

A detailed description of the system used for fouling of Anodisc™ membranes is given in Lamminen et al. [83]. Briefly, all membranes were fouled in a 10 mL stirred dead-end Amicon Ultra filtration (Bedford, MA) cell. Solution which had been ionic strength and pH-adjusted was fed from a Nalgene polypropylene 4 L mixing vessel into the filtration cell. The system was pressurized using ultra high purity nitrogen gas at a constant pressure of 0.7 atm (10 psig).

After initial flux measurements, the membrane was removed, inspected visually for defects, and placed back into the filtration cell. The latex particle solution was then passed through the membrane. The solution consisted of 10 mg L⁻¹ sulfate polystyrene latex particles suspended in Milli-Q water at a designated pH and ionic strength. The membrane was fouled until 550 mL of solution had passed through the membrane. Thus, each fouled surface had the same number of particles attached. The pH did not change over the course of the experiments.
3.3.2 Ultrasonic Cleaning Experiments

A detailed description of the ultrasonic cleaning system is given in Lamminen et al. [83]. The water jacketed cleaning vessel, ultrasonic generator and transducer were manufactured by L3 Communications Elac Nautik (Kiel, Germany). After fouling, the membrane was removed from the Amicon cell and clamped to a stainless-steel stand which was then placed into the glass cleaning vessel that was open to the atmosphere. The cleaning vessel was then filled with 500 mL of Milli-Q water adjusted to the same pH and ionic strength as during fouling. The stainless-steel stand holding the membrane was suspended 10.5 cm away from the transducer. Ultrasound was set at a frequency of 620 kHz, a power intensity of 0.21 W cm\(^{-2}\) and duration of 5 seconds for all experiments performed. Power intensity input into the solution was measured using calorimetry [71]. Due to the rapid nature of ultrasonic cleaning and near complete particle removal occurred for all treatments at optimal cleaning conditions, the runs were performed under sub-optimal cleaning conditions.

3.3.3 Analysis of Cleaning

After the membrane had been treated with ultrasound, the flux was measured using the filtration cell with pH-adjusted and ionic strength-adjusted solution without latex particles. The flux of the cleaned membrane was then compared to the initial flux measured without latex particles. The “cleaned flux ratio” was calculated as \(J/J_0\) where \(J\) is the flux of particle-free solution through the membrane following ultrasonic treatment and \(J_0\) is the flux of particle-free solution through the membrane prior to fouling with particles. Because the cleaned flux ratio is not able to distinguish between an experiment with little flux decline but poor ultrasonic cleaning, and an experiment with significant
flux decline and effective ultrasonic cleaning (i.e. both give cleaned flux ratios near 1.0), results are also presented as the cleaned flux/fouled flux ratio. The cleaned flux/fouled flux ratio was calculated as \( J/J_F \) where \( J_F \) is the flux at the end of the fouling run. This ratio is equal to one if there is no cleaning occurring and increases with increasing cleaning to a maximum of the initial clean water flux divided by the fouled flux. Following ultrasonic cleaning, membranes were air dried for two days and weighed. Using the mass difference before and after treatment, the amount of particles removed was estimated.

Membrane samples were prepared for scanning electron microscopy (SEM) by coating the surface with gold to a thickness of several hundred angstroms. A XL-30 FEG scanning electron microscope (Philips Electron Optics, Netherlands) was used for SEM analysis at voltages of 1-5V. The entire membrane was visible under the lowest magnification using SEM. Cross sections of several membranes were also examined by breaking fouled membranes in half and placing the membrane in an orientation so that it could be viewed by SEM. The entire thickness and diameter of the membrane could be viewed under SEM. The thickness of the membrane was given as 60 \( \mu \)m and used as a guide to the thickness of the fouling layers.

The zeta potentials of the latex particles at different pH values were determined from measurements using a ZetaPlus (Brookhaven Instruments Corp, Holtsville, NY). An electro kinetic analyzer (EKA) (Brookhaven Instruments Corp, Holtsville, NY) combined with a clamping cell was used to determine the zeta potential of the membrane at different pH values [87].
3.4 Results and Discussion

3.4.1 pH Effect on Cleaning

Figure 3.1 shows the ultrasonic cleaning of membranes fouled using 0.53 µm particles and 1 mM KCl at different pH values. The ultrasonic cleaning of the latex particles was found to be the most effective at either high or low pH values. For example, at pH 3.5 the cleaned flux ratio was 0.94 indicating that the water flux after cleaning was nearly the same as an unfouled surface. The ratio of the cleaned flux to the fouled flux at pH 3.5 was greater than 5.0 indicating that the water flux after cleaning increased more than 5 times compared to the flux before cleaning. At neutral pH, ultrasonic cleaning was not as effective with a cleaned flux ratio of 0.5. At high pH both the cleaned flux ratio and the cleaned flux/fouled flux ratio increased indicating that the improvement in membrane performance was due to cleaning and not less fouling or changes in specific resistance of the membrane.

The effectiveness of ultrasonic cleaning at different pH values is visualized with SEM images of the surfaces after cleaning shown in Figure 3.2. The lowest pH (panel A) resulted in the most particle-free surface; in contrast, neutral pH (panel B) had no exposed membrane surface. At the highest pH (panel C) there were areas of exposed membrane surface, but had more particles remaining after cleaning than at the lowest pH. These images are consistent with cleaning ratio trends observed in Figure 3.1.

The zeta potentials of the membrane and particles play a significant role in controlling membrane fouling [88], and therefore, affect the ultrasonic cleaning process. Zeta potentials of the membrane and the latex particles were measured as a function of pH at two ionic strengths are shown in Figure 3.3. The lines in Figure 3.3 represent fits to
the data obtained by performing a least squares analysis, and are shown to illustrate trends. The membrane (open and filled circles) is positively charged below pH=8.1 and negatively charged at higher pH values for both ionic strengths examined. These data are consistent with the range of values for the point of zero charge of γ-alumina reported by Kasprzyk-Hordern [89]. The latex particles were negatively charged for all pH values measured, slightly decreasing in magnitude with decreasing pH. Increasing ionic strength decreased the magnitude of the zeta potentials for both the membrane and particles.

