ABSTRACT

KAUFMANN, ANDREW JACOB. Remediation of Spent Pickling Brine using Crossflow Filtration and Activated Carbon. (Under the direction of Dr. Brian Farkas).

The pickle industry is considering sustainable methods to reuse cucumber fermentation brines that may aid in the management of waste waters with a high chloride content. Spent brine properties change with the completion of fermentation, its direct contact with the unwashed fresh fruits, and the long term storage of the fermented goods in such liquid. Additional changes in the brine may occur due to undesired microbial activity at any time during the active fermentation process and long term storage, and chemical changes such as oxidation, proceeding during long term storage in aerated open top tanks. These changes cause economical losses for pickling companies due to unproductive processing and discharge costs and increase the need for spent brine treatment.

Development of a reclaim process that specifically addresses the concerns previously mentioned for cucumber fermentation brines would allow continued reuse of the ingredients and water needed to create fresh brines while reducing production and waste management costs. The objectives of this study were to (1) characterize of spent brine from current commercial operations and to test (2) the ability of crossflow filtration to remove undissolved particles and microbial load which contributes to brine deterioration and (3) the effectiveness of activated carbon to eliminate the chemical components that deteriorate the quality of spent brine.

Spent brines were passed through a 0.8 µm ceramic filter using a benchtop crossflow filtration unit. The efficiency of the filter to remove particulates was determined by reduction in turbidity and particle size analysis. Turbidity of the spent brines were reduced from an

average of 730 ± 813 NTU to 2.69 ± 2.77 NTU; a reduction of 99.6%. The ceramic filter also removed 98% of the undissolved particles in the spent brine as determined by particle size analysis. Filtration greatly reduced microbial counts. On average, 4 Log CFU/mL of microbes including lactic acid bacteria, total aerobic, and yeasts and molds were removed from the spent pickling brine using the 0.8 µm filter. Although sterility of the brines was not confirmed, the microbial levels dropped to below detectable limits at 2 Log CFU/mL.

Activated carbon batch isotherm testing was done to identify an ideal carbon use rate to employ. The amount of 16g/100 ml was identified as the appropriate amount to be used for the brine types tested. Using this treatment, the total organic carbon (TOC) levels were reduced from an average of 5273 to 2507 mg TOC/L; a 53% reduction. On average, the initial lactic and acetic acid concentrations were 75.28 and 23.99 mM, respectively. The use of 16g/100 ml reduced the average lactic acid concentration to 48.86 mM, for a decrease of 35%, and the average acetic acid concentration to 8.75 mM for a 64% reduction. A few of the brines tested positive for polygalacturonase (PG) before the use of activated carbon. After the carbon treatment, no activity was observed. Transmittance at 254 nm was used to identify the efficiency of activated carbon as a precursor to UV disinfection. % transmittance of brine increased from 0% across all brines prior to the carbon treatment to an average of 89.5% ± 2.11%. All of these results express the effectiveness crossflow filtration and activated carbon have in treating spent brine. Filtration effectively removed the undissolved particles present in the spent brine and reduced microbial counts; and the activated carbon reduced the organic compounds that may contribute to off flavors and odors of recycled brines.

Remediation of Spent Pickling Brine using Crossflow Filtration and Activated Carbon

by
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BIOGRAPHY

Andrew Kaufmann was born in Detroit, MI and grew up in Raleigh, NC. He earned his Bachelor of Science degree in Biological Engineering from North Carolina State University. During that time, he took part in a summer internship with McCormick & Co., Inc. which sparked his interest in working with food. This led to his participation in undergraduate research under Dr. Brian Farkas in the Department of Food, Bioprocessing and Nutrition Sciences (FBNS) at NC State University. The time spent working under Dr. Farkas and in FBNS encouraged Andrew to pursue a Master of Science degree in Food Science.

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Chapter 1

Introduction

Brine used for pickle fermentations contains about 6% NaCl. The fermentations are conducted in tanks that can hold about 40,000 liters (Lu et al., 2012). In colder climates, up to 12% NaCl is required to prevent freezing (Zhou et al., 2000). This high salt concentration makes discharging of spent brine an issue. The US Environmental Protection Agency has put limits on the amount of chloride that is allowed in lakes or streams. Commercial pickle producers can regularly exceed these limits (Humphries and Fleming, 1989).

Additional issues related to the need to develop spent brine reclaim methods involve reports of (1) spoilage of fermented cucumbers associated with the development of unpleasant odors (Franco et al., 2012); (2) susceptibility of pickle to oxidation reactions that have negative effects on quality during fermentation, storage, and processing (Buescher and Hamilton, 2000). The reuse of brine will create a more sustainable system in which the salts and water used for the preparation of fresh brines can be reused (Ratnani et al., 1980).

Several methods have been developed for remediating spent brine. Durkee et al. (1973) examined the use of a combustion system which involved the evaporation of liquid and rey of salt. The cost of evaporating significant amounts of brine was unaffordable for commercial scale production and inefficient in terms of speed. Palnitkar and McFeeters (1975) evaluated the commercial clarification of spent brine to address the concerns that contribute to waste by increasing the pH to 11.0 through the addition of NaOH. This approach allowed for the coagulation of the proteins followed by their removal by decanting. The pH was re-adjusted to pH 7.0 with HCl prior to re-use. Although a simpler process, the costs of NaOH and HCl, and their management in commercial facilities in significant volumes and concentrated solutions do not make this method viable.

More recently, researchers have evaluated remediating spent brine by means of filtration and activated carbon. Fasina et al. (2003) crossflow filtered brine from cucumber fermentation through membranes with pore sizes of 0.05 and 0.2 µm. The filtration process removed the sediments and microbial cells from the spent brine but had no effect on the chemical characteristics which may result in off-flavors to be carried over in the brine. The filter pore sizes were too small to be applied to the commercial scale because the throughput was too low to be used.

Ratnani et al. (1980) tested the filtration of spent brine through activated carbon beds in series. Spent brine was continuously fed through the activated carbon beds and efficiency was based on the ratio of the outlet total organic carbon (TOC) concentration and initial TOC concentration. The results from this study give an understanding of how well activated carbon removes organics as a whole but it did not investigate the specific components that were removed.

No research was found that combined the processes of filtration followed by activated carbon treatment. In this study, spent brine was first filtered through a crossflow system with a 0.8 µm ceramic membrane followed by an activated carbon batch isotherm. The objective of this study was to determine the largest filter size that would effectively remediate the spent brine. A larger filter pore size, as compared to that used by Fasina et al. (2003), would allow for significant throughputs and efficient production of filtered liquid. The spent brine filtered through the selected membrane was tested to determine how well the filter removed the suspended particles that contribute to turbidity. The brine was also evaluated to determine the efficacy of the filter to reduce microbial counts. The objective of the activated carbon system was to remove the chemical components that lead to brine deterioration and off-flavors.

Batch testing was completed to assess how well activated carbon could remove the components that make up the TOC.

The goal of this study was to formulate a process that could be used to remediate spent brine for full reuse in future fermentations. This was done by understanding the components that lead to brine deterioration and spoilage and addressing each of them. Filtration was used to address the physical and microbiological issues and the use of activated carbon was to target the chemical components of concern. It was hypothesized that if spent brine was crossflow filtered and treated with activated carbon, the full amount of the brine used in a fermentation would be capable of being reused.

Chapter 2

Literature Review

2.1 Cucumbers & Pickling

The cucumber, *Cucumis sativus*, is the vegetable most widely preserved by pickling in the United States. China contributes about 70% of the worldwide production. Iran produces the second amount worldwide with Turkey and Russia coming next, respectively. The U.S. produces the 5th most cucumbers worldwide (FAOSTAT, 2013). Over the past 10 years, cucumber production in the U.S. for pickles has been increasing from 1,297 million pounds in 2003 to 1,964 million pounds in 2011 (USDA, 2012).

There are three methods in which cucumbers are pickled. These include pickles made from fermented cucumbers, fresh-pack pickles, and refrigerated pickles (Fleming and Moore, 1983). For the fermented type, cucumbers are brined in a salt solution. Ingredients such as dill herb or other spices and flavorings may be added to comprise a specific type of pickle. After brining, the pickles are washed and jarred. Fresh-pack pickles are made from unfermented cucumbers. Fresh cucumbers are packed in a vinegar solution with specific ingredients to constitute a particular type of pickle. Since these pickles do not undergo the fermentation process, they must be pasteurized in their jars to assure complete preservation. Refrigerated pickles are packed similarly to that of fresh-pack pickles but are preserved by the addition of salt and preservatives such as acetic acid, sodium benzoate or potassium sorbate and stored, distributed, and displayed under refrigeration (USDA, 1991). Up until the early 1940's, all cucumbers used for pickling were preserved by fermentation. At that point in time, fresh-pack pickles started to become prominent. Around 1960, refrigeration was introduced as a new means of preservation for pickles. Currently, about 35% of commercially processed pickles are fermented, 40% are pasteurized (fresh-pack), and 25% are refrigerated (Fleming et al., 2002).

For fermented pickles, cucumbers are placed in vats with a brine solution that is about 6% NaCl. The sodium chloride selects for naturally occurring lactic acid bacteria such as *Lactobacillus plantarum* necessary for fermentation. This part of the fermentation process lasts about 10-21 days, depending on the ambient temperature. Additional NaCl, up to 12 to 16%, is added to the brines in commercial tanks to prevent the spoilage of the cucumbers (Fasina et al., 2003). This salt helps the cucumbers maintain their firmness and crispiness while they are stored in their fermentation brines for extended periods of time as well as preventing freezing on the processed fruits during the winter (McFeeters and Pérez-Díaz, 2010).

L. plantarum is a homofermentative, lactic acid bacterium present on the skin of cucumbers which uses such vegetables as a substrate. *L. plantarum* and other lactic acid bacteria convert the fermentable carbohydrates in the cucumbers into lactic and acetic acids, CO_2, and ethanol (Humphries and Fleming, 1989). Due to its high acid tolerance, *L. plantarum* is more abundant than other microorganisms during fermentation (Todorov and Franco, 2010).

2.2 Waste Issues

There are many characteristics of spent brine that make discharge a continuous issue. Spent brine contains about 10-18% NaCl, a pH ranging from 3.4 – 3.8, 2,000 mg/L suspended solids, 7,000 - 10,000 mg/L BOD, and 10,000 - 15,000 mg/L COD (Ratnani et al., 1980). Of all these issues, the NaCl levels are what concern the Environmental Protection Agency (EPA) the most. The U.S. EPA has set a chloride limit for the release of wastewater into freshwater systems. This limit is set at 230 mg/L of chloride which has been hard to meet for the pickle industry (EPA, 1987). There are three main areas where wastewater

accumulates. These areas are brining, “processing” or freshening, and finishing (Little et al., 1976). Higher costs are affiliated with water discharge containing high amounts of salt and organic wastes (Fleming et al., 2002). As a result of this issue, recycling of fermentation brines is a widely accepted practice among major pickle producers. This reduces the amount of spent brine discharged and cuts down on costs dramatically (McFeeters and Pérez-Díaz, 2010).

Despite recycling spent brine, cucumbers need to be desalted after fermentation due to their high salt contents. Only 1 to 4% NaCl remains in the finished product so desalting must occur (Fasina et al., 2003). Salt is removed from the cucumbers and along with the organic residues, this waste is discharged directly into municipal waste systems or streams (Fleming et al., 1995). The discharge from desalting contains a significant biological oxygen demand (BOD) and a salt concentration too low for the waste to be recycled so discharge is the only option (McFeeters and Pérez-Díaz, 2010).

A couple of processes have been tested for the treatment of spent brine prior to recycling. One of these includes the rey of salt in solid form. A solution containing about 60% NaCl is produced and incinerated at 1,200 °F for about 5 minutes so that all of the organic matter is wiped out and the salt remains. The leftover salt is used to produce the new brine by using the neutralized and filtrated solution after incineration. This resultant brine has been used for fermentation with no negative effects found in the final products (Durkee et al., 1973). Application of this process at the commercial scale has proven cost prohibitive (McFeeters et al., 1978). Another process for recycling spent brine that has shown success is recycling the brine while it is still in the liquid phase. NaOH is added to the brine to promote protein followed by pH adjustment to 11.0. Once the proteins have settled, the clear brine is

decanted and the pH is dropped to 7.0 using HCl. Like the previous method, this recycled brine has been used to ferment cucumbers and has shown to yield pickles with no issues. Despite this method being simpler and resulting in lower capital and operating costs, it requires pH adjustments with concentration NaOH and HCl solutions and management of significant volumes of such solutions at a commercial scale (Palnitkar and McFeeters, 1975).

2.3 Filtration

Over the years, filtration has become a more viable option than conventional separation options such as centrifugation, incineration, extraction, and distillation. Filtration has the advantage of being highly selective of particles, it can be run in a continuous process, and the capital costs are much lower than that of other processes such as centrifugation. Two types of commonly used filtration processes based on pore size are ultrafiltration and microfiltration (Bowen and Jenner, 1995). Ultrafiltration removes particles between 1 and 100 nm in size and microfiltration filters out particles from 0.1 to 10 μm in size (Eykamp, 1995).

Filter membranes come in either organic or inorganic forms. Organic filter mediums, such as polycarbonate or cellulose, are advantageous due to easy disposability and lower initial costs. Inorganic membranes have become more popular due to their ability to withstand higher temperatures and pressures and increased resistance to fouling. Some examples of inorganic membranes include ceramic and aluminum-oxide. Depending on the solution being used, these membranes come in different designs ranging from tubular modules to hollow fiber modules to plate-and-frame modules (Bowen and Jenner, 1995).

2.3.1 Deadend Filtration

Deadend filtration is a separation method that is preferable due to its high selectivity and economic scalability. It also has lower energy and capital costs when compared to crossflow filtration systems (Blankert et al., 2006). A deadend filtration process involves a feed flowing towards a filter medium (Figure 2.1). As the feed flows through the filter, a cake forms on the filter. This cake is the retentate of the feed and the feed that flows through the filter medium is the permeate. As the cake increases throughout the filtration process, so does the pressure loss across the cake. A result of this includes the permeate flow rate concurrently decreasing. The pressure drop across the filter decreases until it equals zero which means that the pressure delivered by the pump equals the pressure loss from the filter. This is when the feed can no longer flow through the filter and the filtration process must be terminated (Wakeman and Tarleton, 2005).

The reoccurring issue with deadend filtration is the problem of cake formation. As the cake thickness increases on the filter medium, the flux of the permeate decreases (Figure 2.1). For cake filtration models in deadend filtration, Darcy's law (Equation 1) is used to interpret data (Polyakov, 2006).

$$j = \frac{\Delta p}{\mu(R_c + R_m)} \tag{1}$$

j is the volumetric permeate flux, Δp is the pressure drop, μ is the viscosity of the permeate, R_m is the resistance of the clean membrane, and R_c is the resistance of the filter cake. The addition of R_m and R_c comprise the overall resistance, R (Reymann and Koenders, 2000). As the filtration process progresses, there is an increase in cake formation which in turn increases R_c (Figure 2.2). Since the volumetric flux is inversely related to cake resistance, j

decreases. R_c is proportional to the mass of the deposited particles on the membrane (Equation 2). As a solution is filtered, particles are deposited and increase its overall cake mass. This causes the resistance of polarized solids to increase (Bowen and Jenner, 1995).

$$R_c = \alpha \frac{m}{A} \tag{2}$$

Here, m is the filter cake mass, A is the membrane area, and α is the specific resistance of the cake. This specific cake resistance can be found using the Carman-Kozeny relationship (Equation 3) (Carman, 1938).

$$\alpha = \frac{180(1-\varepsilon)}{\rho_p d_p^2 \varepsilon^3} \tag{3}$$

In this equation, ρ_p is the density of the particles, d_p is the average particle diameter, and ε is the void volume of the cake (Bowen and Jenner, 1995). As size of the particles increase, so does the specific cake resistance.

An increase in R_c results in a decrease in flux, deadend filters must be cleaned regularly to prevent the filter from fouling completely. There are some mechanical methods that could prove beneficial when dealing with fouling issues. Some of these methods include backwashing the filter to remove cake formations and pulsating the inlet flow to break up the cake (Ben Amar et al., 1993). In order to backwash a filter, the filtration process must be stopped and all of the product must be removed. It is then that the backwashing can occur. The increased time it takes to backwash means an increase of downtime meaning that less time is available to filter the product when compared to crossflow filtration (Mondor et al., 2000).

2.3.2 Crossflow Filtration

Crossflow filtration involves a feed flowing parallel (tangentially) to a filter (Figure 2.3).The retentate forms a cake deposit on the filter similar to that of deadend filtration (Fasina et al., 2003). At the start of the process, the cake thickness increases on the filter medium until a steady state condition is achieved (Figure 2.3). At this point, the flowrate of the permeate maintains a steady stream (Wakeman and Tarleton, 2005). The occurrence of fouling or buildup of a cake layer commonly found in deadend filtration is greatly reduced due to the shear, tangential force (Redkar and Davis, 1993). Due to this reduction of the cake layer, increased filtration rates of crossflow filtration systems are obtained when compared to deadend filtration systems (Fasina et al., 2003).

In order for membrane separations to be economically possible, the permeate needs to possess a high flux. As mentioned earlier for crossflow filtration, the permeate flux decreases in the beginning stages of filtration until it reaches a near steady state. This is established by the degree of fouling. Fouling encompasses both cake formation (external fouling) and deposition of the particulates in the filter (internal fouling). External fouling can be resolved with methods mentioned earlier such as a pulsating flow or backwashing. Internal fouling can be semi-permanent and can degrade the filter medium (Wakeman and Tarleton, 2005).

The filtration process starts with the solution possessing a concentration, C_w, at the surface of the filter medium. As the process progresses, the solution reaches a concentration, C_g, at the surface of the cake formation. So long as C_g is greater than C_w, the flux of the feed will increase with the increase in pressure drop across the filter. Once C_w equals C_g, an increase in pressure drop will result in an increase of the cake thickness which means the flux can no longer increase (Murkes, 1990).

When a solvent that is pure like water is filtered, the flux, J_w, is proportional to the transmembrane pressure, ΔP_A, applied across the filter medium (Equation 4) (Taddei et al., 1989).

$$J_w = \frac{\Delta P_A}{\mu_w R_m} \tag{4}$$

Using the flux, pressure drop, and the viscosity of the water, μ_w, the hydraulic resistance of the clean membrane, R_m, can be found (Daufin et al., 1991). However, when mixtures are being filtered, fouling and cake formation occurs. Due to these factors, a new flux equation has to be used (Equation 5) (Taddei et al., 1989).

$$J = \frac{\Delta P_A - \Delta\Pi}{\mu_p(R_m + R_f)} = \frac{\Delta P_E}{\mu_p(R_m + R_f)} \tag{5}$$

In this equation, $\Delta\Pi$ is the transmembrane osmotic pressure drop is induced by the buildup of undissolved particles over the membrane (Kozinski and Lightfoot, 1972). The other variables include μ_p, the viscosity of the permeate, R_f, the hydraulic resistance caused by polarization and ΔP_E, which is the effective pressure. $\Delta\Pi$ is caused by the cake formation at the surface of the filter and reaches a constant value once the flux reaches a steady state. A critical osmotic pressure can be reached on the filter causing layers of irreversibly aggregated particles to form (Bessiere et al., 2005). To find R_f, a similar approach to finding R_m can be used (Equation 6).

$$R_f = \frac{\Delta P_E}{\mu_p * J} \tag{6}$$

The permeate viscosity is expressed by μ_p and J is the transmembrane flux as a function of time. This polarization resistance is reversible but fouling is irreversible. In this case, the

membrane is rinsed with water and that permeate flux, J'_w, is measured under the pressure drop ΔP_A to find the irreversible fouling resistance, R'_f (Equation 7) (Taddei et al., 1989).

$$J'_w = \frac{\Delta P_A}{\mu_w (R_m + R'_f)} \quad (7)$$

By determining both R_f and R'_f with respect to time, it can be concluded which resistance is truly taking place. R_f will increase as the process time increases. To understand how well a specific filter medium withstands certain products, R'_f needs to be determined. The more R'_f increases, the more the filter medium is being irreversibly damaged (Taddei et al., 1989).

Fasina et al. (2003) crossflow filtered brine from cucumber fermentation using 0.05 and 0.2 μm hollow fiber polysulfone filtration membranes. The objectives were to investigate efficiency parameters such as the effect of flow rate, transmembrane pressure, and membrane pore size on the permeate flux as well as microbial loads and chemical characteristics. The filters were able to remove the suspended particles and microbial cells.

2.4 Activated Carbon

Activated carbon has been used on large scales as an adsorbent to remove contaminants that affect taste and odor (Matsushita et al., 2008). It has mainly been used in conjunction with waste water treatments but has also been used with food and brines such as pickling and table olive brines (Ratnani et al., 1980; Garrido et al., 1992) Activated carbon is made from thermal processing of carbonaceous raw materials like wood, nut shells, and coal. This is done by carbonization which involves the raw material being pyrolyzed at temperatures of 600-900°C in the absence of oxygen followed by hot steam to oxidize/activate the carbon (Ramalho, 1983).

Physical adsorption with activated carbon can be carried out as either a batch or continuous process. For a batch process, the activated carbon is mostly in powdered form. It is mixed with the solution and left to settle. Continuous operations are generally carried out in columns containing activated carbon in the granular form. The continuous method is most widely used in the industry setting due to it being more economical. For both processes, the percent removal of contaminants depends on the amount of time the solution is in contact with the activated carbon and the amount of organic matter in the solution (Ramalho, 1983). Naturally occurring organic matter can significantly reduce the effectiveness of activated carbon. This is generally quantified in terms of total organic carbon (TOC) but can also be measured by the individual components that make up the TOC (Kilduff et al., 1998).

Adsorption is the adhesion of solutes (adsorbates) to the surface of a solid (adsorbent). This is due to the imbalance of surface forces on the solid (Figure 2.4). Within the solid, molecules are surrounded by like molecules forming balanced forces. The surface molecules are not fully surrounded by other molecules so they experience unbalanced forces. Adsorbates can then be retained within the solid due to these forces. This process is referred to as physical adsorption (Ramalho, 1983).

2.4.1 Batch Testing

The first screening test to evaluate activated carbon's ability to adsorb the target contaminant is completing a batch test. Accurate batch tests are essential in determining activated carbon feasibility. They help understand carbon bed life and predict location of the breakthrough curve which depicts the progression of the contaminant concentration as a function of adsorption parameters. This can include contact time and amount of carbon used (Peel, 1980). Data compiled from liquid phase isotherms are typically interpreted using the

Freundlich equation (Achife and Ibemesi, 1989). In the Freundlich equation (Equation 8), the amount of adsorbate bound per unit weight of adsorbent, x/m, is a logarithmic function of the contaminant residual concentration in the fluid phase at equilibrium, c (Proctor and Toro-Vasquez, 1996).

$$\frac{x}{m} = kc^{1/n} \tag{8}$$

The parameters, k and n, are indicators of adsorption capacity and energy of adsorption, respectively. These values can be obtained by fitting the logarithmic form (Equation 9) of the Freundlich equation to the experimental data (Proctor, 1996).

$$\log\frac{x}{m} = \log k + \frac{1}{n}\log c \tag{9}$$

2.4.2 Pilot Testing

Once isotherm testing is complete, it is determined whether or not activated carbon will sufficiently remove the target contaminant. If it will, pilot tests are the follow-up to determine the operating conditions that utilize the most efficient usage of granular activated carbon. The use powdered activated carbon results in carbon loss as waste sludge due to its fine nature. Granular activated carbon is typically used in adsorption processes because it is easier to handle and the carbon loss problem is not as significant as powdered activated carbon (Chern and Chien, 2002).

Designing a carbon adsorption system depends on running bench-scale tests with columns with the same conditions of those in actual plant processes. The Bohart-Adams model is used to model fixed bed breakthrough curves (Equation 10). In solving this model, the design procedure for activated carbon columns can be achieved (Chu, 2010).

$$\mathrm{Ln}\left[\left(\frac{C_o}{C_E}\right) - 1\right] = \ln\left(e^{\frac{KN_oD}{V}} - 1\right) - KC_o t \quad (10)$$

In this equation, t is the service time, N_o is the adsorptive capacity of the carbon, C_o is the influent solute concentration, C_E is the desired effluent solute concentration, V is the linear flow rate, D is the depth of the carbon bed, and K is the rate constant. Some of the parameters, N_o and K, are unknown and are determined via laboratory testing. Ramalho (1983) used three columns in series and recorded three times, t_1, t_2, and t_3, where the effluents of each column equal the desired solute concentration, C_E. A constant velocity, V, is used for each run and the initial solute concentration, C_o, is known. Four experiments were run using different flowrates and amounts of carbon for each column. Once each time, t, was found for each flow rate and carbon depth, a graph was formed with the abscissa being the depth of the carbon, D, and the ordinate being time, t. Each experiment formed a straight line on the graph and the slope, s, and intercept, i, could be determined (Equations 11 and 12) (Ramalho, 1983).

$$s = \frac{N_o}{C_o V} \quad \& \quad i = -\frac{\ln\left[\left(\frac{C_o}{C_E}\right) - 1\right]}{KC_o} \quad (11), (12)$$

Using these equations, the parameters N_o and K can be solved (Equations 13 & 14). Knowing the adsorptive capacity (N_o) and rate constant (K) help determine the most efficient flowrates with respect to time and carbon depth (Ramalho, 1983).

$$N_o = C_o V s \quad \& \quad K = -\frac{\ln\left[\left(\frac{C_o}{C_E}\right) - 1\right]}{iC_o} \quad (13), (14)$$

Ratnani et al. (1980) tested the filtration of spent brine from commercial fermentations through activated carbon filters in a continuous process (Figure 2.5). Spent brine was continuously fed through the activated carbon beds for 12 hours. Efficiency was

based on the ratio of the outlet total organic carbon (TOC) concentration and initial TOC concentration. TOC is the organic matter responsible for the off-odor and color of the spent brine. The effect regeneration has on used activated carbon efficiency was also investigated. Regeneration involved the thermal reactivation of the spent activated carbon in an oven at 870°C for 2 hours.

After the first hour of operation, the TOC removal efficiency was about 99% at the outlet of the third column. At about the sixth hour, the removal efficiency plateaued around 70% for the rest of the process. When regenerated activated carbon was used, the same results were found for about the first hour. After the first hour, the TOC removal competencies of the regenerated carbon showed to be about 5-10% lower than the fresh carbon (Ratnani et al., 1980).

2.5 Ultraviolet (UV) Radiation

Ultraviolet radiation has the potential to inactivate any microorganisms present in spent brine after filtration due to its capabilities of treating large amounts of liquid. UV radiation is electromagnetic energy at wavelengths between 100 and 400 nm (Harm, 1980). UV radiation is present in three parts, UV-A (320 – 400 nm), UV-B (290 – 320 nm), and UV-C (100 – 290 nm) (Mahmoud and Ghaly, 2004). UV light at wavelengths between 180 and 320 nm inactivates bacteria and other microorganisms with the optimum wavelength being 254 nm (Meulemans, 1987). This wavelength is the most efficient in regards to bacteria disinfection since photons are most proficiently absorbed by the DNA of microorganisms at this wavelength (Koutchma et al., 2009).

Some sources of UV light include low/medium-pressure mercury discharge, pulsed xenon arc discharge, xenon excimer, and submerged arc. Low and medium pressure mercury

arcs are the most common sources of UV light. About 95% of the UV light emitted from mercury arcs is at 253.7 nm wavelength. UV light has been shown to inactivate bacteria and yeasts while not affecting the sensory or nutrient characteristics of the product (McKinney et al., 2009). UV light disinfection is carried out by the inactivation of microorganisms. Thymine bases on the DNA and RNA are very reactive to UV light. The UV energy causes the thymine to form dimmers (thymine=thymine double bonds) which inhibit transcription (Figure 2.6). This causes the microorganism to become sterile which means the infection of this microorganism is no longer an issue (Lingireddy, 2002).

A common set-up for continuous UV radiation testing systems was implemented in the work of Mahmoud and Ghaly (2004) (Figure 2.7). This work involved the liquid in the feed tank being pumped through a tubular UV reactor. In the reactor, a UV lamp is encased in a quartz sleeve so that the liquid does not have direct contact with the bulb. The liquid is pumped through the UV reactor so that maximum exposure to UV light is achieved while maintaining efficient flow rates (Mahmoud and Ghaly, 2004).

UV light's effectiveness is directly related to the characteristics of the product being tested. Particles in the product can have adverse effects on the UV efficiency by scattering, absorbing, reflecting, and diffusing any UV light. Target organisms are susceptible to being shielded by other particles which decreases the level of inactivation (Kollu and Örmeci, 2012). Once UV light is absorbed by a microorganism, it can no longer inactivate other microorganisms. If UV light is not absorbed, it can still reflect, refract, and scatter in different directions and still disinfect other microorganisms.

Transmittance is the ratio of the transmitted to the incident light irradiance (Equation 15) (Koutchma et al., 2004).

$$T = I_1/I_0 \quad (15)$$

Where $I_1$is the irradiance of the transmitted light and I_0 is the incident light irradiance. The transmittance of UV light is altered by the scattering and absorbing of light by particles in the liquid. Since transmittance directly influences the UV intensity delivered to the microorganisms in the liquid, a decrease in transmittance decreases the UV intensity (Koutchma et al., 2004). Liquids such as pharmaceuticals, juices, brines, and liquid sugars are promising products for UV disinfection. However, these liquids usually transmit little UV light due to their varying characteristics such as color compounds, suspended matter, and organic solutes. Research is being done to address this low transmittance which results in a lower efficiency of performance of the UV disinfection (Koutchma, et al., 2009).

2.5.1 UV Dose Determination

Establishing the UV dose for a specific liquid is an important aspect to determine for implementing a full scale UV disinfection system. There are four methods to determine UV dosage: mathematical, biological, electronic, and chemical. These methods are generally done independently of each other but they can be done in conjunction to validate one another. The simplest method of the four would be the electronic method (Lingireddy, 2002). A radiometer is used at a specific wavelength to determine the fluence rate of the UV bulb. The fluence rate is the total power emitted from the UV bulb per unit area. Its units are mW/cm^2 (McDonald et al., 2000). Once this is established, it is multiplied by the time of exposure to obtain the UV dose (Koutchma et al., 2009). The electronic method provides simple, cost-effective means of monitoring UV effectiveness but several issues are apparent. Sensors are needed throughout UV reactors to send data to the radiometer. Determining where to place the sensors to quantify the UV irradiance is difficult due to factors such as lamp and reactor

geometry, liquid characteristics, and reflections. These sensors are not reliable for long term use and need to be inspected frequently (Lingireddy, 2002).

The biological determination method incorporates the use of bioassay procedures to find a linear relationship between UV doses and the log inactivation of the microorganisms (Harris et al., 1987). This method accounts for most of the factors that affect UV dose; but it is time consuming, costly, and not adequate for real-time UV dosage determination (Lingireddy, 2002).

The chemical method involves the use of chemical actinometry which is one means of measuring UV dosage. An actinometer is a prepared solution in which the amount of photons in a beam can be determined for a set period of time. For chemical actinometry, the fluence is directly related to the amount of photons absorbed (Kuhn et al., 1989). Some of the most frequently used chemical actinometers include potassium ferrioxalate or malachite, uridine, and peroxydisulfate/t-butanol (Harris et al., 1987; Linden and Darby, 1997; Hoyer et al., 1992). This method provides information regarding the distribution of UV dose throughout the product. Knowing this information helps predict the inactivation efficiency of many microorganisms (Jin et al., 2006). The disadvantage to using this method is that chemical actinometry is impractical for larger applications due to the price and toxicity of the actinometric reagents (Lingireddy, 2002).

The mathematical method is capable of predicting fluid and particle velocities, mixing, and residence times for ideal design of UV reactors (Unluturk et al., 2004). Jacob and Dranoff (1970) created the first successful model for irradiance distribution in a UV reactor. This model has been refined to apply to different reactors over time with the Multiple Point Source Summation Approximation (MPSS model) being the new model others expand

on for specific applications primarily dealing with wastewater UV reactors (Scheible et al., 1985; Suidan and Severin, 1986). A limitation to this method is the difficulty to calibrate and verify the specific and sophisticated models (Linireddy, 2002).

References

Achife, E. C., Ibemesi, J. A. 1989. Applicability of the Freundlich and Langmuir adsorption isotherms in the bleaching of rubber and melon seed oils. *Journal of the American Oil Chemists Society*. 66(2): 247-252.

Ben Amar, R., Gupta, B. B., Jaffrin, M. Y. 1990. Apple juice clarification using mineral membrane: fouling control by backwashing and pulsating flow. *Journal of Food Science*. 55(6): 1620-1625.

Bessiere, Y., Abidine, N., Bacchin, P. 2005. Low fouling conditions in dead-end filtration: Evidence for a critical filtered volume and interpretation using critical osmotic pressure. *Journal of Membrane Science*. 264: 37-47.

Blankert, B., Betlem, B. H. L., Roffel, B. 2006. Dynamic optimization of a dead-end filtration trajectory: Blocking filtration laws. *Journal of Membrane Science*. 285(1-2): 90-95.

Bowen, W. R., Jenner, F. 1995. Theoretical Descriptions of Membrane Filtration of Colloids and Fine Particles: An Assessment and Review. *Advances in Colloid and Interface Science*. 56: 141-200.

Carman, P.C. 1938. Fundamental principles of industrial filtration. *Transactions of the Institution of Chemical Engineers.* 16: 168-188.

Chern, J-M., Chien, Y-W. 2002. Adsorption of nitrophenol onto activated carbon: isotherms and breakthrough curves. *Water Research*. 36: 647-655.

Chu, K. H. 2010. Fixed bed sorption: Setting the record straight on the Bohart-Adams and Thomas models. *Journal of Hazardous Materials.* 117: 1006-1012.

Daufin, G., Labbe, J. P., Quemerais, A., Michel, F. 1991. Fouling of an Inorganic Membrane During Ultrafiltration of Deffated Whey Protein Concentrates. *Netherland Milk and Dairy Journal*. 45: 259-272.

Durkee, E. L., Lowe, E., Baker, K. A., Burgess, J. W. 1973. Field Tests of Salt Rey System for Spent Pickling brine. *Journal of Food Science*. 38(3): 507-511.

EPA. 1987. Water Quality Criteria: Availability of Document. Fed. Reg. 52:37655–37656.

Eykamp, W. 1995. Chapter 1 Microfiltration and ultrafiltration. *Membrane Science and Technology*. 2: 1-43.

FAOSTAT, 2013. Production – Crops. Last updated January 2013. Food and Agriculture Organization of the United Nations.

Fasina, O. O., Fleming, H. P., Humphries, E. G., Thompson, R. L., Reina, L. R. 2003. Crossflow Filtration of Brine from Cucumber Fermentation. *Applied Engineering in Agriculture.* 19 (1): 107-113.

Fleming, H. P. 1984. Developments in Cucumber Fermentation. *Journal of Chemical Technology and Biotechnology*. 34 (4): 241–252.

Fleming, H. P., Humphries, E. G., Fasina, O. O., McFeeters, R. F., Thompson, R. L., and Breidt, Jr., F. 2002. BAG-IN-BOX TECHNOLOGY: Pilot System for Process-Ready, Fermented Cucumbers. *Pickle Pak Science.* VIII (1): 1-8.

Fleming, H. P., McDonald, L. C., McFeeters, R. F., Thompson, R. L., Humphries, E. G. 1995. Fermentation of Cucumbers without Sodium Chloride. *Journal of Food Science*. 60 (2): 312-315, 319.

Fleming, H. P., Moore Jr, W. R. 1983. Pickling. In *Processing of Horticultural Crops in the United States* eds. G. Fuller and G. G. Dull. *CRC Handbook of Processing and Utilization in Agriculture*, Vol. II, Part 2, Plant Products, ed. I. A. Wolff, 397–463. Boca Raton, Fla.: CRC Press, Inc.

Garrido, A., Garcia, P., Brenes, M. 1992. The recycling of table olive brine using ultrafiltration and activated carbon adsorption. *Journal of Food Engineering*. 17(4): 291-305.

Harm, W. *Biological Effects of Ultraviolet Radiation*; Cambridge University Press: New York, NY, 1980.

Harris, G. D., Adams, V. D., Moore, W. M., Sorensen, D. L. 1987. Potassium ferrioxalate as chemical actinometer in ultraviolet reactors. *Journal of Environmental Engineering.* 113(3): 612-627.

Hoyer, O., Kryschi, R., Piecha, I., Mark, G., Schuchmann, M. N. 1992. UV fluence rate determination of the low-pressure mercury arc in the UV disinfection of drinking water. *Aqua – Journal of Water Supply: Research and Technology.* 41(2): 75-81.

Humphries, E. G. Fleming H. P. 1989. Anaerobic Tanks for Cucumber Fermentation and Storage. *Journal of Agricultural Engineering Research.* 44: 133-140.

Jacob, S. M., Dranoff, J. S. 1970. Light intensity profiles in a perfectly mixed photoreactor. *AIChE Journal*. 16(3): 359-363.

Jin, S., Mofidi, A. A., Linden, K. G. 2006. Polychromatic UV Fluence Measurement Using Chemical Actinometry, Biodosimetry, and Mathematical Techniques. *Journal of Environmental Engineering*. 132: 831-841.

Kilduff, J. E., Karanfil, T., Weber, W. J. 1998. Competitive Effects of Nondisplaceable Organic Compounds on Trichloroethylene Uptake by Activated Carbon. I. Thermodynamic Predictions and Model Sensitivity Analyses. *Journal of Colloid and Interface Science*. 205(2): 271-279.

Kollu, K., Örmeci, B. 2012. Effect of Particles and Bioflocculation on Ultraviolet Disinfection of *Escherichia coli*. *Water Research*. 46: 750-760.

Koutchma, T., Keller, S., Chirtel, S., Parisi, B. 2004. Ultraviolet disinfection of juice products in laminar and turbulent flow reactors. *Innovative Food Science & Emerging Technologies*. 5(2): 179-189.

Koutchma, T. N., Forney, L. J., Moraru, C. I. 2009. *Ultraviolet Light in Food Technology: Principles and Applications.*

Kozinski, A. A., Lightfoot, E. N. 1972. Protein ultrafiltration: a general example of boundary layer filtration. *AIChE Journal*. 18(5): 1030-1040.

Kuhn, H. J., Braslavsky, S. E., Schmidt, R. 1989. Chemical Actinometry. *Pure and Applied Chemistry*. 61 (2): 187-210.

Linden, K. G., Darby, J. L. 1997. Estimating effective germicidal dose from medium pressure UV lamps. *Journal of Environmental Engineering*. 123(11): 612-619.

Lingireddy, S. 2002. Control of Microorganisms in Drinking Water. 213-240.

Little, L.W., Lamb III, J.C., Horney, L.F., 1976. Characterization and treatment of brine wastewaters from the cucumber pickle industry. UNC Wastewater Research Center, Department of Environmental Sciences and Engineering, School of Public Health University of North Carolina at Chapel Hill. ESE Publication No. 399.

Lu, Z., Pérez-Díaz, I. M., Hayes, J. S., Breidt, F. 2012. Bacteriophage Ecology in a Commercial Cucumber Fermentation. *Applied Environmental Microbiology*. 78 (24): 8571-8578.

Mahmoud, N. S., Ghaly, A. E. 2004. On-Line Sterilization of Cheese Whey Using Ultraviolet Radiation. *Biotechnology Progress*. 20 (2): 550-560.

Matsushita, T., Matsui, Y., Sawaoka, D., Ohno, K. 2008. Simultaneous removal of cyanobacteria and an earthy odor compound by a combination of activated carbon adsorption, coagulation, and ceramic microfiltration. *Journal of Water Supply: Research and Technology – AQUA*. 57(7): 481-487.

McDonald, K., Clevenger, T., Curry, R. 2000. Ultraviolet Light Technologies for Water Treatment. *Environmental and Pipeline Engineering*. 299-311.

McFeeters, R. F., Coon, W., Palnitkar, M. P., Velting, M., Fehringer, N. 1978. Reuse of fermentation brines in the cucumber pickling industry. EPA-600/2-78-207, Cincinnati, Ohio.

McFeeters, R. F., Pérez-Díaz, I. 2010. Fermentation of Cucumbers Brined with Calcium Chloride Instead of Sodium Chloride. *Journal of Food Science.* 75 (3): 291-296.