Zeta potential data provide mechanistic insight into the role solution conditions play in ultrasonic cleaning. At the lowest pH investigated (3.5), the particles had the smallest magnitude zeta potential (least negative) while the membrane was highly positively charged. Therefore, particle-particle repulsive forces were lower than at higher pH values. As a result, greater force is required to remove individual particles from the cake layer. Visual observations made during ultrasonic cleaning at pH 3.5 showed large, millimeter-scale particle aggregates detaching from the membrane surface and the flocs slowly disaggregating in solution. The stronger particle-particle interactions at this low pH apparently facilitated patch removal of aggregates from the surface. This removal mechanism resulted in very effective membrane cleaning with a cleaned flux ratio of 0.94 and a cleaned flux which was more than 5 times greater than the fouled flux.

Ultrasonic cleaning was poorest at intermediate pH values. At pH values up to 8.1, the particles were increasingly negatively charged, while the membrane was less positively charged than at lower pH. As a result of the increased particle charge, more repulsive interparticle forces resulted in weaker particle-particle binding than at lower pH values. At these intermediate pH values, visual observations showed that individual
particles or very small aggregates were released during the cleaning process rather than large flocs. At pH 7.0, the cleaned flux ratio was only 0.60, and the cleaned flux was only about 3 times greater than the flux observed for the fouled membrane. At this pH, the attractive particle-membrane interactions prevent floc removal from the fouling layer, but the particle-particle interactions govern the release of particles from the fouling layer at intermediate pH values.

At the highest pH (9.5), the particles had a very strong negative charge and the membrane was also negatively charged at this pH. Therefore, particle-membrane interactions were repulsive. In this case, particles were more easily detached from the fouling surface in smaller clusters and the membrane was cleaned effectively. With a cleaned flux ratio of 0.72 and a cleaned flux 3.6 times greater than the fouled flux, the cleaning was not as complete as with the lowest pH. At the short cleaning times used in this study, large aggregate removal was more effective at cleaning than removal of individual particles. As a note, increasing the time of cleaning from 5 seconds to 5 minutes completely restored the initial flux for all of the pH values tested.

Several researchers have observed that membrane and particle interactions can affect membrane fouling and cleaning. Faibish et al. observed that membranes and particles of the same charge did not experience irreversible fouling due to strong electrostatic repulsive forces between the membrane and particles [90]. Martin et al. observed little fouling at pH values in a cross-flow system where both the membrane and the particles had the same charge [91]. Elzo et al., observed that at pH values where the membrane and particles were both negatively charged, the decreasing zeta potential
difference between the two required more hydrodynamic turbulence to remove particles from the surface than at pH values where the zeta potential difference was greater [92].

However, contrary to these studies, our findings suggest that regardless of membrane-particle interactions, particle-particle interactions largely determine how well the surface was cleaned by ultrasound. Unlike these previous studies, our research used a dead-end filtration cell to force the particle-laden solution through the membrane. Therefore, greater fouling under repulsive particle-particle and particle-membrane interactions was likely observed as compared to the cross-flow systems used in the studies cited above. Also, it was observed that with the majority of the cake layer removed, the remaining particles on the surface had little impact on the flux through the membrane. Therefore, particle-membrane interactions had little effect on flux recovery.

3.4.2 Ionic Strength Effect on Ultrasonic Cleaning

The effect of ionic strength, at constant pH (7.0), on ultrasonic cleaning was examined from 1 mM to 1 M potassium chloride. All membranes were fouled with 550 mL of 10 mg L⁻¹ latex particles. Figure 3.4 shows that there was an initial decrease in the cleaned flux ratio with increasing ionic strength, followed by a sharp increase at ionic strengths greater than 0.1 M. The improved cleaned flux ratio at low ionic strength is attributed to more effective cleaning. However, at high ionic strength the increase in cleaned flux ratio was not a result of increased ultrasonic cleaning, but rather little flux decline during membrane fouling at the higher salt concentrations.

Because the cleaned flux ratio did not show the true effect of ultrasonic cleaning on the fouling layer, comparing cleaned flux to fouled flux was used to quantify differences in the flux improvement at high ionic strengths (see Figure 3.5). At ionic
strengths greater than 0.2 M, the cleaned flux/fouled flux ratio was constant and close to 1.0 indicating no improvement in flux upon cleaning. Figure 3.5 demonstrates that little particle release from the membrane surface occurred at high ionic strength, as determined from the fraction of weight of particles remaining on the membrane surface. The ratio of the cleaned flux / fouled flux is reproduced in Figure 3.5 for comparison.

Figure 3.6 shows the SEM images of membranes fouled with 10 mg L^{-1} particles at 1 mM KCl (panel A), 0.1 M KCl (panel B) and 1 M KCl (panel C). The 1mM and 0.1 M ionic strength images show a well packed, ordered surface while the high ionic strength (1 M KCl) image shows dark areas which are openings in the fouling layer. The higher ionic strengths in our experiments exceeded the salt concentration above which the particles destabilized (0.3 M as stated by manufacturer). Therefore, at least some particles agglomerated in solution above the membrane with subsequent floc deposition onto the surface. This floc formation caused the fouling layer in the higher ionic strength system (1 M KCl) to be 2.5 times thicker (and less dense) than at lower ionic strengths (1 mM KCl), as determined by SEM cross sections.

Faibish et al. [90] found that with increasing ionic strength the cake thickness decreased and cake layer resistance increased. Also, a decrease in the interparticle distance within the cake layer with increasing ionic strength occurred [90]. All of their experiments were done at ionic strengths below which the particles flocculate. Hwang et al. found that coagulation of particles due to compression of the electric double layer resulted in high cake porosity and low specific filtration resistance of the cake layer [15]. Further, Elzo et al. observed that at higher ionic strength, more hydrodynamic turbulence was required to remove particles from surfaces than at low ionic strengths [92]. This was
attributed to compression of the double layer and less particle-particle repulsion at the higher ionic strengths.

The findings of these studies are generally consistent with our results. The initial decrease of cleaned flux ratio with increasing ionic strength is an indication of less repulsion among the particles. This in turn leads to a reduction in ultrasonic cleaning. A lack of flake removal at higher ionic strengths (as there is with low pH) may be because particles are strongly bound to one another at high ionic strength within a primary energy minimum. With low pH a flake may detach from neighboring particles because there are still repulsive forces between particles even though they may be weaker. At high ionic strength, the repulsive forces are significantly reduced; in order to have flake removal large forces are required to detach nearly the entire cake layer at once from the membrane. Ultrasonic cleaning mechanisms do not appear to be strong enough to overcome these particle-particle interactions. There may be an ionic strength at which flake removal is possible, but it was not observed in this study.

The reduction in ultrasonic cleaning with increased ionic strength also may be influenced by a reduction in cavitation activity. With increasing ionic strength there is an increase in the surface tension of solution. There is an increase of 1.8 dynes/cm in surface tension from pure water to 1 M KCl [86]. This increase in surface tension results in more energy needed to form cavitation bubbles. However, the resulting bubbles produce more erosive turbulence [93]. It has been demonstrated that these cavitation bubbles are largely responsible for the ultrasonic cleaning of the membranes [83]. Cavitation bubbles that are formed under higher ionic strength collapse more violently, and are expected to clean more effectively than bubbles formed at lower ionic strengths.
It has also been shown that cavitation bubbles do not coalesce as readily as ionic strength increases [94]. This decrease in coalescence reduces one of the significant contributors to ultrasonic cleaning, microstreamers. Microstreamers are bubbles that travel in solution and coalesce with other bubbles. They have the ability to scour the membrane surface and detach fouling materials. This mechanism was shown to contribute greatly to the cleaning of membranes in our previous work [83].

In order to determine if cleaning was dependent on changes in cavitational activity, experiments were performed with membranes fouled with high ionic strength solution (1 M KCl), but ultrasonically cleaned in Milli-Q water. To ensure that there were no structural changes in the fouling layer as a result of the Milli-Q water, membranes which had been fouled with particles at 1 M KCl, were removed from the fouling cell, soaked in Milli-Q water for 10 minutes and placed back into the cell to test fluxes with particle-free 1 M KCl solution. There was no change in the flux of the solution suggesting little alteration of the cake layer structure due to changing the solution to Milli-Q water. The fouled membrane which was cleaned in Milli-Q water was found to be resistant to ultrasonic cleaning. Cleaning in both the high ionic strength and Milli-Q water solutions resulted in cleaned flux / fouled flux ratios of around 1.0, indicating no significant cleaning. This result suggests that the reduction in cleaning was not a result of changes in cavitation with increasing ionic strength alone. The fouling layer, even when soaked in Milli-Q water may not have had all of the salt removed from the membrane structure. In the ultrasonic cleaning vessel, even though the ultrasonic activity may not have been reduced by the Milli-Q water, the fouling layer may have still behaved like as
if it were in a high ionic strength solution where the particles are very tightly bound to one another and therefore difficult to remove with ultrasound.

### 3.4.3 Particle Size Effect on the Ultrasonic Cleaning of Membranes

Particles of different sizes were used to determine their effect on ultrasonic cleaning. Particles of different size tend to create fouling layers of differing compositional structures [90]. These layers may influence ultrasonic removal due to the different packing densities, permeabilities and particle interactions.

Figure 3.7 shows the initial clean solution flux (first 10 minutes) followed by the flux during fouling using different sized particles at concentrations of 10 mg l\(^{-1}\). From Figure 3.7, the largest particle size (1.0 µm) fouling layer maintained higher permeate flux than smaller particle size (0.3 µm) fouling layers. The smallest particle size fouled the membrane the most and took the longest to filter 550 mL of solution. With respect to ultrasonic cleaning, the largest recovery in flux was seen with the medium sized particles (0.53 µm). Both the largest and smallest particles experienced very small increases in flux as a result of ultrasonic treatment.

Figure 3.8 shows the cross sections of fouling layers formed from different sized particles prior to ultrasonic cleaning. The cake layer is the block of material on the left hand side of each image. Using the membrane as a reference thickness of 60 µm, the thickness of each of the fouling layers was calculated from several different points along the fracture interface. The thickness was largest for the 0.53 µm particles (45 µm), followed by the 1.0 µm particles (38 µm) and then the smallest particles 0.3 µm (29 µm). All of the membranes had approximately the same mass of particles on the surface, which was verified gravimetrically. Thus, intermediate size particles (0.53 µm) had the
most porous cake layer structure, with larger (1.0 µm) and smaller (0.3 µm) particles having more dense cake layers.

Faibish et al. found that cake layer porosity and cake layer thickness increased with decreasing particle size, while permeability decreases [90]. They did find, however, that the permeate fluxes using their two smallest particles 47 nm and 110 nm maintained similar values for the same ionic strength while the largest particle size maintained the highest fluxes with little variation with ionic strength. Li et al. showed that in their cross flow membrane system, increasing the cross flow velocity led to a larger fraction of smaller sized particles remaining on the surface [16]. Larger particles were more easily removed by fluid movement.