McKinney, J., Williams, R. C., Boardman, G. D., Eifert, J. D., Sumner, S. S. 2009. Dose of UV Light Required to Inactivate Listeria monocytogenes in Distilled Water, Fresh Brine, and Spent Brine. *Journal of Food Protection.* 72 (10): 2144-2150.

Meulemans, C. C. E. 1987. The Basic Principles of UV–Disinfection of Water. *Ozone: Science & Engineering: The Journal of the International Ozone Association*. 9 (4): 299-313.

Mondor, M., Girard, B., Moresoli, C. 2000. Modeling Flux Behavior for Membrane Filtration of Apple Juice. *Food Research International.* 33 (7): 539-548.

Murkes, J. 1990. Fundamentals of Crossflow Filtration. *Separation and Purification Methods*. 19 (1): 1-29.

Palnitkar M. P., McFeeters, R. F. 1975. Recycling spent brines in cucumber fermentations. Journal of Food Science. 40(6):1311–1315.

Peel, R. G., Benedek, A. 1980. Attainment of Equilibrium in Activated Carbon Isotherm Studies. *Environmental Science & Technology*. 14(1): 66-71.

Polyakov, Y. S. 2006. Deadend outside-in hollow fiber membrane filter: Mathematical model. *Journal of Membrane Science.* 279 (1-2): 615-624.

Proctor, A., Toro-Vazquez, J. F. 1996. The Freundlich Isotherm in Studying Adsorption in Oil Processing. *Journal of the American Oil Chemists' Society*. 73(12): 1627-1633.

Ramalho, R. S. 1983. Introduction to Wastewater Treatment Processes. 2nd Edition. 485-502.

Ratnani, K.,LeDuy, A., Ramalho, R. S. 1980. Activated carbon adsorption treatment of spent pickling brine. *The Canadian Journal of Chemical Engineering.* 58 (3): 325-331.
Redkar, S. G., Davis, R. H. 1993. Crossflow microfiltration of yeast suspensions in tubular filters. *Biotechnology Progress.* 9(6):625–634.

Reymann, S., Koenders, C. 2000. Filter Cake Formation and Volume-Time Curves in Dead-End Filtration. *Chemical Engineering and Technology*. 23 (6): 501-504.

Suidan, M. T., Severin, B. F. 1986. Light intensity models for annular UV disinfection reactors. *AIChE Journal*. 32(11): 1902-1909.

Scheible, O. K., Casey, M. C., Forndran, A. 1985. Ultraviolet disinfection of wastewaters from secondary effluent and combined sewer overflows. Report No. EPA/600/2-86/005, NTIS, Springfield, VA.

Taddei, C., Daufin, G., Aimar, P., Sanchez, V. 1989. Role of Some Whey Components on Mass Transfer in Ultrafiltration. *Biotechnology and Bioengineering.* 34 (2): 171-179.

Todorov, S. D., Franco, B. D. G. M. 2010. *Lactobacillus plantarum*: Characterization of the Species and Application in Food Production. *Food Reviews International*. 26 (3): 205-229.

Unluturk, S. K., Arastoopour, H., Koutchma, T. 2004. Modeling of UV dose distribution in a thin-film UV reactor for processing of apple cider. *Journal of Food Engineering.* 65: 125-136.

USDA, National Agricultural Statistics Service, Vegetable Yearbook 2012. "U.S. cucumbers for pickles: Supply, utilization, and price, farm weight, 1979-2011."

Wakeman, R. J., Tarleton, E. S. 2005. Solid/Liquid Separation: Principles of Industrial Filtration.

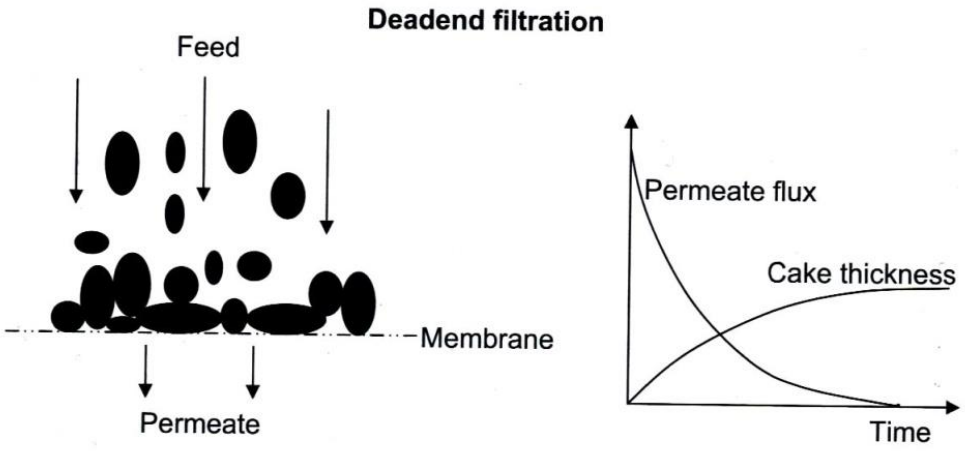

Figure 2.1 Deadend filtration diagram with relationship of cake thickness and permeate flux with respect to time (Wakeman and Tarleton, 2005)

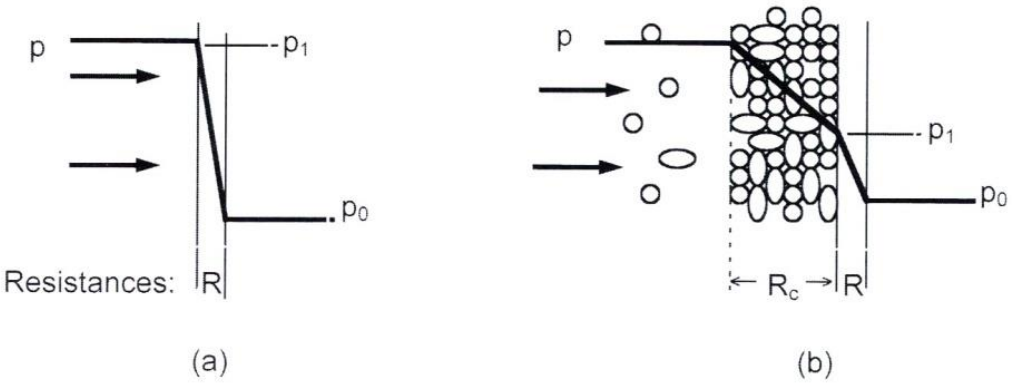

Figure 2.2 Effects of cake formation and membrane resistance on pressure differences (Wakeman and Tarleton, 2005)

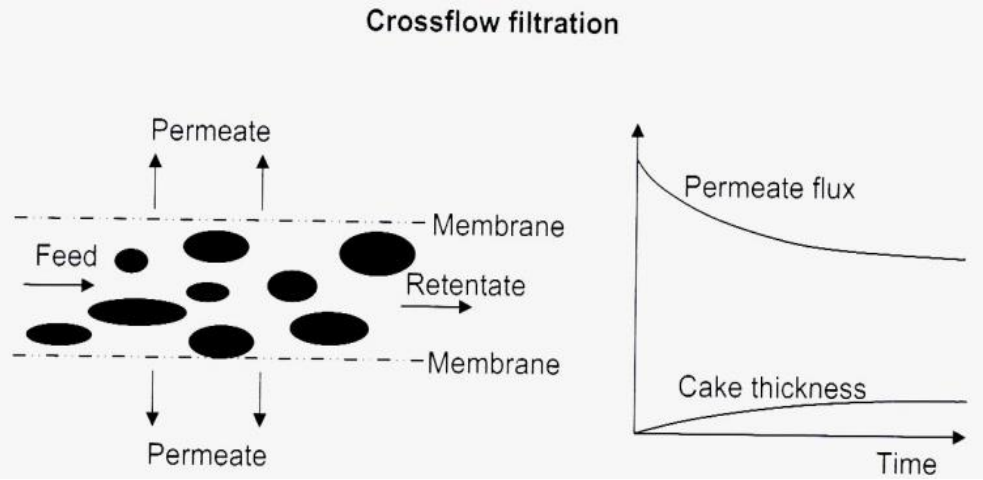

Figure 2.3 Crossflow filtration diagram with relationship of cake thickness and permeate flux with respect to time (Wakeman and Tarleton, 2005)

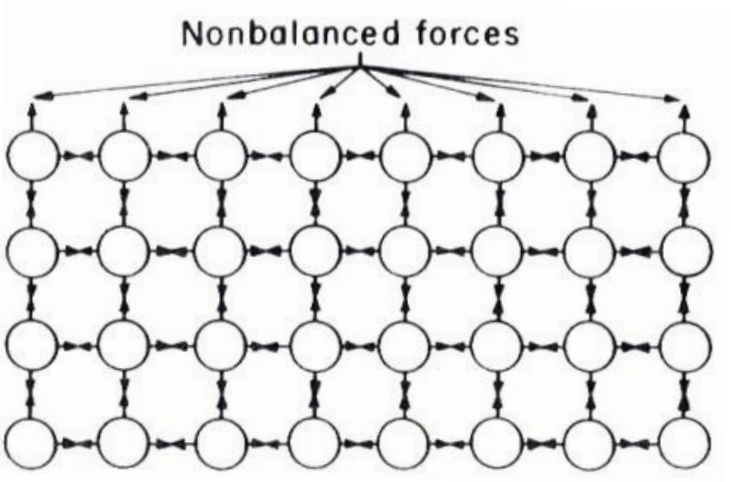

Figure 2.4 Nonbalanced forces in activated carbon that assist in the adsorption of solutes (Ramalho, 1983)

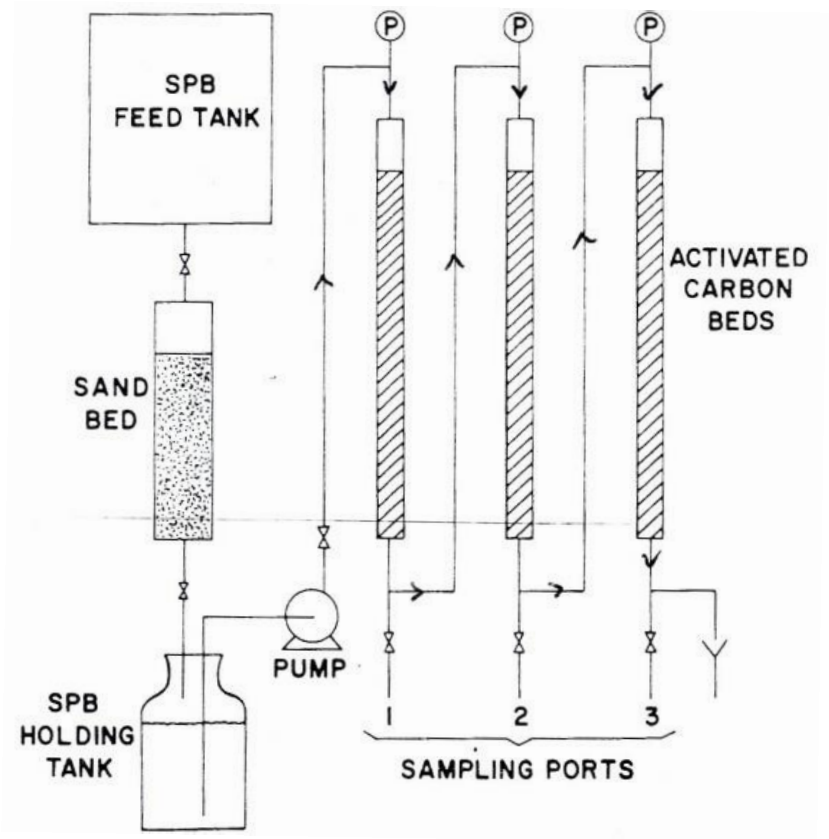

Figure 2.5 Adsorption column system used in the pilot testing of activated carbon in determining efficiency (Ratnani et al., 1980)

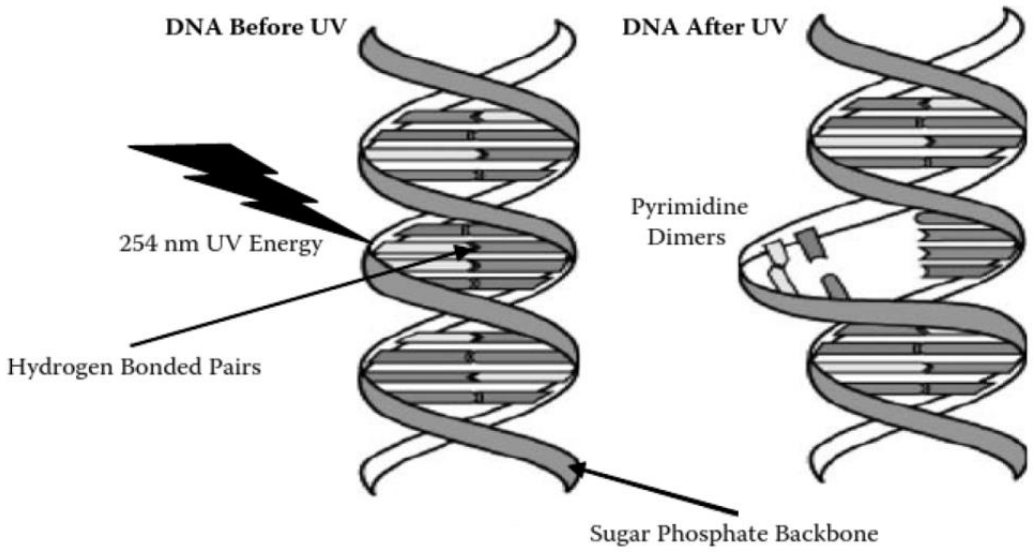

Figure 2.6 UV energy inactivating microorganisms by inhibiting transcription (Koutchma et al., 2009)

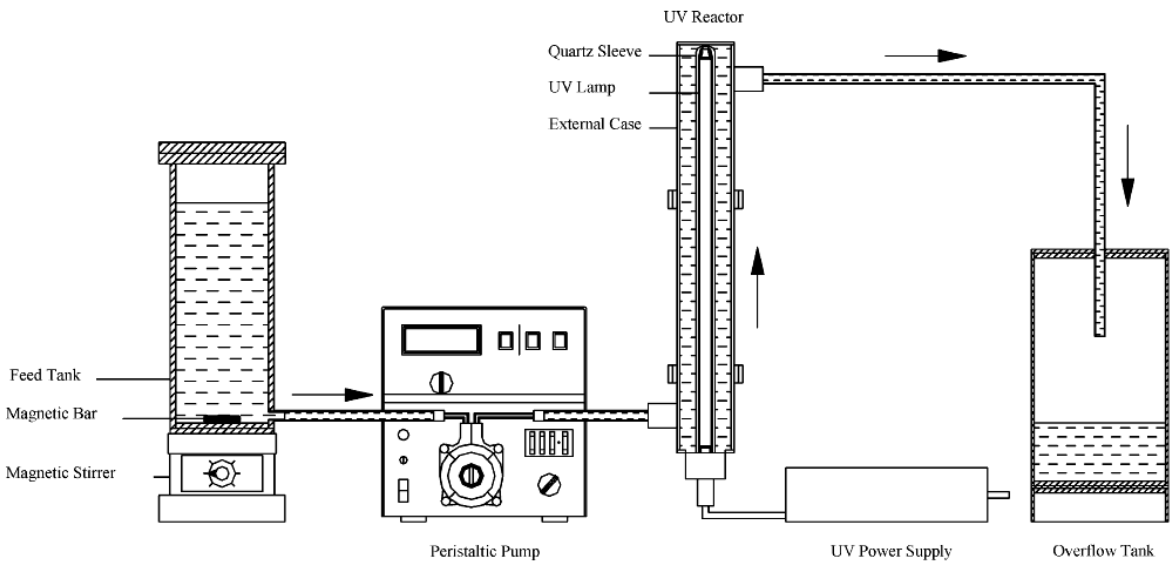

Figure 2.7 Common UV radiation set-up for microbial disinfection in liquids (Mahmoud and Ghaly, 2004)

Chapter 3

Physical and Microbiological Remediation of Spent Pickling Brine using Crossflow Filtration

3.1 Abstract

Pickle companies may benefit from the development of ways to reclaim spent pickling brine. Reclaiming spent brine represents an opportunity to diminish the environmental impact and cost of commercial production. The objective of this study was to (1) characterize spent brine from commercial cucumber fermentation operation and (2) determine the efficacy of crossflow filtration for remediation of spent brine. A particle size distribution analysis was completed to define the appropriate filter pore size. Testing was done using a benchtop crossflow filtration unit with a ceramic filter (0.8 µm pore size) selected for remediation of pickling brines. Turbidity measurements by nephelometry were used as indicators of brine clarification and monitoring tools for brine reclamation. Brine samples were then plated for microbiological analysis. The ceramic filter with the 0.8 µm pore size removed 98% of the undissolved particles in the spent brines as determined by particle size analysis. Corresponding to visual observations of very cloudy to clear, respectively, turbidity of the brine was reduced from an average of 730 ± 813 NTU to 2.69 ± 2.77 NTU; a reduction of 99.6%. Microbiological testing showed that filtration greatly reduced microbial counts. On average, 4 Log CFU/mL of lactic acid bacteria, total aerobic, and yeasts and molds were removed from the pickling brine using the 0.8 µm filter. The filtered brines were not sterile, but the microbial counts were below detectable limits (2 Log CFU/mL). The results from this research show that filtration is a viable option in physically and microbiologically remediating spent pickling brine.

3.2 Introduction

Spent brine used for cucumber fermentations contains about 6% NaCl. The fermentations occur in tanks that hold about 40,000 liters (Lu et al., 2012). In colder climates,

up to 12% NaCl is required to prevent freezing (Zhou et al., 2000). High salt concentration makes discharging of spent brine an issue. The US regulatory agencies have set stricter limits on the amount of chloride allowed for discharge in lakes or streams. Discharge from commercial pickle production facilities can regularly exceed such limits (Humphries and Fleming, 1989). Reusing the brine can __ the difficulties with the discharge of waste water with high chloride content and reduce the cost of such operation. It will also allow pickling companies to retain the salts and water in the brine which will reduce the cost of brine preparation (Ratnani et al., 1980).

Although recycling brine involving the use of incineration has been proposed to re salt while removing organic matter, it has been deemed cost prohibitive at the commercial scale (Durkee et al., 1973). Clarification of brines by alkalinization followed by decantation to eliminate coagulated proteins and acidification have been proposed to reclaim spent brine. Although this method is simpler, the cost of NaOH and HCl represents an important fraction of the total expense (Palnitkar and McFeeters, 1975).

The concept of filtration was explored here due to its efficiency in removing particles with specific sizes in a continuous process. Filter membranes come in either organic (cellulose and polycarbonate) or inorganic (ceramic and aluminum oxide) forms (Bowen and Jenner, 1995). The two main types of filtration include deadend and crossflow. Deadend filtration involves the feed flowing towards a filter membrane. As the feed flows through the filter, a cake layer forms on the filter. Over time, this cake increases until the feed can no longer flow through the filter (Wakeman and Tarleton, 2005). At this point, the run is terminated and the filter needs to be replaced. A backwash can be used to reduce cake formation but can result in long downtime (Mondor et al., 2000). Crossflow filtration entails

a high pressure feed flowing parallel to the filter. A cake layer forms on the membrane like deadend filtration but a shear force across the surface from the liquid flow reduces cake formation. This allows for a high flowrate through the filter membrane to be maintained (Fasina et al., 2003). Although crossflow systems tend to be more efficient than deadend systems, designing crossflow systems is more complex than that of deadend systems due to the consideration of three process streams: the feed, the permeate, and the retentate. Deadend systems involve only the feed and permeate streams (Zeman and Zydney, 1996). Fasina et al. (2003) crossflow filtered brine from cucumber fermentation using 0.05 and 0.2 μm hollow fiber polysulfone filtration membranes. The filtration process removed the sediments and microbial cells from the brine. However, if larger filter sizes could be used to remove the microbial cells and suspended particles, a higher throughput could be achieved. More brine would be able to be filtered before the process needs to be stopped to clean the filter and remove the fouling layer.