Although medium particles (0.53 µm) in our study were not expected to have the thickest fouling layer, it may be due to these particles having the most negatively charged zeta potential (68 mV at pH = 5.5). Higher zeta potentials create a thicker, more porous fouling layer due to the increased particle-particle repulsion and larger interparticle distances [90,95]. Also, with highly charged particles, ultrasonic cleaning was faster because the particles readily detached from one another. The largest particles (1.0 µm) and the smallest particles (0.3 µm) both possessed zeta potentials that were similar (-36 mV for pH = 5.6 and -41 mV for pH =5.5 respectively), but lower than that of the medium sized particles (0.53 µm). The fouling layers that were formed by these particles were similar in thickness and showed little improvement with ultrasonic cleaning. This suggests that the zeta potentials of the particles was more important in determining the effectiveness of membrane cleaning than particle size.
3.5 Conclusions

This research has shown that ionic strength, pH and particle interactions have significant impacts on the ultrasonic cleaning of membranes. Ultrasonic cleaning was greatly affected by the pH of the solution, which is attributed to changes in particle-particle and particle-membrane interactions. Cleaning was most effective at low and high pH. Ultrasonic cleaning at higher ionic strength was not as effective as cleaning fouling layers formed at lower ionic strengths. High ionic strength caused particles to coagulate in solution and settle as flocs on the membrane surface. These flocs were resistant to ultrasonic cleaning as a result of their strong particle-particle and particle-membrane interactions. Particle size experiments showed that the zeta potentials of the particles were a significant factor for increased ultrasonic cleaning. The repulsive particle-particle interactions of the highly charged particles made for better removal than with lesser charged particles regardless of size.
Figure 3.1. Cleaned flux ratio of ultrasonically cleaned membranes (620 kHz, 0.21 W cm$^2$, 5 sec treatment) at different pH values.
Figure 3.2. SEM images of ultrasonically cleaned membranes at different pHs; (A) pH = 3.5; (B) pH = 7.0; (C) pH = 9.5.
Figure 3.3. Zeta Potentials of membrane and sulfate latex particles at 1 mM KCl and 100 mM KCl.
Figure 3.4. Cleaned flux ratio of ultrasonically cleaned (620 kHz, 0.21 W cm\(^{-2}\), 5 sec treatment) membranes at different ionic strengths at pH 7.0.
Figure 3.5. The fraction of the weight of particles remaining on the membrane surface and the ultrasonically cleaned flux / fouled flux at different ionic strengths at pH 7.0.
Figure 3.6. SEM images of fouling layers in which the membranes were fouled with particles; (A) 1 mM KCl fouling solution with 10 mg L\(^{-1}\) 0.53 mm latex particles; (B) 0.1 M KCl fouling solution with 10 mg L\(^{-1}\) 0.53 mm latex particles; (C) 1 M KCl fouling solution with 10 mg L\(^{-1}\) 0.53 mm latex particles.
Figure 3.7. Permeate flux of the membranes during initial particle free flux test followed by fouling with particles of sizes, 1.0 µm, 0.53 µm, and 0.3 µm, followed by ultrasonic cleaning at 620 kHz, 0.21 W cm$^{-2}$, and a duration of 5 seconds and then a particle free permeate flux test.
Figure 3.8. SEM cross sections of the fouling layers created by the different sized particles. (A) 0.3 μm, (B) 0.53 μm and (C) 1.0 μm.
CHAPTER 4

CLEANING OF PARTICLE-FOULED POLYMERIC MEMBRANES USING AN ULTRASONIC TRANSDUCER EMBEDDED IN A CROSS-FLOW FILTRATION CELL

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4.1 Abstract

Ultrasound was introduced into a cross-flow membrane cell using a Navy Type I lead zirconate titanate transducer embedded opposite the membrane surface. The transducer, only 4.1 mm in thickness, required minimal modification of the existing filtration cell. Hydrogen peroxide was detected in solution, indicating the transducer was capable of inducing cavitation. Increases in hydrogen peroxide concentration were observed with increasing applied voltages. Chemiluminescence, formed through reactions with radical species created during cavitation, showed that increased voltages applied to the transducer resulted in larger zones of cavitation. For all voltages tested, chemiluminescence measurements indicated that the surface of the membrane was within the zone of cavitation. Membrane cleaning results showed that the thin transducer system was able to increase permeate flux of the membrane with flux increasing with increasing
applied voltage to the transducer. Both pulsed and continuous operation of the transducer improved flux (with continuous operation experiencing slightly more improvement), although it may be beneficial to operate the system in pulsed mode for energy savings purposes. With operation at the highest voltages, some evidence of damage to the membrane was observed. At lower applied voltages no damage to the membrane was found.

4.2 Introduction

Membrane filtration is widely accepted as a treatment technology and will approach $6 billion in US sales by the year 2006 [96]. Many industrial processes that rely on purification are switching to membrane filtration because of the versatility that membranes provide and because membranes are able to produce a consistent end product. The main drawback of membranes is fouling which results in a reduction in permeate flux. There has been a significant amount of research done on fouling and alleviation of fouling [97,98,99,100]. Decreased productivity as a result of fouling requires that a membrane be cleaned using hydraulic, chemical, mechanical or other treatments. Although these techniques are sometimes able to restore membrane fluxes, they have drawbacks. For example, these treatments require that the membrane process be stopped or may require the purchase of additional equipment or chemicals, decreasing productivity and increasing costs.

Ultrasonic cleaning has been used for many different components from dental instruments [101] to pickling of steel strip [29]. Ultrasonic cleaning generally uses a frequency in the range of 16 – 70 kHz. Frequencies on the order of 400-1000 kHz have
been used very successfully in the silicon wafer industry to clean microscopic particles from wafer surfaces without damaging the surface of the wafer [102,103]. With higher frequency cleaning, acoustic streaming (a large scale movement of solution), plays a significant role in particle removal. With ultrasonic cleaning, extremely violent cavitation events such as shock waves, microstreamers, microstreaming and micro-jets play significant roles in the removal of particles from a surface [83]. However, there is well-documented evidence as to the damage that cavitation can cause to metals, organic compounds and other surfaces [104,105,106]. With higher ultrasonic frequencies, cavitation occurs but the collapses are less violent than that with lower ultrasonic frequencies [107,77]. Therefore, cleaning in the high frequency range may be less damaging.