The objectives of this study were to (1) characterize spent pickling brines to determine an appropriate pore size for crossflow filtration and (2) test the ability of a bench top crossflow filtration unit with a ceramic membrane to improve the quality of the spent brine.

3.3 Materials and Methods

Spent Pickling Brines. Spent pickling brines used in this study were collected from two independent companies. Within each company, different brine types were acquired to represent the wide varieties of spent brines that may be encountered during commercial scale production. Two batches of brine samples were used from each company. Batch 1 from each company was received first and used for the laboratory scale deadend filtration test. Batch 2

was acquired later and used in the benchtop crossflow filtration system. Table 3.1 shows a list of the brine types used and their descriptions. The brines retrieved from Companies A and B were stored in five gallon buckets and one gallon jugs, respectively, and refrigerated at 4°C.

Particle Size Distribution. The particle size distribution of each brine was determined using a Mastersizer 3000, Hydro EV (Malvern Instruments Ltd., Malvern, Worcestershire, UK). The Mastersizer 3000 was capable of measuring particle sizes ranging from 0.01 – 3500 µm. A 600 mL beaker with 500 mL of deionized water was placed on the Hydro EV unit and the head of the unit was lowered in the beaker. The brine was added at 22 °C to the deionized water until the program read a % obscuration of 2-20%. Particle size distributions were collected and analyzed using the Mastersizer 3000 v.2.20 software. The refractive index of the brine samples was measured to allow for accurate particle size determination. It was measured at 22 °C using an Abbemat 550 refractometer (Anton-Paar, Graz, Austria). Droplets of brine were added to the measuring prism using a disposable pipette. The measurement prism was cleaned between measurements using a nonabrasive wipe.

Turbidity. Turbidity was determined using a 2100P Portable Turbidimeter (Hach Company, Loveland, CO). The turbidimeter was first calibrated using standards of 1, 10, 100, and 1000 NTU. Approximately 15 mL of brine at 22 °C was put into a clean glass vial which accompanied the turbidimeter. Nephelometric Turbidity Units (NTU) readings were automatically provided by the instrument and an average of independent duplicates were calculated for each brine type. The 2100P Portable Turbidimeter was capable of reading

turbidities ≤1000 NTU. Brine samples A9, B8, and B9 were diluted 3:1, 2:1, and 1:3, respectively, with deionized water to obtain accurate readings.

Microbiological Analysis. Brine samples were collected in 50 mL sterile conical tubes, serially diluted in 0.85% sterile saline solution, and spiral plated using an Eddy Jet 2 (IUL, S.A., Barcelona, Spain). Lactic acid bacteria were enumerated on Lactobacilli deMan Rogosa and Sharpe agar (MRS, Becton Dickinson and Co., Franklin Lakes, NJ) supplemented with 0.001% cycloheximide (0.1% solution, OXOID LTD., Basingstoke, Hampshire, England) to inhibit the growth of yeasts. MRS plates were incubated anaerobically using a Coy anaerobic chamber (Coy Laboratory Products, Inc., Grass Lakes, MI) at 30°C for 5 days. Yeasts were enumerated using yeast and mold agar (YMA, Becton Dickinson and Co.) supplemented with 0.01% chloramphenicol (Sigma-Aldrich, St. Louis, MO) and 0.01% chlortetracycline (Sigma-Aldrich) to inhibit bacterial growth. YMA plates were incubated aerobically at 30°C for 48 h. Total aerobic counts were determined by plating on Plate Count Agar (PCA, Becton Dickinson and Co., Franklin Lakes, NJ) and incubating for 24-48h at 30°C. All microorganisms were counted using a Flash and Go automated colony counter (IUL, S.A., Barcelona, Spain).

A 10ml portion of selected processed brine samples were centrifuged at 6,000 rpm for 15 min at 22 °C (Eppendorf Benchtop Centrifuge Model 5810R, Hauppauge, NY) to concentrate the remaining cells. The cell pellets were suspended in 0.85% saline solution to 1/10th of the original brine volume and spiral plated on the culture media described above to increase the limit of detection.

Deadend Filtration. Each brine type from Batch 1 was filtered through a Grade GF/B glass microfiber binder free 1 μm filter (GE Healthcare, Little Chalfont, UK) using a

vacuum Buchner funnel and flask. After filtering, each brine sample was placed in a 1 L Nalgene bottle (Nalge Nunc International, Rochester, NY) and refrigerated at 4°C.

Crossflow Filtration. A Membralox XLAB 5 Benchtop crossflow pilot unit (Pall Corporation, Port Washington, NY) equipped with a 0.8 µm ceramic membrane tube filter was used for experimentation. The brine was added into the feed tank where it was then pumped through the filter membrane core. The system was pressurized to 2.2 bar using a membrane valve located after the filter. The concentrated brine retentate was collected in a five gallon bucket and used as the feedstock for the next run. A backpulse device was attached to the filter housing to assist with efficiency optimization. A timer was set so that every 30 seconds a hydraulic piston re-injected 3 ml of permeate to minimize membrane fouling. This whole process was conducted 10 times for each brine type.

The order of runs for the brines was randomized. This was completed by using the =RANDBETWEEN ( ) function in Microsoft Excel. Each brine was assigned a random number between 1 and 2,000 using this function. The brines were then sorted from the lowest to highest using the assigned random number. The lowest assigned number brine was run first and the highest assigned number brine was run last.

Filtrate flowrate. The filtrate flowrate was determined using an EJ-2000 digital scale (A&D Company, Tokyo, Japan). The filtrate outlet was sent to a 600 ml beaker placed on the scale which was accompanied by a stopwatch. As soon as a run started, the stopwatch was started so that the mass of the filtrate (grams, g) was known over time (seconds, s). The mass of the filtrate over time was converted to volume (milliliters, ml) over time giving the flowrate (ml/s) over the course of a run.

Cleaning. Cleaning the membrane took place between brine types according to the manual accompanying the filtration unit. A 1% caustic solution containing potassium hydroxide and sodium hypochlorite was run through the system for one hour followed by a water run of one hour. Cleaning efficiency was determined by comparing the flow of water out of the filter with the initial flow of water through the filter before the system was first used.

Data Analysis. Data was compiled in an electronic spreadsheet. Calculations, averages and standard deviations were calculated in MS Excel.

3.4 Results and Discussion

Physical Remediation of Spent Pickling brine

The particle size distributions of spent pickling brines showed some similarities among the samples from both Companies A and B with 0.25 – 1.94% of the particles at 1 μm or smaller (Table 3.2). Particles of 1-2 μm in size showed to have the greatest relative proportion ranging from 43.9% for Batch 1 of Company A to 79.52% for Batch 1 of Company B. The majority of particles in the brine from Company B were < 3 μm. About 1.44% and 7.11% of the particles were greater than 3 μm for the brine in Batch 1 and 2, respectively. About 6.49% and 15.19% of the particles were greater than 5 μm for the brine in Batch 1 and 2, respectively. The large standard deviations shown in Table 3.2 for Batch 2 of Company A can be attributed to the addition of the spent blancher brines (A6 and A7). The blancher brines had greater concentrations of larger particles; especially A7 (Figure 3.1). This large variation caused an increase in standard deviations. All of this particle size data was new information for brine. Ratnani et al. (1980) evaluated the suspended solids (mg/L) and total solids (%) but a particle size distribution was not undertaken. Particle size distributions help determine the amount of particles removed using specific filter pore sizes.

These data suggest using a filter with a pore size of 1 μm would remove >98% of existing particles. Every 1 μm increase in pore size would be an expected significant decrease in the amount of particles retained. A filter with a pore size of 2 μm would only remove about 18.54% of all particles present in Batch 1 of Company B. Sequential filters could be used in series prior to the 1 μm pore size to allow for a better throughput compared to using the 1 μm filter alone. According to the particle size data (Table 3.2), using filters with pore sizes of 4, 3, and 2 μm would help alleviate the amount of fouling on the 1 μm filter.

Filtration of the brines from Batch 1 of both companies using a 1 μm membrane revealed the absence of detectable particle distributions by the Mastersizer 3000 which relies on 2% obscuration The 1 μm deadend filtered brine was unable to reach this percent obscuration when passed through the particle size analyzer. Thus it is concluded that the 1 μm filter did remove nearly all of the particles as hypothesized.

The turbidities of the brines from Batch 1 for both companies were significantly reduced after deadend filtration through the 1 μm filter (Figure 3.2). The unfiltered, spent brine samples in Batch 1 had a wide range of 9.89 – 823 NTU with a median value of about 400 NTU. Although the majority of the turbidities were >100 NTU, there were instances where the turbidity of an unfiltered, spent brine was as low as 9.89 NTU. After filtration, the brine was found to have significantly lower values. The turbidity of the brine ranged from 1.22 – 14.17 NTU with a median value of about 4.3 NTU.

The unfiltered, spent brines in Batch 2 from Company A and B were found to have a wider array of turbidities than Batch 1. The values ranged from 50.4 – 2760 NTU with a median value of 451 NTU (Figure 3.2). This wider range of turbidities in Batch 1 can be attributed to the particle size distributions (Table 3.2). For Batch 1, the majority of the

particles are in the lower size range (<3 μm). The particles in Batch 2 are more evenly distributed among all of the size ranges which would result is a wider range of turbidities. The brines from Batch 2 were crossflow filtered through the 0.8 μm pore size. After filtration, the turbidities decreased significantly. The turbidities of the filtered brine ranged from 1.12 – 10.68 NTU with a median value of 1.37 NTU. These 0.8 μm filtered turbidities had a higher concentration of lower values compared to the turbidities of the 1 μm filtered brine. While the 0.8 μm crossflow filtered brine had 75% of the turbidities below 2.73 NTU, the 1 μm deadend filtered brine had 75% below 7.41 NTU in agreement with the smaller filter pore size.

The appearance of the unfiltered spent brines were similar for most of the samples and were described as cloudy with a yellow tint. After both deadend and crossflow filtration, the yellow tint was still apparent but the cloudiness was absent (Figures 3.4 & 3.5). All filtered brines had a similar appearance. There was no noticeable visual difference between the filtered brine with the lowest turbidity (1.12 NTU) and highest turbidity (14.17 NTU) based on color and clarity.

Crossflow Filtration System Performance

Although, the crossflow filtration system utilized could not to be used for scaling a full size production system, qualitative lab scale testing provided sufficient information for an initial assessment. The 0.8 μm ceramic membrane tube, having a filtration surface area of only 50 cm^2, was too small to be scaled up. However, performance data such as permeate flowrates were still collected and analyzed.

For the crossflow system, the flowrate of the filtrates for the brines followed a similar pattern. About 5 gallons of each brine from Company A was available for use compared to

about 2 gallons for Company B. This resulted in longer run times for Company A (Figure 3.5) than Company B (Figure 3.6). As each run progressed, the filtrate flowrate decreased. Once the backpulse occurred, the flowrate increased to a maximum flowrate where it then began to decrease again until the next backpulse occurred. This cycle repeated itself until all of the brine was used up. A similar trend was seen in the work of Fasina et al. (2003). Although their system cycled the retentate and permeate back into the feed tank, there was a noticeable decrease in flow rate as each run progressed as a result of membrane fouling. Past crossflow filtration experiments of microbial cells had similar results as well (Makardij et al., 1999; Patel et al., 1987; Zahka and Leahy, 1985; Taddei et al., 1990).

Hoffman et al. (1987) used crossflow filtration for yeast fermentations and found that flowrates decreased over time with high cell concentrations. It was also found that backpulsing could be used to assist in higher flowrates. The membrane fouling in this current study resulted in an impeded flow through the filter until the backpulse occurred which forced filtered brine through the filter in the opposite direction, removing some of this build-up. As each run was completed, the overall flowrates decreased. Even though backpulses were occurring throughout each run, they were not fully removing the particles retained by the membrane. The maximum amount of filtrate produced occurred in the first pass of brine through the filter (Run 1). As each run was completed, the average amount of filtrate produced decreased. The implications of this on a commercial scale are that if a filter of this pore size is to be used, backpulsing and filter cleaning will still need to be completed. This will result in less time available for spent brine treatment. The decision if this is a viable option is up to whether or not the commercial facility has the time and resources available to properly treat the filters when fouling occurs.

Microbiology of Spent Pickling Brine

The 1 µm deadend filtration reduced all microbial counts tested (Table 3.3). Initial counts from the unfiltered brines of Batch 1 from Company A were consistently higher than those from Company B. This suggests that the lower microbial counts found after filtration are a function of lower initial counts. On average, 1µm deadend filtration removed 3 Log CFU/mL of microbial cells from the brines. The filtrate produced by Fasina et al. (2003) was free of microbial cells after crossflow filtration. Membranes with pore sizes of 0.05 and 0.2 µm were used so the effectiveness of a 0.8 µm filter to remove microbial cells from pickling brine was unknown. The 0.8 µm ceramic filter reduced microbial loads from Batch 2 to levels below the minimum detection level of 1.60 Log CFU/mL (Table 3.3). An average of 4 Log CFU/mL was present in the unfiltered brines. Once the samples were filtered in the crossflow filtration unit, all microbial counts were reduced to levels below detection. This does not mean that the brine is a sterile solution upon exiting the 0.8 µm ceramic filter. Minimal microbial counts could still be present which would not be a concern for tankyard reuse. The brine used for cucumber fermentations is not a sterile solution so using this filtered brine would be acceptable for future fermentations.

3.5 Conclusions

The crossflow filtration of spent brine has the possibility of addressing the issue of spent brine quality deterioration during fermentation and bulk storage. The opportunity to reduce waste and cost of commercial production is possible through the reclamation of spent brine. The crossflow filtration of spent brine was known to significantly reduce microbiological counts but small filter sizes were used that would make its use on a commercial scale very challenging. In this study, it was found that the use of a 0.8 µm

crossflow filter can physically remediate brine by removing nearly all undissolved particles which contribute to turbidity. Microbial counts were also decreased below detectable limits (2 Log CFU/mL).

This understanding of the efficacy of the 0.8 µm crossflow filter treating spent brine can assist in understanding if this crossflow filtration system can be used on a commercial scale. The size of the crossflow filtration system used did not make it possible to scale up the completed operations, however, this study did make it known what the quality of the spent brine would be like before and after a 0.8 µm crossflow, ceramic filter. Future work will need to be completed involving the use of a pilot scale system using a 0.8 µm crossflow ceramic filter. This would be done on-site at the fermentation yard and would help determine if a full-scale system would be economically possible.

References

Bowen, W. R., Jenner, F. 1995. Theoretical Descriptions of Membrane Filtration of Colloids and Fine Particles: An Assessment and Review. *Advances in Colloid and Interface Science*. 56: 141-200.

Durkee, E. L., Lowe, E., Baker, K. A., Burgess, J. W. 1973. Field Tests of Salt Rey System for Spent Pickling brine. *Journal of Food Science*. 38(3): 507-511.

Fasina, O. O., Fleming, H. P., Humpries, E. G., Thompson, R. L., Reina, L. R. 2003. Crossflow Filtration of Brine from Cucumber Fermentation. *Applied Engineering in Agriculture.* 19 (1): 107-113.

Hoffman, H., Scheper, T., Schugerl, K. 1987. Use of membranes to improve bioreactor performance. *Chemical Engineering Journal*. 34: B13-B19.

Humphries, E. G., Fleming, Henry P. 1989. Anaerobic Tanks for Cucumber Fermentation and Storage. *Journal of Agricultural Engineering Research*. 44: 133-140.

Lu, Z., Pérez-Díaz, I. M., Hayes, J. S., Breidt, F. 2012.Bacteriophage Ecology in a Commercial Cucumber Fermentation. *Applied Environmental Microbiology.* 78 (24): 8571-8578.

Makardij, A., Chen, X. D., Farid, M. M. 1999. Microfiltration and ultrafiltration of milk: some aspects of fouling and cleaning. *Transactions of the Institute of Chemical Engineers*. 77 (C2): 107-113.

McFeeters, R. F., Pérez-Díaz, I. 2010. Fermentation of Cucumbers Brined with Calcium Chloride Instead of Sodium Chloride. *Journal of Food Science.*75 (3): 291-296.

Mondor, M., Girard, B., Moresoli, C. 2000.Modeling Flux Behavior for Membrane Filtration of Apple Juice. *Food Research International.* 33 (7): 539-548.

Palnitkar M. P., McFeeters R. F. 1975. Recycling spent brines in cucumber fermentations. Journal of Food Science. 40 (6): 1311–1315.

Patel, P. N., Mehaia, M. A., Cheryan, M. 1987. Cross-flow membrane filtration of yeast suspensions. *Journal of Biotechnology.* 5 (1): 1-16.

Ratnani, K., LeDuy, A., Ramalho, R. S. 1980. Activated carbon adsorption treatment of spent pickling brine. *The Canadian Journal of Chemical Engineering.* 58 (3): 325-331.

Taddei, C., Daufin, G., Aimar, P., Sanchez, V. 1989. Role of Some Whey Components on Mass Transfer in Ultrafiltration. *Biotechnology and Bioengineering.* 34 (2): 171-179.

Wakeman, R. J., Tarleton, E. S. 2005. Solid/Liquid Separation: Principles of Industrial Filtration.

Zahka, J., Leahy, T. J. 1985. Practical aspects of tangential flow filtration in cell separations. In *Purification of Fermentation Products: Applications to Large Scale Processes,* eds.

Zeman, L. J., Zydney, A. L. 1996. Microfiltration and Ultrafiltration Principles and Applications. New York: Marcel and Dekker, Inc.

Zhou A., McFeeters R. F., Fleming H. P. 2000. Development of oxidized odor and volatile aldehydes in fermented cucumber tissue exposed to oxygen. *Journal of Agricultural Food Chemistry*. 48(2): 193-197.

Table 3.1 Representative spent brines from two commercial pickle producers

Source	Brine	Description
Company A, Batch 1[1]	A1	Brine from the brine station where it is "refreshed"
	A2	Clear brine taken from a prolonged fermentation tank
	A3	Cover brine in which cucumbers are imported from overseas
	A4	Brine typically seen in a tank after an average fermentation time
Company A, Batch 2[2]	A5	45 degree salometer brine (approx. 13% salt – <1 grains of acid; made using the barrel brine) for tanking of fresh cucumbers
	A6	45 degree salometer brine (approx. 13 % salt – <1 grain of acid; made using the blancher brine) for tanking of fresh cucumbers
	A7	Blancher brine (approx. 14% salt) – brine that was used to make fresh cucumbers easier to pack.
	A8	Used brine (7% salt – approx. 5 grains of acid - more turbid)
	A9	Barrel brine (no vinegar) - (7 – 10% salt and 2 – 6 grains) from imported brined stock
	A10	Used brine (7% salt - approx. 5 grains of acid – somewhat clear)
	A11	Vinegar brine (approx. 25 gr – 4% salt) from imported cucumbers that are considered fresh
Company B, Batch 1[1]	B1	Brine from an aisle with a high rate of softening enzyme
	B2	Brine from an aisle with a high rate of softening enzyme
	B3	Brine typically seen after an average fermentation time
	B4	Comingled brine from newly fermented tanks
	B5	Comingled brine from a previous season that was not yet used in a new tank of pickles to be "refreshed"
	B6	Brine from a newly fermented tank
Company B, Batch 2[2]	B7	Old brine with very high level of softening enzyme
	B8	Old brine with high level of softening enzyme
	B9	Brine typically after an average fermentation time and bulk storage
	B10	Brine typically after an average fermentation time and bulk storage

[1]Deadend filtered through 1 µm pore size
[2]Crossflow filtered through 0.8 µm pore size

Table 3.2 Cumulative particle size distribution in spent brines (n=21) from two commercial pickle companies

	Company A		Company B	
Size Range	Batch 1 (n=4)	Batch 2 (n=7)	Batch 1 (n=6)	Batch 2 (n=4)
>1 µm	99.75 ± 0.35	98.74 ± 0.61	98.06 ± 0.25	99.43 ± 0.58
>2 µm	55.85 ± 12.9	33.11 ± 14.7	18.54 ± 4.03	33.83 ± 4.76
>3 µm	19.91 ± 3.22	13.45 ± 14.4	1.44 ± 3.23	7.11 ± 4.24
>4 µm	9.19 ± 4.63	17.07 ± 12.4	1.27 ± 2.84	6.12 ± 1.39
>5 µm	6.49 ± 4.61	15.19 ± 12.3	0.92 ± 2.06	4.63 ± 1.06

Table 3.3 Microbial counts (Log CFU/mL) for the spent pickling brines filtered in Deadend (n=10) and Crossflow (n=11) systems

	1 μm (Deadend Filtration)		0.8 μm (Crossflow Filtration)	
	Unfiltered	Filtered	Unfiltered	Filtered
		Lactic Acid Bacteria		
Company A	4.01 ± 1.41	3.13 ± 0.37	<1.60	<1.60
Company B	3.27 ± 1.10	<1.60	3.32 ± 0.91	<1.60
		Total Aerobic		
Company A	5.50 ± 0.35	2.86 ± 0.45	4.76 ± 0.09	<1.60
Company B	3.87 ± 0.57	<1.60	4.43 ± 1.17	<1.60
		Yeasts and Mold		
Company A	5.07 ± 0.63	3.06 ± 0.29	4.74 ± 0.17	<1.60
Company B	3.64 ± 1.20	<1.60	4.11 ± 1.4	<1.60

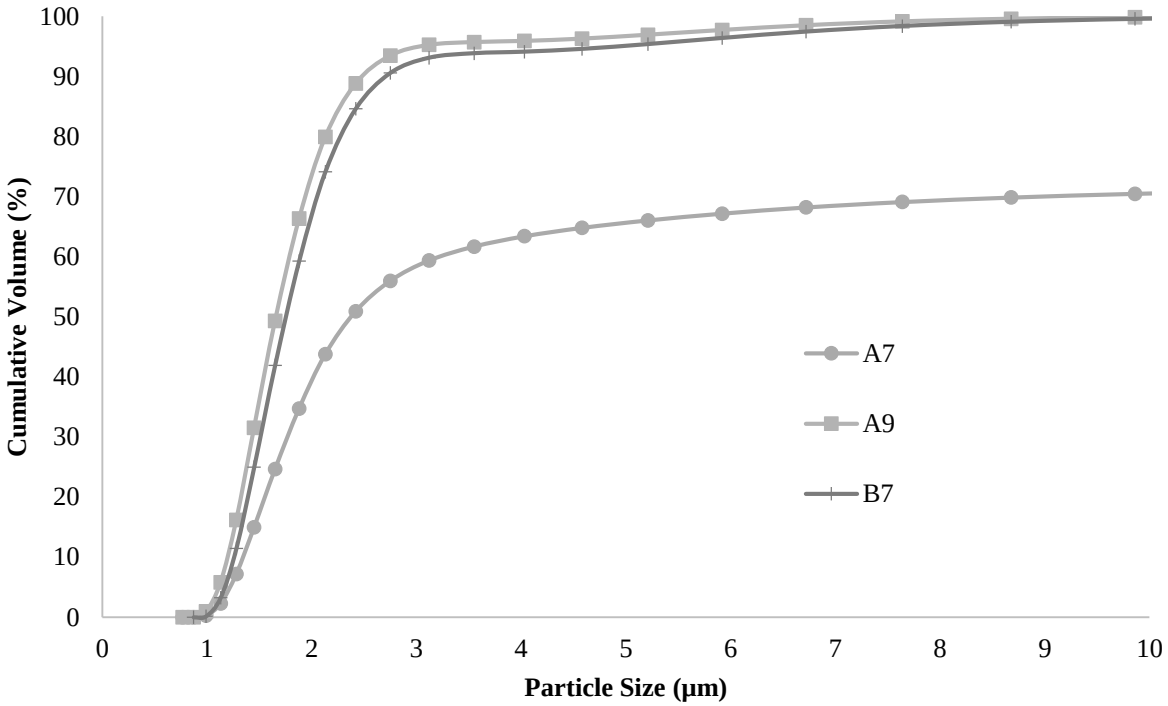

Figure 3.1 Particle size distribution comparison between the spent blancher brine (A7) and two common spent fermentation brines (A9 & B7)

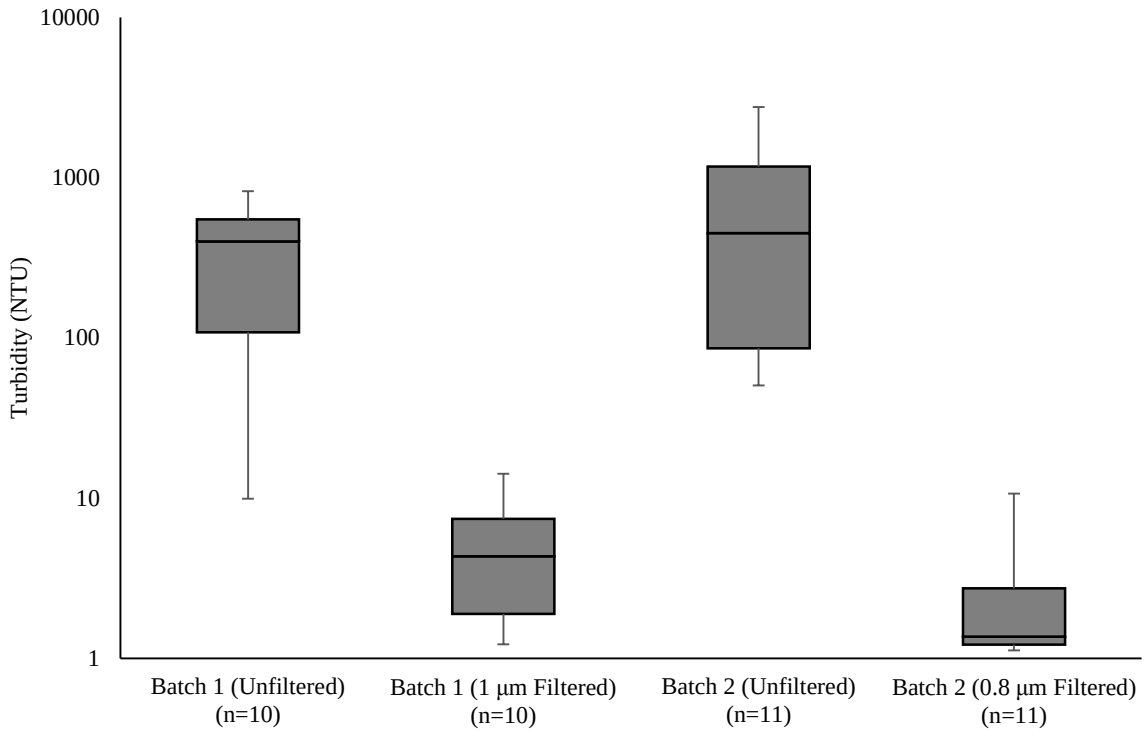

Figure 3.2 Turbidity distributions of the spent pickling brines before and after filtration from two geographically distant commercial facilities

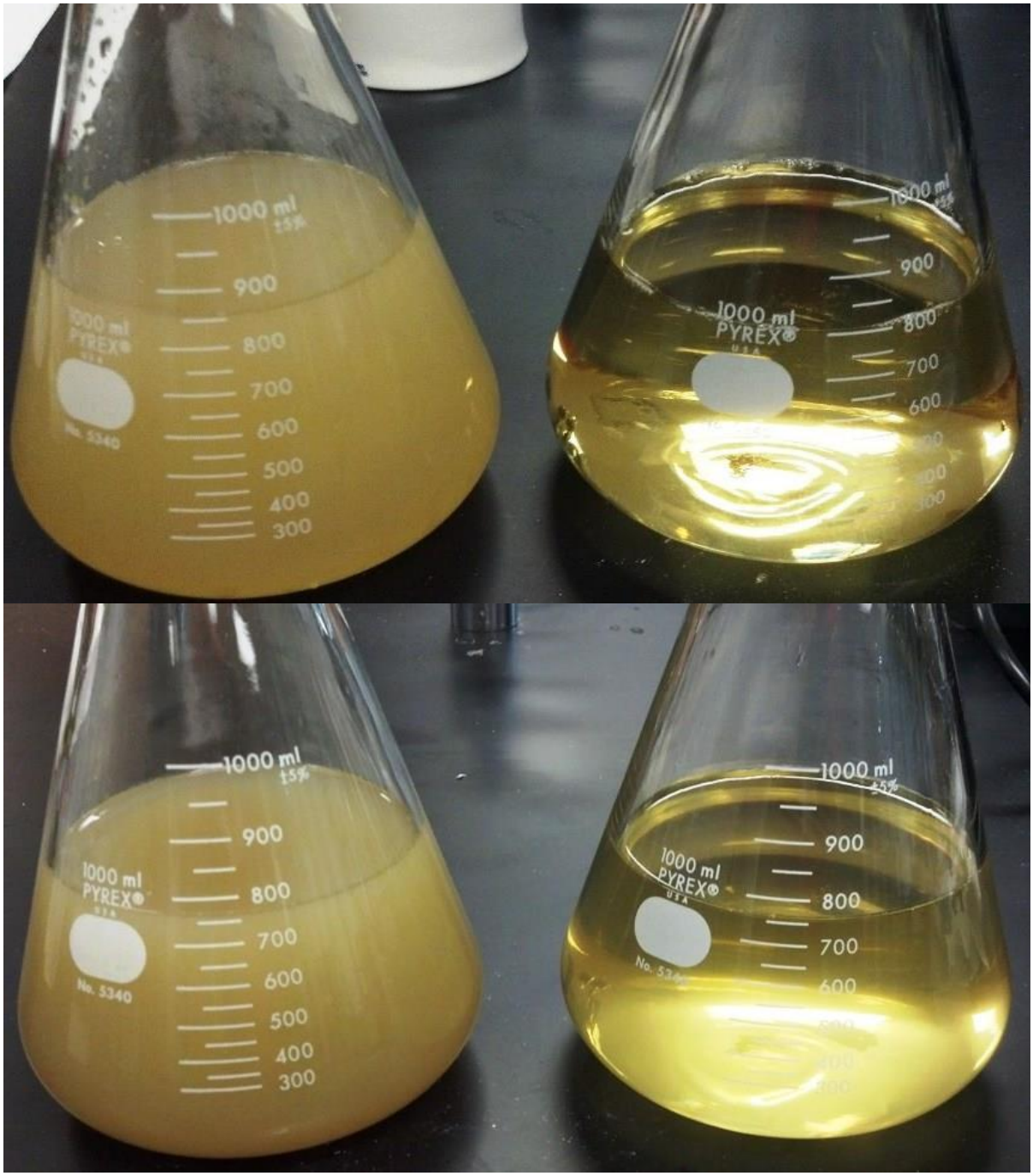

Figure 3.3 Unfiltered brine from Batch 1 with turbidities of 474 NTU (top left) and 823 NTU (bottom left) deadend filtered with a 1 μm filter to give turbidities of 1.95 NTU (top right) and 14.2 NTU (bottom right), respectively

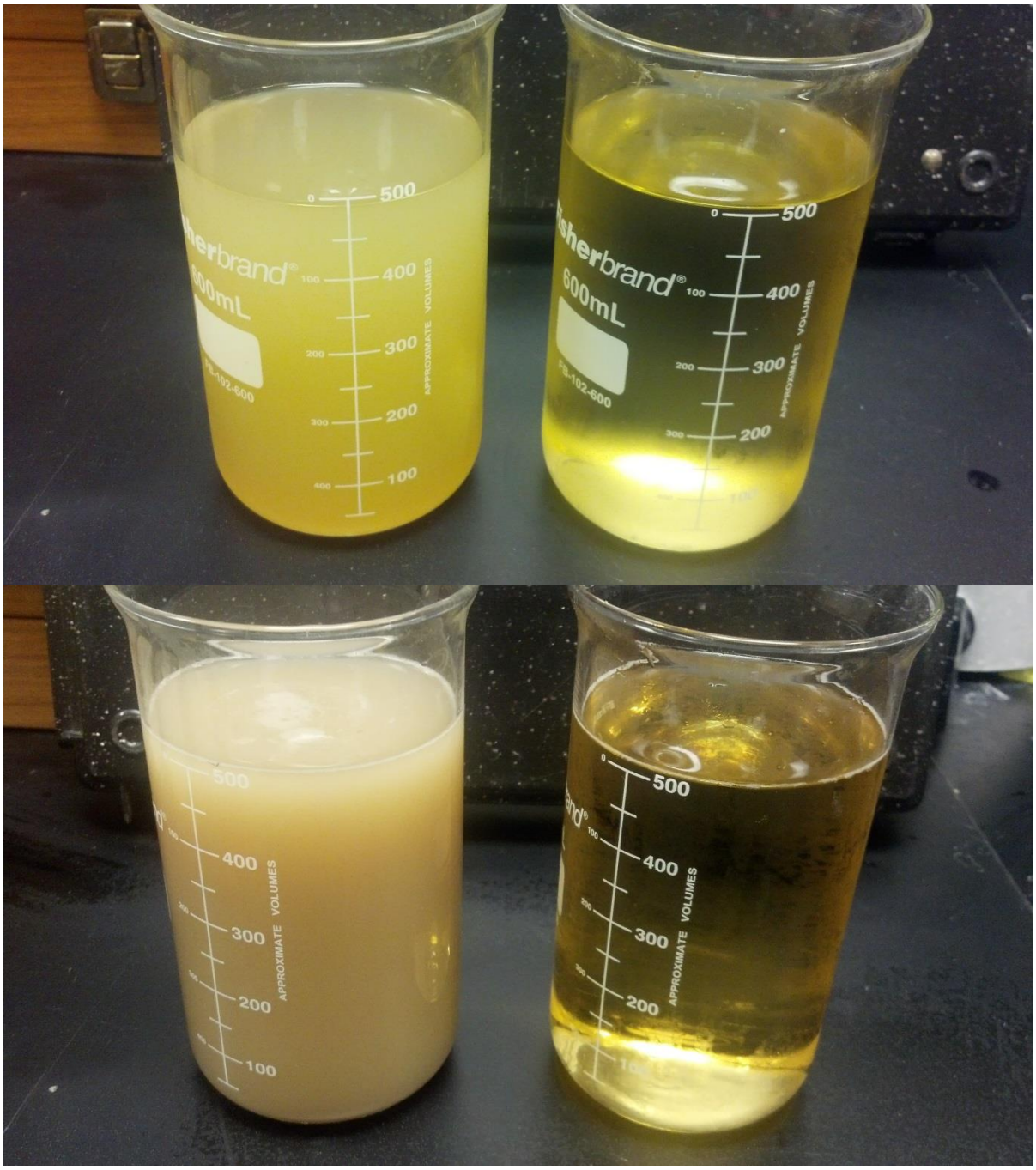

Figure 3.4 Unfiltered brine from Batch 2 with turbidities of 451 NTU (top left) and 2760 NTU (bottom left) crossflow filtered with a 0.8 μm filter to give turbidities of 10.68 NTU (top right) and 2.34 NTU (bottom right), respectively

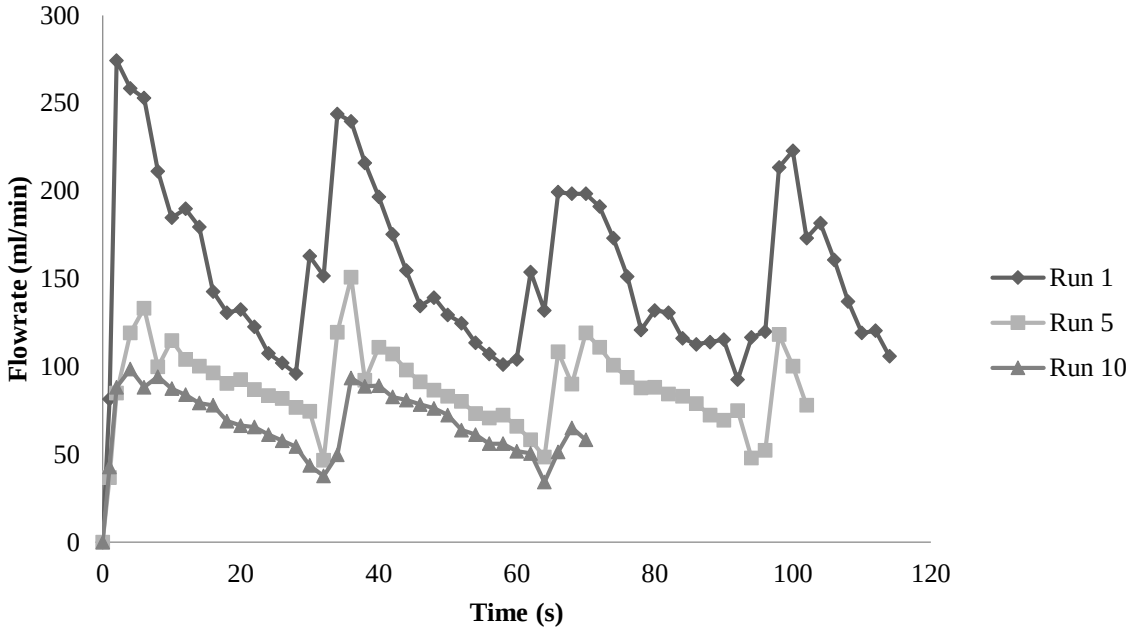

Figure 3.5 Average filtrate flowrates from the crossflow filtration system with a 50 cm^2 ceramic filter area and 0.8 µm pore size for the brines of Batch 2 from Company A

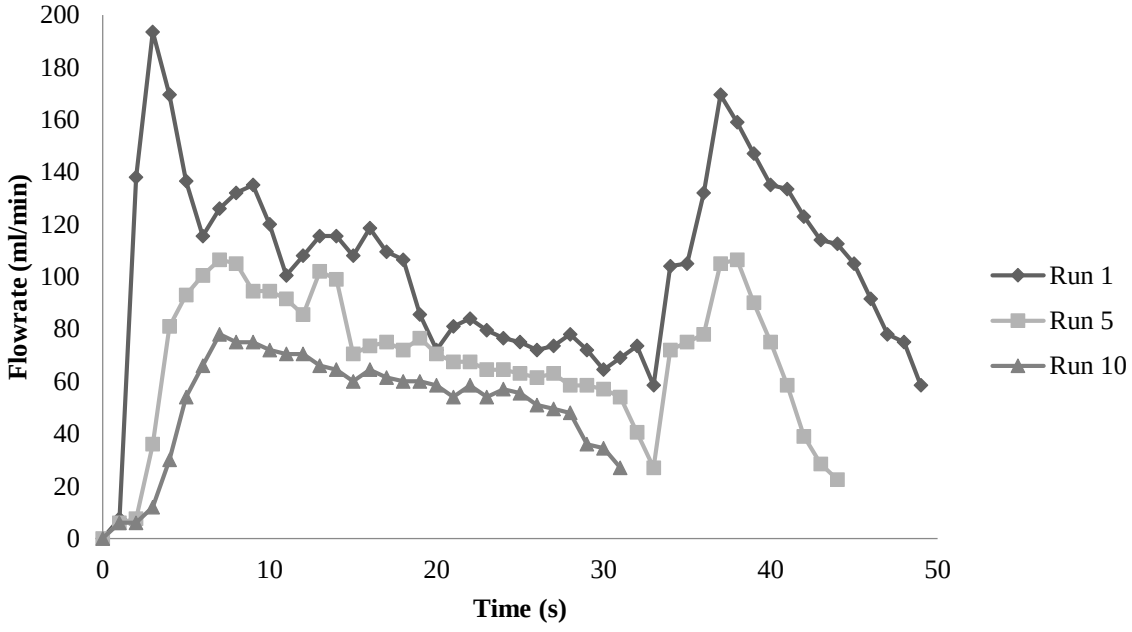

Figure 3.6 Average filtrate flowrates from the crossflow filtration system with a 50 cm^2 ceramic filter area and 0.8 µm pore size for the brines of Batch 2 from Company B

Chapter 4

Remediation of Filtered, Spent Pickling Brines

Using Activated Carbon

4.1 Abstract

The pickle industry is considering methods for remediating spent brine that deteriorates in quality during cucumber fermentations. This deterioration is the result of chemical changes during bulk storage which includes occasional changes in pH with concurrent conversion of organic acids post-fermentation that may lead to off-odors and flavors. Inability of companies to reclaim spent brines resulting from oxidation represents higher operational costs for pickle processors. The goal of this study was to test the ability of activated carbon to remove organic compounds in the spent brine that have been related to off-odors. Batch testing of two types of activated carbon in increasing amounts (2 – 32 g/100 ml) was competed and changes in total organic carbon (TOC) were used to identify an ideal carbon use rate to employ. The amount of 16g/100 ml was identified as the appropriate amount to be used for all brine types because it provided the maximum reduction or near maximum reduction of the parameters tested. Using this treatment, the TOC levels were reduced from an average of 5273 to 2507 mg TOC/L; a 53% reduction. Activated carbon was known to reduce TOC levels in spent brine but the specific components that make up the total TOC have not been examined. These include lactic and acetic acid and volatile compounds. On average, the initial lactic and acetic acid concentrations were 75.28 and 23.99 mM, respectively. The use of 16 g/100 ml reduced the average lactic and acetic acid concentration to 48.86 mM and 8.75 mM for a reduction of 35 and 64%. The volatile compounds that contribute to off flavors and odors were also reduced. Of the 142 compounds detected, 68 were reduced to below detectable limits and 47 were partially removed. All of these results express the effectiveness of activated carbon in treating spent brine to address the issues related to the deterioration of spent brine quality.