Several researchers have looked at ultrasonic cleaning to reduce fouling or clean fouled membranes. Kobayshi and Chai et al. [49,50,51,52] submerged a membrane module into an ultrasonic bath. They found increased fluxes and overall improved performance of the membrane system with ultrasound. Other groups have also seen improvements in membrane system performance as a result of ultrasound, including membrane distillation systems with an ultrasonic probe attached to the outside of the module [54] and treating fouled membranes in a water bath with an attached ultrasonic probe [55]. Our previous research has focused on understanding the mechanisms that are important for ultrasonic cleaning [83] and observing the effects of solution conditions and particle size on ultrasonic cleaning [108]. A remaining obstacle to the scale-up and application of this technology is the difficulty in introducing ultrasound into membrane systems without making extensive modifications to existing systems. It would be
desirable to have an ultrasonic system inside a standard membrane module or to have the membrane housing made out of a transducer material. However, currently existing ultrasonic systems are bulky and not easily introduced into standard membrane modules.

In this study, a thin transducer system was developed that could be incorporated into a standard laboratory cross-flow flat sheet membrane system. This transducer was tested outside of the cross-flow system for its ability to produce cavitation and clean fouled membranes. Also, the transducer was placed into the cross-flow membrane cell to test its ability to clean the cross-flow membrane and improve flux. The potential for ultrasound to damage the membranes was assessed directly by imaging the membranes using scanning electron microscopy (SEM).

4.3 Methodology

_Ultrasonic transducer system_

The piezoelectric element was manufactured for this system by Ferroperm Piezoceramics A/S (Kvistgard, Denmark). It is disk shaped and has a diameter of 38 mm and a thickness of 4.1 mm. It was made from a Navy Type I hard lead zirconate titanate (PZT) material and has a silver ink coating on the top and bottom surfaces (Figure 4.1). To keep the transducer as thin as possible, no additional coupling layers were added onto the disk. The thickness can be seen in Figure 4.1 panel B. Electrical connections were made to the top and bottom surfaces using conductive copper tape, onto which wires were soldered. To avoid excess heat caused by single point connections, the copper tape was placed around the perimeter of the top and bottom surfaces of the disk to maximize contact with the surface. The copper tape around the edge of the transducer is seen on
Figure 4.1 panel C. Wire connections were made to both the top and bottom surface of the transducer as shown in Figure 4.1 panel D. The disk was then placed into an external ultrasonic cleaning cell or into a cross-flow membrane cell as shown in Figure 4.2. Wiring to the amplifier exits the cell in the rear of the membrane module. The driving voltage was applied to the surface of the disk and insulated using a silicone sealant to prevent short circuiting during operation. The other surface of the transducer was left exposed and connected to ground. This surface was in direct contact with water in the cross-flow cell.

Different frequencies were applied to the disk using an AG 1021 linear amplifier (T & C Power Conversion, Rochester, New York). The amplifier was used to generate a continuous output to the transducer. A SM-1020 Function/Pulse generator (Signametrics, Seattle, Washington) was used to modify the amplifier output to pulses when desired. At the resonance frequency the disk will experience maximum displacement resulting in the greatest amplitude of the acoustic wave; thus, all experiments were run at the resonance frequency. To determine the resonance frequency of the disk, the disk was placed into an open vessel containing 1 mM KCl solution. A Hewlett Packard 54501A 100 MHz digitizing oscilloscope was used to measure the output of the amplifier which was sent to the transducer. The signal to the oscilloscope increased as the frequency approached the resonance frequency of the disk. The resonance frequency was determined as the frequency that resulted in the maximum output voltage from the amplifier. Using the oscilloscope, the resonance frequency was determined to be 476 kHz.
Batch Ultrasonic Cleaning of Membranes

Initial experiments focused on using the transducer system to clean membranes in a separate, external cleaning vessel. Two types of membranes were used in these experiments. 25 mm diameter membrane disks were cut from larger polyvinylidene difluoride (PVDF) membranes from Osmonics (GE Water, Minnetonka, MN) with a pore size around 0.3 µm. 25 mm Anodisc™ γ-alumina ceramic membranes were obtained from Whatman (Clifton, NJ) with a 0.2 µm pore size. To begin an experiment, particle-free water at pH 6.0 with 1 mM KCl was passed through the membranes at 0.7 atm (10 psig) in an Amicon Ultra Filtration 10 mL dead-end cell (Bedford, MA) until the flux stabilized. The membranes were then fouled using 10 mg L⁻¹ 0.53 µm sulfate polystyrene latex particles from Interfacial Dynamics Corporation (Portland, OR) until 550 mL of solution passed through the membrane. Next, the membrane was removed from the filtration cell and cleaned in the 2 L batch external ultrasonic cleaning vessel shown in Figure 4.4. The membrane was held in place using a stainless steel stand that was suspended above the transducer in 400 mL of 1 mM KCl solution with the fouled membrane surface 3 mm away from the transducer surface. Following ultrasonic cleaning, the membrane was removed from the cleaning vessel and placed back into the dead-end filtration cell. The stable flux was measured again using 1 mM KCl solution fed at 0.7 atm (10 psig) to determine the efficiency of cleaning.

Cross-Flow Cell PVDF membranes

All of the cross-flow experiments were performed in an Osmonics (GEwater, Minnetonka, MN) SEPA CF flat sheet test cell shown in Figure 4.4. Because ceramic membranes were not available for this system, all cross-flow experiments were
performed with Osmonics PVDF membranes with a pore size around 0.3 μm and an effective surface area of 155 cm². There is a low foulant spacer on the feed side of the membrane which has a thickness of 0.86 mm and a permeate carrier on the permeate side of the system. The cell was fed by a peristaltic pump (Fisher Scientific, Pittsburgh, PA) at a constant pressure of 0.7 atm (10 psig). The flux though the membrane was allowed to stabilize with 1 mM KCl, pH 6.0 solution for three hours prior to testing. One hour of measurements were then made with the same solution to determine the initial flux. The solution was then dosed with 10 mg L⁻¹ of sulfate latex particles with a diameter of 0.53 μm and run for either two or four hours depending on the experiment. Ultrasound was used during the fouling experiments and in some cases only at the end of the fouling run. The temperature of the feed solution did not change during the course of an experiment.

In the cross-flow membrane cell, the transducer was placed adjacent to the membrane surface in the channel, which was deepened by 5 mm to accommodate the transducer. Styrofoam and silicone sealant were used around the transducer disk to make the surface as flat as possible. Wiring to the disk ran through a port in the cross-flow membrane cell that was sealed with silicon sealant. The amplifier was then connected to the transducer to supply different driving voltages. The PVDF membrane surface was coated with a 300 μm film of silicone sealant in all areas of the membrane except the area directly opposite the transducer to prevent flow from passing through the membrane. Lack of fouling on coated sections of the membrane was verified by filtration of dyed latex particles to visually observe fouling and images of the coated and uncoated membrane can be seen in Figure 4.3.
**Hydrogen Peroxide Measurement**

Hydrogen peroxide was measured in solution to assess if cavitation was produced by the thin transducer system. Experiments were performed in a 1 L beaker filled with 250 mL of Milli Q water. Samples were taken every 5 minutes for 30 minutes. Determination of hydrogen peroxide was done using the triiodide technique [109]. Potassium iodide, sodium hydroxide, ammonium molybdate tetrahydrate, and potassium hydrogen phthalate were all reagent grade and obtained from Fisher Scientific (Pittsburgh, PA). Absorbance measurements were done using a UV–VIS 2401PC double beam spectrophotometer (Shimadzu Corporation, Columbia, MD) at a wavelength of 351 nm.

**Luminescence**

Chemiluminescence was used to directly image the zone of cavitation near the transducer. Chemiluminescence experiments were performed in a dark room using a 2 L beaker filled with 400 mL of $10^{-3}$ M luminol (3-aminophthalhydrazine, 97% Fisher Scientific Pittsburgh, PA) at pH 12.0. Different voltages were applied to the transducer and images were taken of the resulting luminescence. The luminescence was imaged using a 35 mm Minolta Maxxum camera situated 12 inches away from the beaker, using an aperture of 1.7 and exposure times from 1 second to 30 seconds. Fujicolor Superia 1600 high-speed color film was used for all experiments.

**Imaging of Membranes**

Scanning electron microscopy (SEM) was performed using an XL30 FEG ESEM by Philips Electron Optics (Netherlands). Samples were air dried for at least 3 days prior to sputter coating with gold. A plasma current of 15 mA was used with a total coating
time of 100 seconds. SEM images were taken of all of the membranes following treatment. The entire membrane surface was imaged where possible and cut into pieces when it was too large. In all cases, the entire membrane surface was visualized using SEM.

4.4 Results and Discussion

Characterization of the Ultrasonic Transducer System

The constructed ultrasonic transducer system was initially characterized for cavitation formation by measuring hydrogen peroxide and imaging the cavitation zone using chemiluminescence. With increasing applied voltage, there was a clear increase in the amount of hydrogen peroxide produced by the transducer in the batch external reactor. Figure 4.5 shows the formation rate of hydrogen peroxide produced for 30 minutes of continuous transducer operation at different voltages. Hydrogen peroxide is an indicator of cavitation [110]. Cavitation has been shown to be a major mechanism leading to the cleaning of particle-fouled membranes [83]. The rate of hydrogen peroxide production measured in this study was similar to that produced by Petrier et al. [111] in which they utilized a 2 cm diameter PZT transducer system at 514 kHz. The system examined by Petrier et al. produced 0.234 μmoles/min while we were able to produce 0.359 μmoles/min with a larger transducer at our highest applied voltage (16 V).

Figure 4.6 shows the chemiluminescence produced by the transducer system in a batch reactor at a range of voltages: (A) 10 V, (B) 14 V, (C) 22 V, and (D) 30 V. Luminescence was detected for the entire range of applied voltages used. A clear distinction between the different applied voltages was observed at an exposure time of 1
second. A comparison of the different images shows that the cavitational activity generating luminescence reached distances greater than 2 cm from the transducer for the second highest voltage applied to the transducer (16 V). For the lower voltages, the distances at which luminescence was observed from the transducer were smaller. The extension of cavitation observed by luminescence compared to the dimensions of the cross-flow membrane filtration cell indicates that for all of the applied voltages, the membrane is situated within the cavitation zone. It is clear that cavitation was produced by the transducer in aqueous solution; however, because cavitation may damage the membrane, different driving voltages were tested in the membrane module.