4.2 Introduction

Pickling cucumbers are commercially fermented in 40,000 L, open-top tanks using a brine solution of 6% NaCl (Lu et al., 2012). After the fermentation period, more salt could be added up to 12% (Zhou et al., 2000). These salt concentrations are necessary for selecting homofermentative lactic acid bacteria to carry out the fermentation process and to protect against microbial spoilage during long-term storage (Zhou and McFeeters, 1998). Reports of the spoilage of fermented cucumbers associated with unpleasant odors from the fermentation tanks have come forward from the cucumber pickling industry (Franco et al., 2012). A change in brine pH has also been reported as a cause of fermented cucumber deterioration. The production of lactic acid is a reason for this change in pH as well as the production of acetic, butyric, and propionic acids (Fleming et al., 1989).

Cucumber pickles are also susceptible to oxidation reactions that have negative effects on quality during bulk storage, processing, and shelf storage. Fermentation tanks are open to the atmosphere to allow exposure to sunlight and air that unfortunately promote these reactions (Buescher and Hamilton, 2000). The brines also contain traces of prooxidant metals which are responsible for the oxidation of pigments and development of off-flavors (Eisenstat and Fabia, 1953).

The reuse of brine from prior fermentations has become a practice in the cucumber pickle industry. However if spoilage occurs, this option is no longer viable (Lu et al., 2012). Discharge of the spent brine is an alternative to immediate reuse but the high salt waste generated makes this a continuous issue (McFeeters and Pérez-Díaz, 2010). A few methods have been developed to recycle spent brine. Durkee et al. (1973) examined the use of a combustion system which involved the evaporation of liquid and recovery of salt. The cost of

evaporating massive amounts of brine was found prohibitive and inefficient. Palnitkar and McFeeters (1975) proposed clarifying the brine by alkalinization followed by decantation to eliminate coagulated proteins followed by acidification. Although this method is simpler, the cost of NaOH and HCl represents an important fraction of the total cost. Another method investigated involved crossflow filtration of brine from cucumber fermentation through membranes with pore sizes of 0.05 and 0.2 μm (Fasina et al., 2003). The filtration process removed the sediments and microbial cells from the brine but had no effect on the chemical characteristics, which could influence product quality in subsequent fermentations.

The use of activated carbon was employed for this research to address the organic compounds of concern. Activated carbon uses the phenomenon of physical adsorption which is the adhesion of solutes (adsorbates) to the surface of a solid (adsorbent) (Ramalho, 1983). Activated carbon has been used on large scales as an adsorbent to remove contaminants that affect taste and odor. These large scale applications are mainly associated with wastewater and drinking water facilities, where the organic carbon load is relatively low (Matsushita et al., 2008). Isotherm testing is completed first which includes carbon being tested in batches to determine activated carbon feasibility. The isotherm batches help understand carbon bed life and predict location of the breakthrough curve which depicts the progression of the contaminant concentration as a function of adsorption parameters such as contact time and amount of carbon used (Peel, 1980). Naturally occurring organic matter can significantly reduce the effectiveness of activated carbon. This is generally quantified in terms of total organic carbon (TOC) but can also be measured by the individual components that make up the TOC (Kilduff et al., 1998).

Ratnani et al. (1980) tested the filtration of spent brine through activated carbon beds in series. Brine was continuously fed through the activated carbon beds for 12 hours. Efficiency was based on the ratio of the outlet to initial TOC concentrations. Since TOC was solely looked at, other components such as acid concentrations and volatile compounds that make up the total TOC were not analyzed to understand how well activated carbon removes specific components. The objective of this study was to test the efficiency of activated carbon to address the issues that contribute to spent brine quality.

4.3 Materials and Methods

Filtered, Spent Pickling Brines. The brine used in this study was sampled from two different companies. Within each company, different brine types were acquired to represent the wide varieties of brines within each company. Testing results for the brines were combined by company to show trends as averages. The list of brine types and descriptions are shown in Table 4.1. The brines retrieved from both of the participating companies were stored in five gallon buckets and one gallon jugs in a 4°C refrigerator, respectively. All spent brines used were previously filtered through a 0.8 μm ceramic crossflow filter prior to the carbon treatment.

Carbon Testing. The activated carbon used in this study was supplied by Calgon Carbon, Pittsburgh, PA. The two types of powdered activated carbon were BL and WPC. The BL was a coal based carbon and the WPC was a coconut based carbon. The granular activated carbon (Filtrasorb 400 (F400)) used was a coal-based carbon.

Equilibrium testing was completed to determine the contact time needed between the carbon and brine for all surface area of the carbon to be used. Testing was performed on brine sample “A8” (Table 4.1). One hundred mL of the brine was placed in two sets of five

250 mL Erlenmeyer flasks. For one set, 16 g of the BL carbon were placed in each flask and for the other set, 16 g of the F400 carbon were placed in each flask. The flasks were placed on a G10 Gyrotory shaker (New Brunswick Scientific Co., Inc., Edison, NJ) set to 250 rpm. The flasks for each set were run for times of 0.5, 1, 2, 4, and 6 hours. The carbon treated brines were then filtered through a Grade GF/B glass microfiber binder free 1 μm filter (GE Healthcare, Little Chalfont, UK) using a vacuum Buchner funnel and flask to remove the spent carbon. Treated brines were stored in a 4°C refrigerator and analyzed for TOC concentrations.

The next set of experiments involved the testing of carbon in increasing amounts. This was done to determine the effects the different amounts of carbon had on the brines. The two brines used were the "A10" and "B8" (Table 4.1) and the two carbons used were the BL and WPC carbons. For each brine type, 100 mL were placed in two sets of seven 250 mL Erlenmeyer flasks. For each set, weights of 0.5, 1, 2, 4, 8, 16, and 32 g of activated carbon were placed in the flasks. BL carbon was placed in one set and WPC the other. The flasks were placed on the shaker set to 250 rpm for two hours. This was repeated for each brine type. The carbon treated brines were then filtered as before. Treated brines were stored in a 4°C refrigerator for TOC, HPLC, and transmittance analysis. For GC x GC analysis, samples were stored in a -80°C freezer.

The final set of tests was done to understand how the targeted amount of carbon (16 g/100 ml) affected all eleven brine types (Table 4.1). One hundred mL of each brine type was placed in a flask with 16 g of the BL carbon. The flasks were placed on the shaker set to 250 rpm for two hours. This process was done in triplicate. The carbon treated brines were then

filtered. Treated brines were stored in a 4°C refrigerator for TOC, HPLC, polygalacturonase, and transmittance analysis. For GC x GC analysis, samples were stored in a -80°C freezer.

Total Organic Carbon (TOC). TOC was determined by using an Apollo 9000 TOC Combustion Analyzer (Teledyne Instruments, San Diego, CA). The methods followed for testing included EPA 415.1 and 9060A and Standard Method 5310B. An injection volume of 0.05 mL and a sparge volume of 0.01 mL were used. Samples were diluted to 1% due to the high salt content present in the samples. Brine samples were stored in 40 mL Qorpak Clear Borosilicate Vials, Cleaned for Total Organic Compounds (TOC) (Fisher Scientific, Waltham, MA) and placed in a 4°C refrigerator prior to testing.

High Performance Liquid Chromatography (HPLC). Analysis was done using the 1260 Infinity Quaternary LC System (Agilent Technologies, Santa Clara, CA) with a diode array detector. Components of the samples were separated on an Aminex HPX-87H column (Bio-Rad Laboratories, Hercules, CA) with a Bio-Rad Micro-Guard Cation H column. 0.03N sulfuric acid in water was used isocratically at a flow rate of 0.6 mL/min. The column was kept at 37°C. A wavelength of 210 nm was used for detection of organic acids. The samples were held at 4°C in the autosampler tray prior to injection.

Samples were initially stored in a 4°C refrigerator prior to sampling. They were removed from the freezer and allowed to be completely thawed then vortexed. 1 mL of each sample was placed in a microcentrifuge tube and centrifuged at 10,000 rpm for 8 minutes. A 400 µL aliquot of the supernatant was transferred to glass vials compatible with the autosampler attached to the HPLC used.

GC x GC – ToF MS. GC x GC – ToF MS analysis was performed as described by Johanningsmeier and McFeeters (2011) with the following modifications: spent brine

samples (100 µL) were diluted 1:10 with deionized water (886 µL), 3N H_2SO_4 (4 µL), and 5 ppm deuterated hexanoic acid (10 µL) in 10 mL screw-cap headspace vials (Microliter Analytical Supplies, Inc., Suwanee, GA). Blank samples were run every ten samples and they contained 986 µL deionized water, 4 µL 3N sulfuric acid, 10 µL 5ppm deuterated hexanoic acid, and 0.4 g NaCl. Alkane standards (C8 – C40) were run at the beginning and end of the run. A second dimension separation time of 2.75 s was used instead of the 1.5 s time used in Johanningsmeier and McFeeters (2011).

Data Processing. GCxGC – ToF MS data processing and statistical analysis was performed as outlined by Johanningsmeier (2011).

Polygalacturonase (PG). Diffusion plate assay procedure for polygalacturonase activity in brines was performed as outlined in Buescher and Burgin (1992). Samples were stored at 4°C prior to testing.

Transmittance and Absorbance. Brine transmittance and absorbance were determined using a Lambda XLS UV/Vis Spectrophotometer (PerkinElmer, Waltham, MA). Approximately 4 mL of deionized water was used in a quartz cuvette as a reference. Approximately 4 mL of the brine sample at 22 °C was put into another quartz cuvette and the transmittance and absorbance were measured over the wavelength spectrum of 200 nm to 950 nm. The data were then exported to Microsoft Excel where they were collected and analyzed. Samples were stored in a 4°C refrigerator prior to testing.

4.4 Results and Discussion

Activated Carbon Equilibrium Testing

Equilibrium times of both powdered (BL) and granular (F400) activated carbon (16 g/100mL) were determined using reductions in TOC concentrations as indicators (Figure

4.1). The A8 brine was chosen for equilibrium testing given that its initial TOC concentration was the highest of all samples. After 0.5 hours of incubation, the TOC concentrations remained nearly constant for 6 hour of testing. The BL and F400 carbons reduced the TOC concentrations from 6680 mg/L to about 2091 and 2665 mg/L, respectively, after 0.5 hours. Powdered activated carbon has a higher external surface area than granular carbon which is more readily available for absorption than the internal pore structure. Granular carbon contains a larger internal pore structure than powdered which can cause equilibrium testing to take days to allow all of the internal surface area of granular carbon to be used (Cameron Carbon, 2006). Since equilibrium was shown to have been reached in 2 hours with the powdered activated carbon, the BL and WPC carbons were used to determine their effectiveness of adsorbing the chemical components of the brine.

Effect of Increasing Amounts of Activated Carbon on Spent Pickling brine

As increasing amounts of carbon were used, a greater reduction in TOC was achieved (Figure 4.2). The BL carbon removed more TOC from both brine types than the WPC. The A10 and B8 brines had initial TOC concentrations of 6647 and 6333 mg TOC/L, respectively. When the A10 brine was treated with 16 and 32 g/100 ml carbon, there was a reduction to 2820 and 2394 mg TOC/L, respectively, for the BL carbon and 3144 and 2726 mg TOC/L, respectively, for the WPC carbon. The B8 brine saw similar reductions to the A10 brine. When treated with 16 and 32 g/100 ml BL carbon, the B8 TOC levels were reduced to 2825 and 2368 mg TOC/L, respectively. The use of the WPC carbon saw reductions to 3191 and 2744 mg TOC/L, respectively, for the 16 and 32 g/100 ml treatments. On average, the BL carbon achieved about 5% more TOC reduction than the WPC carbon. These TOC reductions were similar to those seen in the study of Ratnani et al. (1980). The

brine used by Ratnani et al. had an initial TOC concentration of 5427 mg TOC/L which was lower than the initial concentrations of A10 and B8. Ratnani et al. saw the TOC concentration drop sharply with the initial amounts of carbon and as more carbon was used, the TOC levels started to level off until the maximum of 30 g of carbon was used which is in line with the observations made here.

The lactic acid reduction showed similar trends to that of the TOC (Figure 4.3). There was a decrease in lactic acid concentrations as carbon amounts increased with the BL carbon removing more lactic acid than the WPC. The initial lactic acid concentrations for the A10 and B8 brines were 103.3 and 107.9 mM, respectively, which is typical of the content of cucumber fermentation brines. For the 16 and 32 g/100 ml treatments, the lactic acid concentrations were reduced to an overall average of about 62.7 and 54.9mM, respectively, for the BL carbon and 68.3 and 62.3 mM, respectively, for the WPC carbon. Unlike the lactic acid, acetic acid concentrations reached a minimum at 16 g/100 ml for both carbon types (Figure 4.4). Concentration levels decreased with increasing amounts of carbon until 16 g/100 ml were used and then the concentration either plateaued or increased for the 32 g/100 ml treatments. The acetic acid levels had initial concentrations of 25.1 and 26.6 mM for the A10 and B8 brines, respectively. For the A10 and B8 brines, the treatment of 16 g/100 ml reduced those concentrations to 7.05 and 6.67 mM, respectively, for the BL carbon and 9.07 and 7.47 mM, respectively, for the WPC carbon. On average for both acids, the BL carbon achieved about 6% more acid reduction than the WPC carbon. This can be attributed to the tight, more microporous structure of coconut (WPC) than coal (BL) carbon. Solutions with only trace amounts of organic compounds can be better treated with WPC due to the smaller

pore structure (Cameron Carbon, 2006). The brines used in this study have high amount of organic acids which make BL a more suitable option.

The removal of TOC, lactic, and acetic acid all had different efficiencies. The acetic acid concentration was reduced by an average of 73.5% using the 16 g/100 ml treatment (BL carbon) compared to an average reduction of 56.5% for the TOC and 40.6% for lactic acid. The 32 g/100 ml treatment continued to remove the TOC and lactic acid but at a slower rate.

Prior to the filtration of the brine, the transmittance for all of the brines was minimal at the 254 nm wavelength. After the brine was filtered through both the 1 and 0.8 µm filters, the transmittance at 254nm was 0% (Kaufmann, Submitted 2015). This indicated that the undissolved particles were not the cause of the low transmittance at the 254 nm wavelength. The "blocking" of UV light is more likely due to a chemical than a physical adsorption. The use of activated carbon resolved this issue. Transmittance levels reached a maximum at the 16 g/100 ml treatments (Figure 4.5). One exception was the A10 brine which achieved a maximum at 51.9% transmittance when 8 g/100 ml of WPC carbon was used and then decreased for the following two treatments. The BL carbon was more effective than the WPC in increasing transmittance. An average maximum transmittance of 92.6% was achieved using 16 g/100 ml of the BL carbon where only 49.1% was reached using the WPC carbon. This is another indication that the spent brine bring treated has more than trace amounts of organic compounds which would make the BL carbon a more suitable option. An increase in carbon to 32 g/100 ml caused the transmittance to decrease to an average of 87.6 and 30.1% for the BL and WPC carbons, respectively. Ratnani et al. (1980) evaluated the % transmittance as an indicator of turbidity at 500 nm instead of 254 nm as done so in this research. Similar to the untreated brines in this study, the untreated brine in the study of

Ratnani et al. had a % transmittance of 0. Once treated with activated carbon, the % transmittance increased to 100 at 500 nm. Although different wavelengths were used, the conclusion can be made that activated carbon removes most or all of the UV blocking chemicals.

Volatile compounds reacted differently when treated with increasing amounts of carbon. Three compounds were selected as examples of each type of removal. Some chemical compounds were partially removed. 2-methyl-1-propanol was evident in the filtered brine before carbon treatment. It was reduced when 0.5 g/100 ml of both the BL and WPC carbon were used and as increasing amounts were used, no dramatic change was noticed (Figure 4.6). Compounds such as 1-butanol-3-methyl were gradually removed as more carbon was used (Figure 4.7) and compounds such as 5-methyl-5-hexen-2-one were nearly completely removed beginning with the lowest amounts of carbon used (Figure 4.8).

Effect of 16 g/100 ml of Activated Carbon on a Wide Range of Spent Pickling Brines

The treatment of 16 g/100 ml of BL carbon was selected to treat all of the brines. This treatment was most effective on acetic acid concentrations and transmittance levels and reduced lactic acid and TOC concentrations to levels comparable to the 32 g/100 ml treatment. When applied to all brines types, this treatment reduced TOC concentrations very similarly across all of the brines (Figure 4.9). Initially, there was a wide range of values from about 1404.8 to 7029.5 mg TOC/L with 70% of these values greater than 5500 mg TOC/L. The use of BL carbon reduced TOC levels by about 53% from an average of 5273.2 to 2507.4 mg TOC/L. For the carbon treated samples, a much smaller range was apparent from a minimum of 501.61 mg TOC/mL to a maximum of 3302.1 mg TOC/L. Of these values, 80% of them were larger than 2100 mg TOC/L.

Lactic acid concentrations in the brines ranged from 17.03 to 112.0 mM to give an average of about 75.28 mM (Figure 4.10). When the brines were treated with 16 g/100 ml of the BL carbon, the range decreased to 8.26 to 65.8 mM with an average of about 48.86 mM. About 60% of the concentrations were greater than 55 mM of lactic acid. Acetic acid concentrations had a smaller initial range likely due to the lower concentrations. Before the carbon treatment, the samples had acetic acid concentrations ranging from 13.47 to 43.16 mM with an average of about 23.99 mM. After carbon, the concentrations were as low as 4.62 mM and as high as 17.7 mM. Of all the carbon treated brines, 60% of the acetic acid concentrations were less than 10.0 mM.

Transmittance levels were 0% at the 254 nm wavelength before carbon treatment. The 16 g/100 ml carbon treatment increased transmittance levels significantly. After carbon treatment, transmittance levels ranged from 85.5 to 93.3% with an average of 89.5% at the 254 nm wavelength.

Before the use of activated carbon, a few of the brines tested positive for polygalacturonase (PG) which is an indicator of texture deterioration in fresh cucumbers. PG activity was not detected in the A10 and B7 brines which were used in the testing of increasing carbon amounts. PG was only detected in four of the other brine types (Table 4.2). Brines that had PG activity had clear zones on the diffusion plate assay proportional to the enzyme activity. The smallest clear zone diameter was 1.94 mm meaning there was slight PG activity. One of the brines (A7) had moderate activity and two others (B9 & B10) had extremely high PG activity with the largest diameter being 17.3 mm. After carbon treatment of 16 g/100 ml, no clear zones were identified meaning no PG activity was present. The removal of PG from cucumber brines by adsorption has been tested before but not with

activated carbon. Buescher and Hamilton (2002) experimented with the adsorption of PG by clay. Although successful, the use of clay requires the clay being washed with alkaline for restoration and does not address the additional concerns of off flavors and odors. Activated carbon can be used to treat spent brines with varying levels of PG activity from extremely high to moderate activity while also addressing the need to remove the volatile compounds that lead to off flavors and odors.