*Batch External Cleaning of Ceramic Membranes*

In initial experiments, ceramic membranes fouled using the dead-end filtration cell were cleaned using the constructed transducer system in a batch cleaning cell. The transducer was tested at two voltages: 24 V and 30 V. The cleaned flux ratios (ultrasonically cleaned flux / initial clean water flux) at both applied voltages were high: 0.93 at 24 V and 0.97 at 30 V. From SEM images of Figure 4.7, we observed that the membrane was fully coated with particles prior to cleaning. Only a thin layer of particles remained after cleaning with ultrasound at 24 V. No particles remained with cleaning at 30 V. No visible damage to the membrane was observed with the lower voltage (24V); however, damage was apparent in the form of pits at the higher voltage (30V). This suggests that the potential for damage exists with high driving voltages, however, the potential for membrane damage at lower voltages is decreased where no damage was observed.
Batch External Ultrasonic Cleaning of PVDF membranes

PVDF membranes were also fouled in the dead-end filtration cell, cleaned using the batch ultrasonic cleaning vessel, and then placed back into the dead-end cell to measure the ultrasonically cleaned flux. As shown in Figure 4.8, an increase in cleaned flux ratio was observed with increasing voltage. After the driving voltage exceeded 18V however, the flux became higher than the initial flux. This same trend of increasing cleaned flux ratio with increasing voltage was also observed with pulsed ultrasonic treatment, (1 second on and 1 second off) although the cleaned flux ratio was lower compared to continuous ultrasonic operation. This reduction in cleaning is expected since half of the energy is used compared to continuous ultrasound. The increase in cleaned flux above the initial flux is an indication of damage to the membrane. The inset in Figure 4.8 is a SEM image showing possible ultrasound-induced damage to the membrane surface at the highest applied voltage (22V). For all experiments carried out, damage to the membranes was not observed for voltages less than 14 V.

Ultrasonic Cross-Flow Membrane Cleaning System

The ultrasonic cross-flow membrane cleaning system was tested in two ways. First, the membrane was fouled with sulfate latex particles, and subsequently, ultrasound was applied at different voltages with particle-laden solution continuing as the feed solution through the system. The flux was measured for each of the different applied voltages (Figure 4.9). The final flux / clean water flux was determined after 10 minutes of applied ultrasound. Figure 4.9 shows that the ultrasonic transducer system improved the flux of the particle-fouled membrane. With increased applied voltage there was an increase in the ratio of the final flux / clean water flux. For each applied voltage, the
improvement in flux occurred in less than 2 minutes and the flux remained stable during the entire measurement period of 10 minutes. Above 12 V, the flux increase exceeded the initial flux of the system. The inset SEM image of the membrane surface at the highest voltage (14 V) shows damage caused as a result of ultrasound. It should be noted that the membrane was initially completely coated with particles but ultrasound still caused damage to the membrane because it quickly removed the fouling layer. These data indicate that at higher voltages, treatment times should be kept short to just remove the fouling layer but not damage the membrane. SEM images at other voltages indicated no damage to the membranes at voltages less than 12 V.

Because the system may be prone to damage with voltages above 14 V with treatment times on the order of minutes, a pulsed system may be desirable. During cleaning, the membrane is expected to have at least a thin layer of particles or other fouling material on the surface. By keeping the ultrasonic treatment time short and maintaining a thin layer of particles on the surface, the time over which the bare membrane surface would be exposed to ultrasound would be minimized.

The second type of experimental test involved the simultaneous application of ultrasound in continuous or pulse mode during fouling for four hours. Figure 4.10 shows the final flux / clean water flux for the system with continuous ultrasound at different voltages and with pulsing for 1 second on and 10 seconds off for a PVDF membrane that is fouled with 10 mg/L latex particles for 4 hours. There is an increase in the final flux / clean water flux with increasing voltage. However, at the highest voltage (12 V) there was an increase over the initial flux similar to the results observed in Figure 4.10 where the treatment time was very short, and the corresponding damage is shown in panels A
and B in Figure 4.11. With pulsing, improvement in flux occurred but there was no resulting damage to the membrane (see panels C and D in Figure 4.11). The system maintained a flux of around 97% of the original clean water flux compared to the untreated membrane which had a flux of 74% of the clean water flux.

4.5 Conclusions

The thin transducer system constructed in this study created cavitation in solution as evidenced by the presence of hydrogen peroxide. Chemiluminescence images verified cavitation formation in the system and showed an increased zone of chemiluminescence with increased applied voltage demonstrating that a membrane in a cross-flow cell was well within the zone of cavitation. Cleaning of ceramic and PVDF membranes using this transducer system was found to be effective in both a batch cleaning system and when incorporated into a cross-flow membrane cell. However, at higher applied voltages, there was evidence of damage to the membrane. Pulsed ultrasound was also shown to improve the flux, but it was slightly less effective than continuous ultrasound.

These results show that transducers can be effectively placed into membrane systems and used to clean membranes during filtration. However, more work needs to be done to optimize the system with respect to the frequency of the transducer and the applied voltage so that damage does not occur to the membrane.
**Figure 4.1** Piezoelectric disk used for membrane cleaning system. A) Disk laid flat on a surface B) Disk standing up on an edge C) Overhead view of copper tape covering top side of the disk D) Side profile of wire connections to both the top and bottom of the disk.
Figure 4.2 Piezoelectric disk embedded in an Osmonics Cross-flow cell. The Disk is at the center of the flow through channel and is surrounded by Styrofoam material. The area directly around the disk is sealed using silicone sealant.
Figure 4.3 Modified membrane with silicone sealant covering entire membrane area except the area directly across from the transducer. Membrane was fouled with 10 mg L$^{-1}$ red dyed latex particles for 2 hours with no ultrasonic treatment.
Figure 4.4. External cleaning vessel and cross-flow membrane system with embedded transducer.
Figure 4.5. \( \text{H}_2\text{O}_2 \) production rate from the transducer in 200 mL of Milli-Q water at different applied voltages.
Figure 4.6. Images of chemiluminescence above the transducer in 400 mL of $10^{-3}$ M luminol at pH 12.0 at different applied voltages A) 10V, B) 14V, C) 22V and D) 30V.
Figure 4.7  SEM images of ceramic membrane surfaces for a membrane fouled with 10 mg L$^{-1}$ sulfate latex particles and A) no cleaning, B) cleaned using external batch cleaning at 24 V, and C) cleaned using external batch cleaning at 30 V.
Figure 4.8 Cleaned flux ratio of PVDF membranes fouled with 10 mg L⁻¹ sulfate latex particles and cleaned using the external batch system with different applied voltages using continuous and pulse treatments of ultrasound. Pulse treatments were done with a pulse length and interval of 1 second at each voltage. Inset is an SEM of the membrane surface which was treated using continuous treatment at 22 V.
Figure 4.9 Final flux / clean water flux of different applied voltages for a membrane initially fouled for 2 hours with 10 mg L$^{-1}$ sulfate latex particles in the cross-flow cell and subsequently subjected to continuous ultrasonic treatment afterwards in the cross-flow cell. Inset is an SEM of the membrane surface for the applied voltage of 14 V.
Figure 4.10 Final flux / clean water flux after 4 hours of fouling with 10 mg L$^{-1}$ sulfate latex particles and simultaneous treatment with ultrasound at differing applied voltages. Under pulse conditions the ultrasound was applied for 1 second on and 10 seconds off.
Figure 4.11  SEM images of membranes treated by applying ultrasound from the onset of fouling. Panels A and B are for continuous operation at 12V, while C and D are for pulse operation at 12V.
CHAPTER 5