Volatile compounds were clustered by filtered, unfiltered, and carbon treated to identify how the 16 g/100 ml affects specific compounds (Figure 4.11). Hierarchical clustering analysis revealed that there were compounds that were minimally, partially, and extensively removed when carbon treated. The hierarchical clustering diagram grouped volatile compounds by likeness. The clusters of volatile compounds were continually grouped together until they were specifically separated. Each compound is associated with a color on a scale from dark red to dark blue. The darker red is associated with a higher frequency and the darker blue is associated is a lower frequency. Of the 142 compounds that were present in the filtered brine before carbon treated, 68 were below detection limits after carbon treatment and 47 compounds were partially removed (Figure 4.12). However, there were 27 compounds that were minimally affected by the carbon and were still present after the treatment such as heptanoic acid, 3-methyl-3-buten-1-ol, amylene hydrate, and 2,3-dimethyl-butane.

4.5 Conclusions

The use of activated carbon on a commercial scale has the potential to address the current concerns related to spent brine quality deterioration during fermentation and bulk storage. The inability to use this poor quality brine causes high operational costs for pickle

processors. When this spent brine is treated with activated carbon, there is a possibility of full reuse. This could cut down on those operational costs and decrease spent brine waste. Activated carbon was known to reduce TOC levels in spent brine but the specific components that make up the total TOC were not examined. Some of these components included lactic and acetic acid and polygalacturonase activity. In this study, all of these were reduced through the use of activated carbon. Volatile compounds that contribute to off flavors and odors were also reduced.

This new knowledge of the effectiveness of activated carbon in treating spent brine can help determine if it is possible to be used industrially. The work done in this study helped understand how activated carbon interacts with spent brine and what components were being removed. It did not evaluate the commercial parameters that would determine if the use of activated carbon is economically feasible. Further work needs to be done involving the use of activated carbon in treating spent brine on site at a pickle producing facility.

References

Buescher, R.W. and C. Burgin. 1992. Diffusion plate assay for measurement of polygalacturonase activities in pickling brines. *Journal of Food Biochemistry*. 16:59-68.

Buescher, R., and Hamilton, C. 2000. Protection of cucumber pickle quality by $CaNa_2EDTA$. *Journal of Food Quality*. 23(4): 429-441.

Buescher, R., and Hamilton, C. 2002. Adsorption of polygalacturonase from recycled cucumber pickling brines by Pure-Flo B80 clay. *Journal of Food Biochemistry*. 26:153–156.

Cameron Carbon Incorporated. 2006. Activated Carbon Manufacture, Structure, & Properties.

Durkee, E. L., Lowe, E., Baker, K. A., Burgess, J. W. 1973. Field Tests of Salt Rey System for Spent Pickling brine. *Journal of Food Science*. 38(3): 507-511.

Eisenstat, L. and Fabian, F. W. 1953a. Factors which produce bleaching of pickles-I. The Glass Packer, April 29-51, 78.

Fasina, O. O., Fleming, H. P., Humphries, E. G., Thompson, R. L., Reina, L. R. 2003. Crossflow Filtration of Brine from Cucumber Fermentation. *Applied Engineering in Agriculture.* 19 (1): 107-113.

Fleming H. P., Daeschel M. A., McFeeters R. F., Pierson M. D. 1989. Butyric acid spoilage of fermented cucumbers. *Journal of Food Science*.54:636 –639.

Franco W., Perez-Diaz I. M., Johanningsmeier S. D., McFeeters R.F. 2012.Characteristics of spoilage-associated secondary cucumber fermentation. *Applied and Environmental Microbiology*. 78(4): 1273-84.

Johanningsmeier, S. D. 2011. Biochemical Characterization of Fermented Cucumber Spoilage using Non-targeted, Comprehensive, Two-dimensional Gas Chromatography-Time-of-Flight Mass Spectrometry: Anaerobic Lactic Acid Utilization by Lactic Acid Bacteria. [PhD Dissertation]. Raleigh, NC: North Carolina State Univ. Available from: NC State Theses and Dissertations, Raleigh, NC.

Johanningsmeier, S. D., McFeeters, R. F. 2011. Detection of volatile spoilage metabolites in fermented cucumbers using nontargeted, comprehensive 2-dimensional gas chromatography-time-of-flight mass spectrometry (GC×GC-TOFMS). *Journal of Food Science.* 76(1): C168-77.

Kaufmann, A. J. Submitted 2015. Physical and Microbiological Remediation of Spent Pickling Brine using Crossflow Filtration. [Thesis]. Raleigh, NC: North Carolina State Univ. Available from: NC State Theses and Dissertations, Raleigh, NC.

Kilduff, J. E., Karanfil, T., Weber, W. J. 1998.Competitive Effects of Nondisplaceable Organic Compounds on Trichloroethylene Uptake by Activated Carbon. I. Thermodynamic

Predictions and Model Sensitivity Analyses. *Journal of Colloid and Interface Science*. 205(2): 271-279.

Lu, Z., Pérez-Díaz, I. M., Hayes, J. S., Breidt, F. 2012.Bacteriophage Ecology in a Commercial Cucumber Fermentation. *Applied Environmental Microbiology.* 78 (24): 8571-8578.

Matsushita, T., Matsui, Y., Sawaoka, D., Ohno, K. 2008. Simultaneous removal of cyanobacteria and an earthy odor compound by a combination of activated carbon adsorption, coagulation, and ceramic microfiltration. *Journal of Water Supply: Research and Technology – AQUA.* 57(7): 481-487.

McFeeters, R. F., Pérez-Díaz, I. 2010. Fermentation of Cucumbers Brined with Calcium Chloride Instead of Sodium Chloride. *Journal of Food Science.*75 (3): 291-296.

Palnitkar, M. P., McFeeters, R. F. 1975. Recycling spent brines in cucumber fermentations. *Journal of Food Science*. 40(6):1311–1315.

Peel, R. G., Benedek, A. 1980. Attainment of Equilibrium in Activated Carbon Isotherm Studies. *Environmental Science & Technology*. 14(1): 66-71.

Ramalho, R. S. 1983. Introduction to Wastewater Treatment Processes.2nd Edition.

Ratnani, K.,LeDuy, A., Ramalho, R. S. 1980. Activated carbon adsorption treatment of spent pickling brine. *The Canadian Journal of Chemical Engineering.* 58 (3): 325-331.

Zhou, A., McFeeters, R. F. 1998. Volatile compounds in cucumbers fermented in low-salt conditions. *Journal of Agricultural Food Chemistry.* 46(6): 2117-2122.

Zhou A., McFeeters R. F., Fleming H. P. 2000. Development of oxidized odor and volatile aldehydes in fermented cucumber tissue exposed to oxygen. *Journal of Agricultural Food Chemistry*. 48(2): 193-197.

Table 4.1 Representative spent brines from two commercial producers

Source	Brine	Description
Company A	A5	45 degree salometer brine (approx. 13% salt – <1 grains of acid; made using the barrel brine) for tanking of fresh cucumbers
	A6	45 degree salometer brine (approx. 13 % salt – <1 grain of acid; made using the blancher brine) for tanking of fresh cucumbers
	A7	Blancher brine (approx. 14% salt) – brine that was used to make fresh cucumbers easier to pack.
	A8	Used brine (7% salt – approx. 5 grains of acid - more turbid)
	A9	Barrel brine (no vinegar) - (7 – 10% salt and 2 – 6 grains) from the imported brined stock
	A10	Used brine (7% salt - approx. 5 grains of acid – somewhat clear)
	A11	Vinegar brine (approx. 25 gr – 4% salt) from imported cucumbers that are considered fresh
Company B	B7	Old brine with very high level of softening enzyme
	B8	Old brine with high level of softening enzyme
	B9	Brine typically after an average fermentation time and bulk storage
	B10	Brine typically after an average fermentation time and bulk storage

Table 4.2 Effect of powdered activated carbon (BL) on brines containing polygalacturonase

	Before Carbon		After Carbon (16 g)	
Brine Type	Net Clear Zone Diameter (mm)	PG Activity[1]	Net Clear Zone Diameter (mm)	PG Activity
A7	4.26	Moderate	0	None to Slight
B7	1.94	None to Slight	0	None to Slight
B9	14.2	Extremely High	0	None to Slight
B10	17.3	Extremely High	0	None to Slight

[1]PG activities based on the net clear zone diameter (0.0 - 2.1 mm = none to slight, 2.4 - 5.0 mm = moderate, 5.3 - 7.6 mm = high, 7.9 - 10.2 mm = very high, >10.2 mm = extremely high) (Buescher and Burgin, 1992)

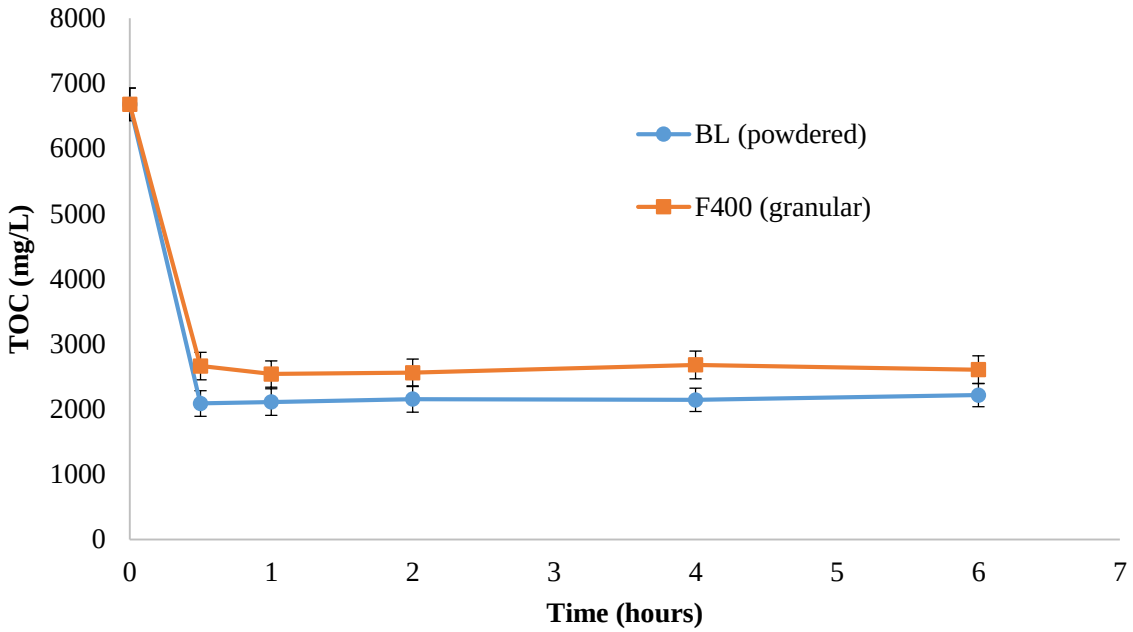

Figure 4.1 Effect of contact time on TOC (mg/L) reduction in spent pickling brine treated with powdered and granular, coal derived, activated carbon (16g carbon/100 ml spent brine)

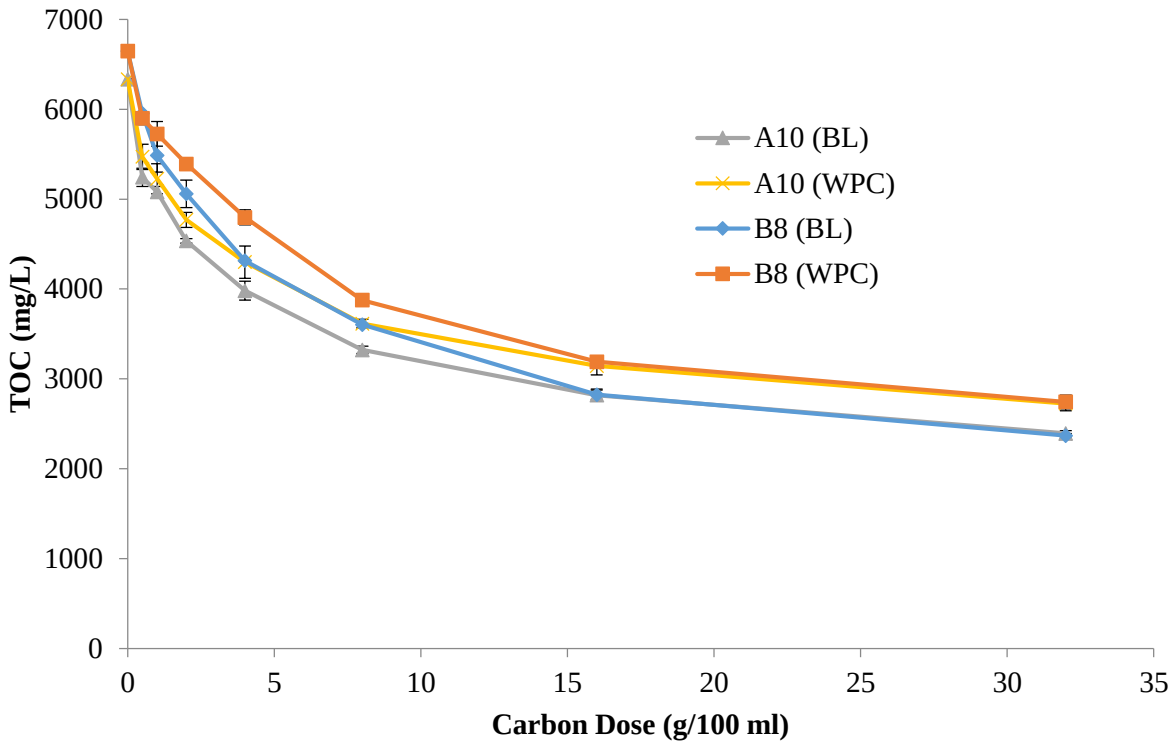

Figure 4.2 Effect of increasing amounts of coal (BL) and coconut (WPC) powdered activated carbon on the TOC concentrations of spent brines (B8 and A10) for a 6 hour test time

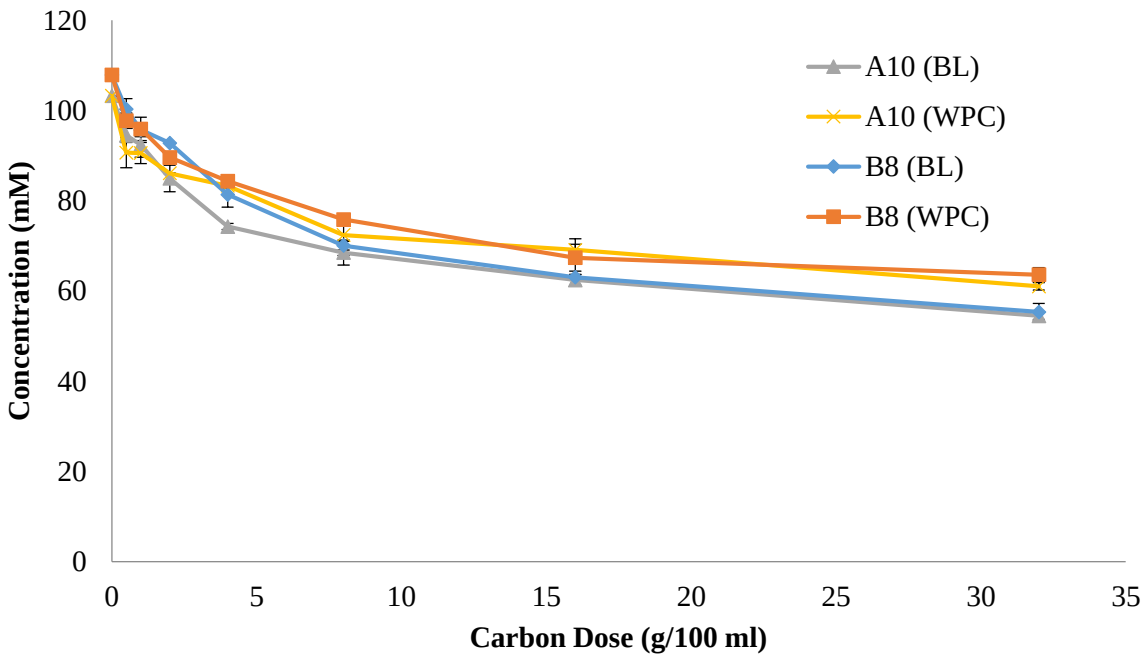

Figure 4.3 Effect of increasing amounts of coal (BL) and coconut (WPC) powdered activated carbon on the lactic acid concentrations of spent brines (B8 and A10) for a 6 hour test time

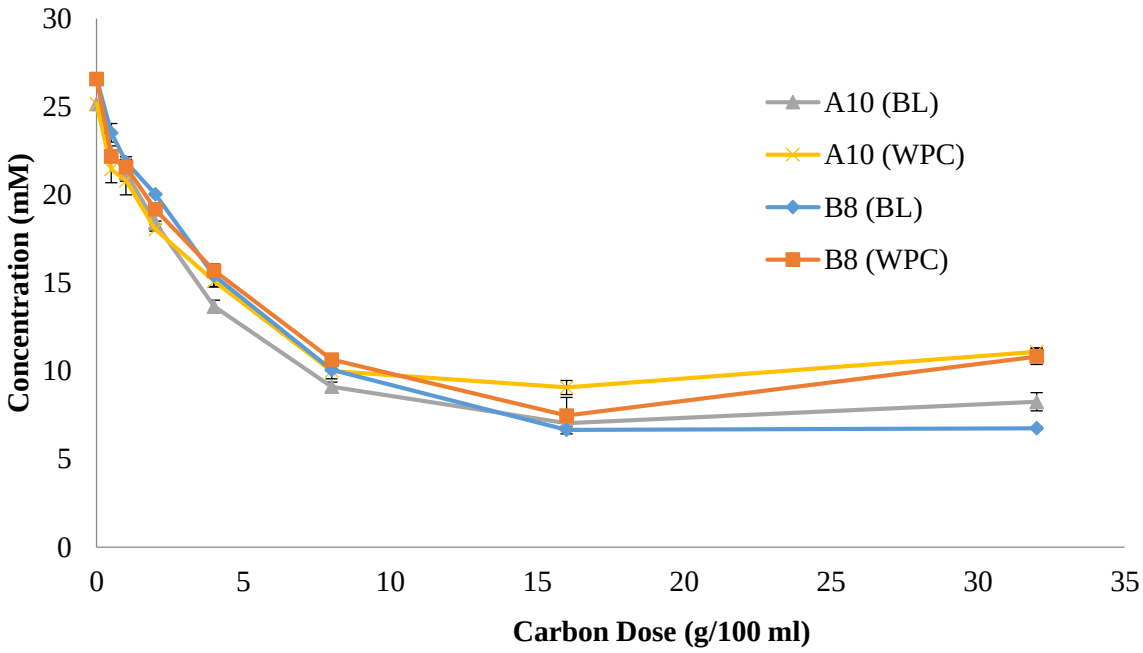

Figure 4.4 Effect of increasing amounts of coal (BL) and coconut (WPC) powdered activated carbon on the acetic acid concentrations of spent brines (B8 and A10) for a 6 hour test time

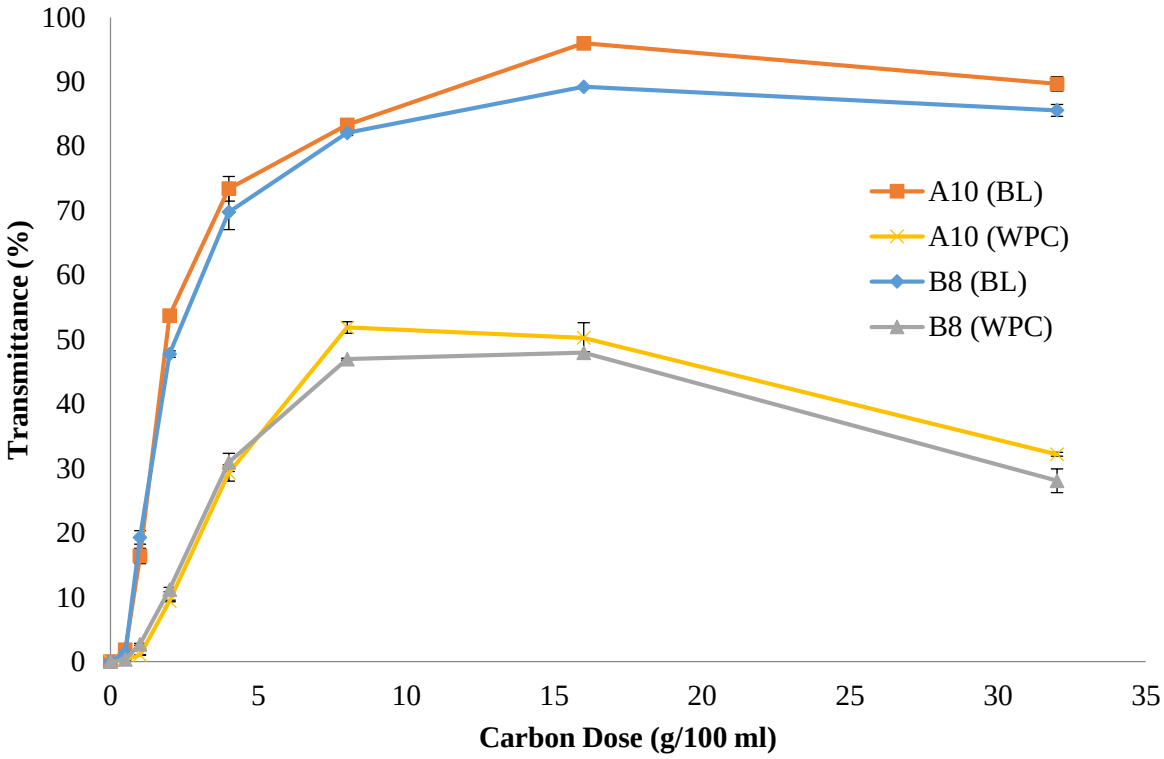

Figure 4.5 Effect of increasing amounts of coal (BL) and coconut (WPC) powdered activated carbon on the transmittance (at 254 nm) of spent brines (B8 and A10) for a 6 hour test time