CONCLUSIONS AND FUTURE WORK

5.1 Conclusions

This research has shown that membranes may be effectively cleaned using ultrasound. Ultrasonic frequencies from 70 kHz up to 620 kHz were able to clean ceramic membranes without damaging them. Lower frequencies had higher cleaning efficiencies than higher frequencies. Although higher frequencies may have more cavitation bubbles collapsing with time, the bubbles are smaller in size and collapse less energetically; thus, they may not be capable of detaching particles from the cake layer as readily as lower frequencies. Increases in power intensity increased the cleaned flux ratio. This increase was attributed to an increase in the number of cavitation bubbles in the system and an increase in acoustic energy in the system. The removal of fouling material from the surface of a membrane was attributed to two factors: 1) detachment or loosening of any particles from the surface by cavitational mechanisms (i.e., microstreamers), and 2) transport away from the surface by acoustic streaming.
In further studies, it was found that solution conditions alter particle interactions greatly and have significant impacts on the ultrasonic cleaning of membranes. Ultrasonic cleaning was greatly affected by the pH of the solution, which was attributed to particle-particle interactions and with the particles and the membrane. Cleaning was most effective at low and high pH. At low pH, the strong particle-particle interactions caused large flocs to be removed from the surface whereas the strong repulsion of particles at higher pHs caused removal of smaller clusters. Ultrasonic cleaning at higher ionic strength was not as effective as cleaning fouling layers formed at lower ionic strengths. High ionic strength caused particles to coagulate in solution and settle as flocs on the membrane surface causing large void spaces in the fouling layer. Ultrasound was not effective at removing this high ionic strength fouling layer due to the stronger particle-particle interactions. Particle size experiments showed that the zeta potentials of the particles were a significant factor for increased ultrasonic cleaning. The repulsive particle-particle interactions of the highly charged particles made for better removal than with lesser charged particles regardless of size.

For incorporation of ultrasound into membrane systems, a thin transducer system was developed. The thin transducer system created cavitation in solution as is evidenced by the presence of hydrogen peroxide measurements. Also, chemiluminescence was present in the system at increasing distances with increasing voltages applied. The distance to the membrane inside of the cross-flow membrane cell is within the zone of cavitation. Cleaning of ceramic and PVDF membranes was found to be effective using the thin transducer system in the external batch cleaning vessel in continuous and pulse modes. Cleaning of PVDF membranes in the cross-flow membrane cell using the
transducer was found to be effective. However, at higher applied voltages, there was evidence of damage to the membrane. No damage was observed at lower voltages.

SUMMARY

In this research ultrasonic cleaning of particle-fouled membranes was evaluated and a new transducer system was developed to be used in cross-flow membrane systems. This work is an initial step in developing ultrasonic membrane cleaning systems that can be incorporated into larger scale systems. It has been shown that ultrasound can effectively clean ceramic membranes without any type of damage, but more work needs to be done on more commonly used polymeric membranes.

6.2 FUTURE WORK

Results of this research suggest that ultrasonic cleaning of membranes is possible through the use of piezoelectric disks embedded into the cross-flow membrane module opposite the fouled membrane surface. These studies were carried out with a single transducer and a modified membrane surface. The addition of more transducers to the membrane module will be required to cover the entire membrane surface.

Also the transducer material was not well coupled with the fouling fluid for the cross-flow experiments, which may cause reflection of acoustic energy back into transducer instead of propagating into the fluid. This is because the acoustic impedance of the PZT is not matched well to the acoustic impedance of the water. This will cause inefficient transfer of energy to the medium. There may also be problems with the deposition of fouling material onto the transducer surface or corrosion over time of the
surface of the transducer. A coupling plate should be added to the system to better match
the PZT to the medium. This plate would be made of steel or another material with an
acoustic impedance between that of water and that of the transducer material. This would
improve transmission of acoustic energy into the fluid and protect the transducer surface.
The plate would also allow for fewer transducers to be used in the membrane cleaning
system because the plate would span over the entire membrane surface while the
transducer could be optimized to fit the cell while effectively cleaning. The optimum
number of transducers that can drive the plate should also be investigated.

Only one frequency was utilized for cleaning the polymeric membrane in the
cross-flow membrane cell. This disk showed that it was possible to damage the
membrane with higher applied voltages. The use of thinner disks which have higher
resonance frequencies should be evaluated. These disks would also fit into the membrane
module, but the cavitation that is created would be less intense than for the thicker
transducer. These disks could also be attached to the coupling plates in order to cover the
entire membrane surface.

Only PVDF membranes were used for the cleaning experiments. Flat stainless
steel membranes have been offered for testing by Bekaert which could be incorporated
into the cross-flow membrane system. These membranes would be more resistant to
damage from ultrasound and may present an easier surface to clean than polymeric
membranes.
BIBLIOGRAPHY