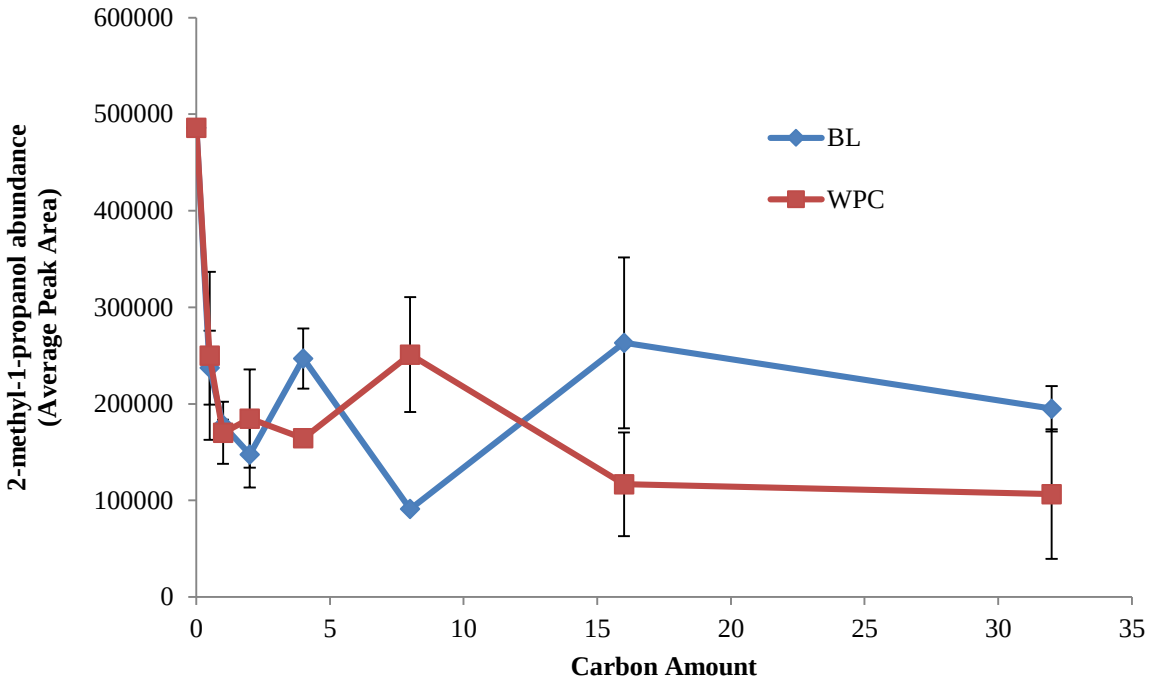

Figure 4.6 Partial removal of 2-methyl-1-propanol from the A10 brine as a result of increasing amount of BL and WPC powdered activated carbon

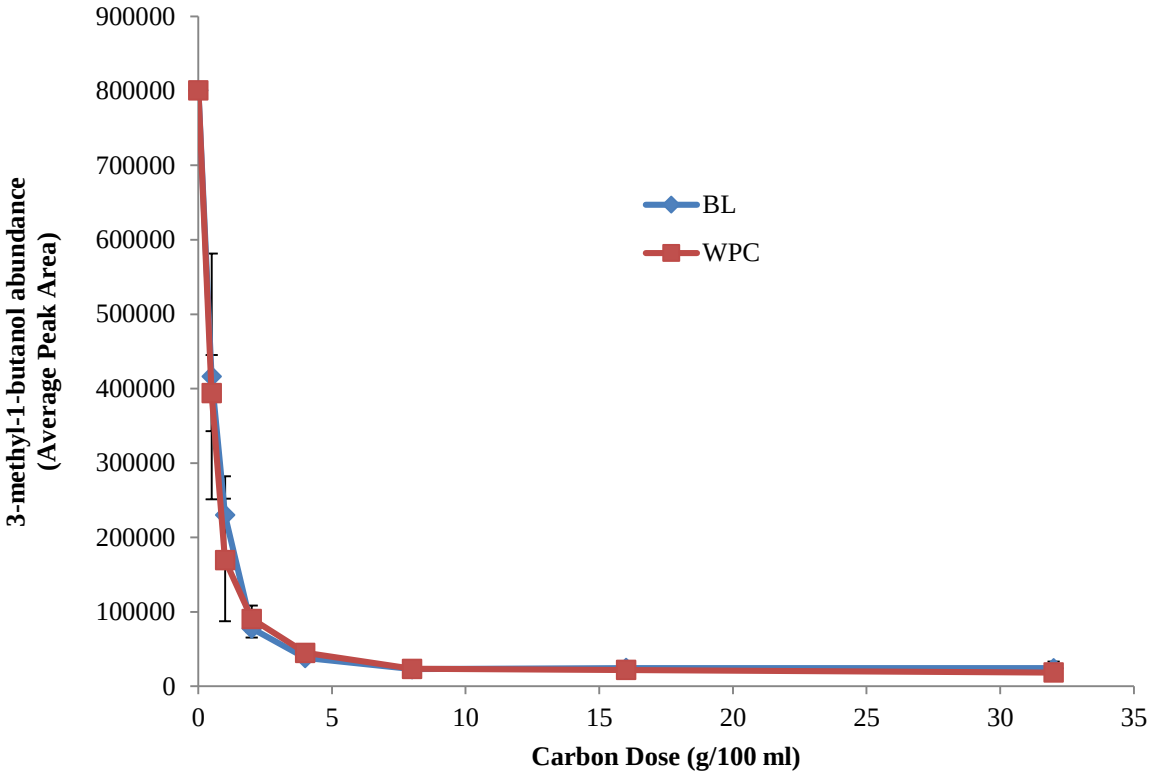

Figure 4.7 Removal of 3-methyl-1-butanol from the B7 brine as a result of increasing amount of BL and WPC powdered activated carbon

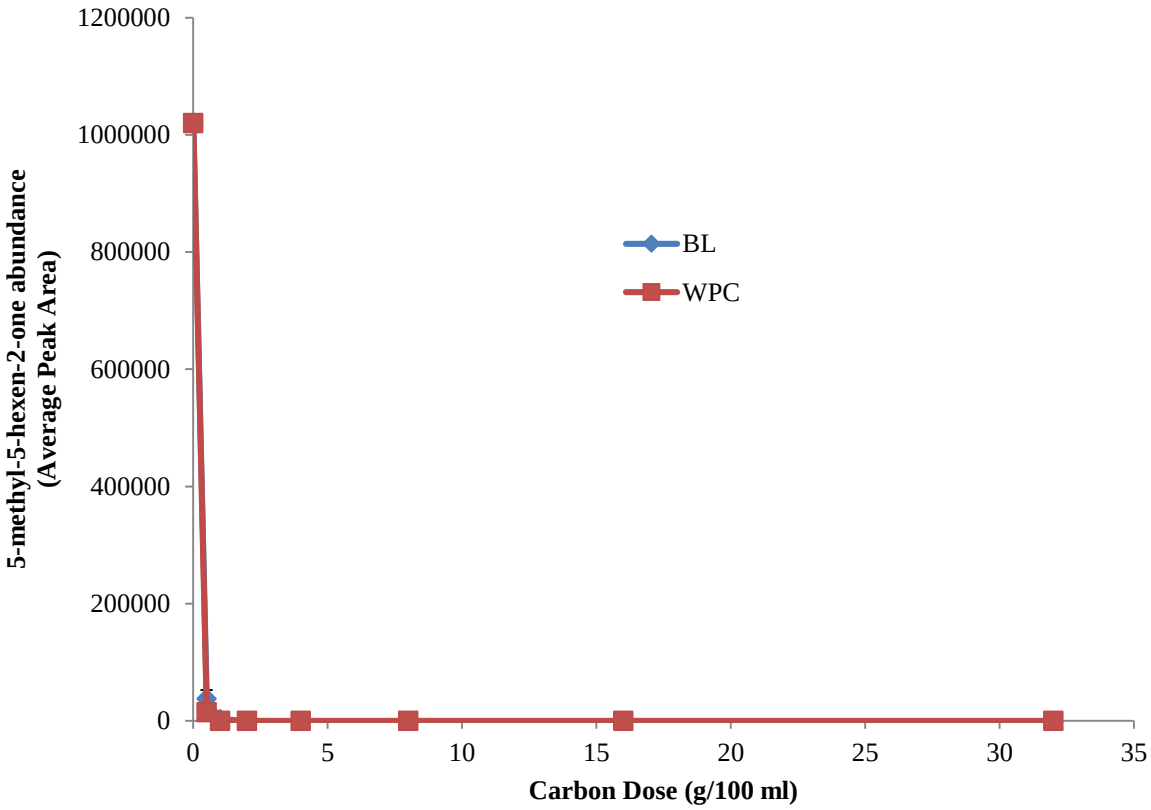

Figure 4.8 Complete removal of 5-methyl-5-hexen-2-one from the B7 brine as a result of increasing amount of BL and WPC powdered activated carbon

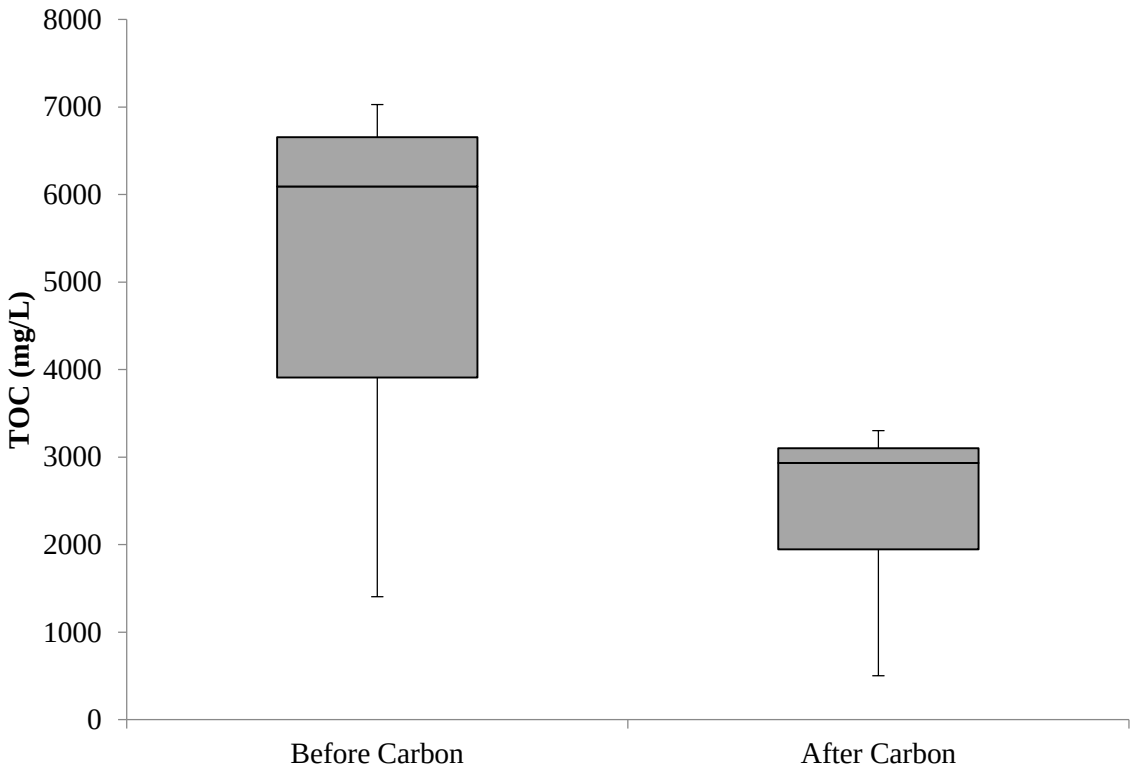

Figure 4.9 Effect of BL powdered activated carbon (16 g/100 ml) on the TOC concentration distributions for all brines

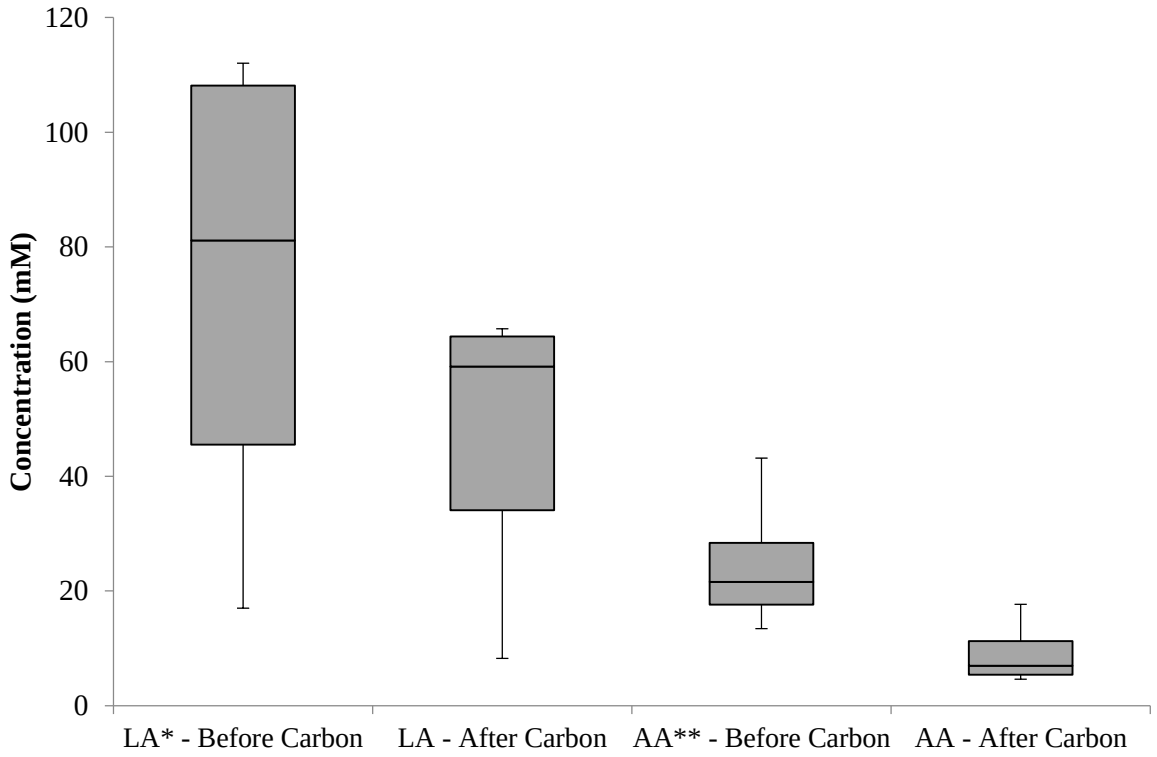

Figure 4.10 Effect of powdered, activated carbon (BL, 16 g/100 ml) on the lactic and acetic acid concentration distributions for all brines

*Lactic Acid
**Acetic Acid

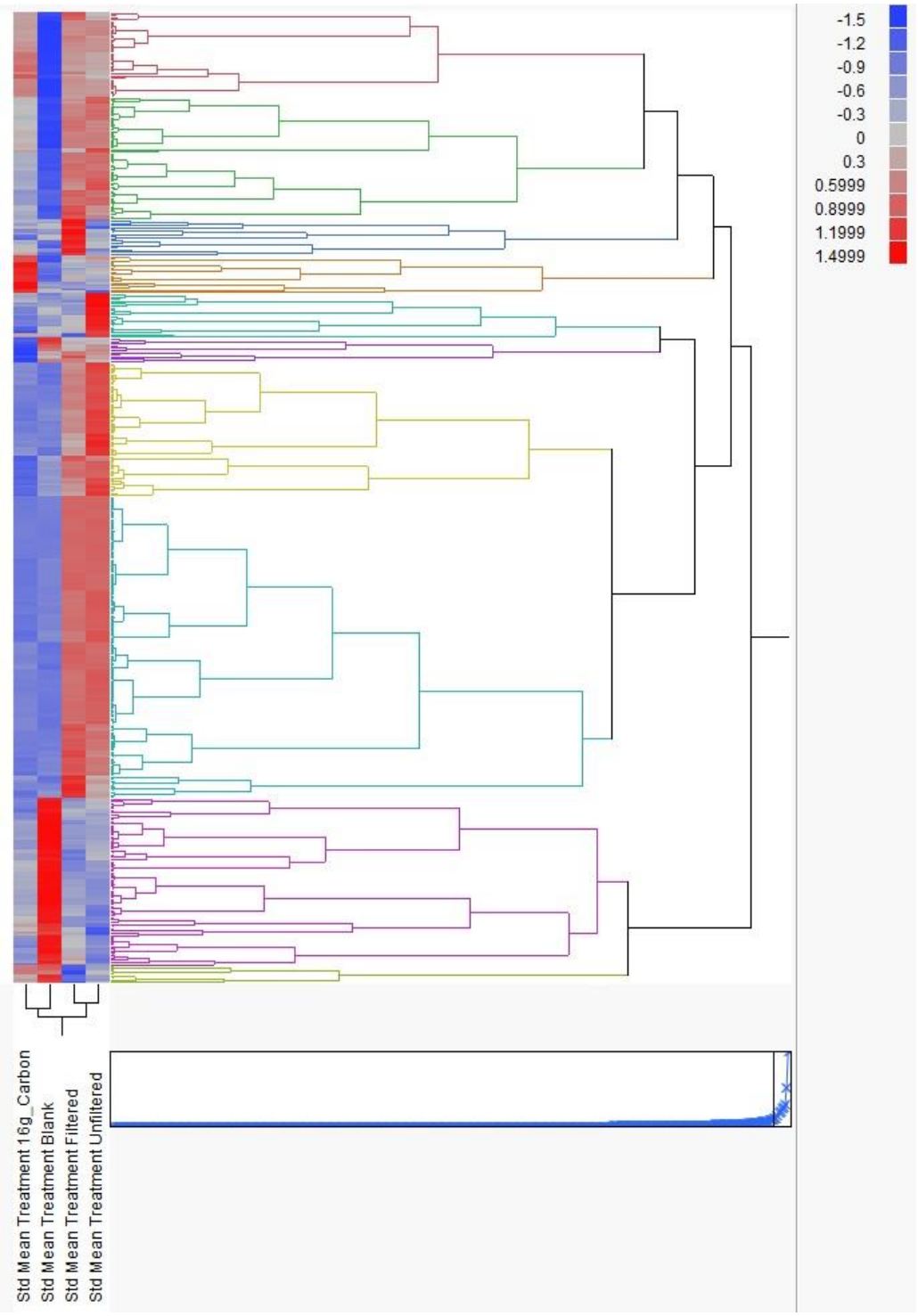

Figure 4.11 Hierarchical clustering of volatile compounds that changed in the unfiltered, filtered, and carbon treated (16 g/100 ml) brines as well as the internal standard blanks

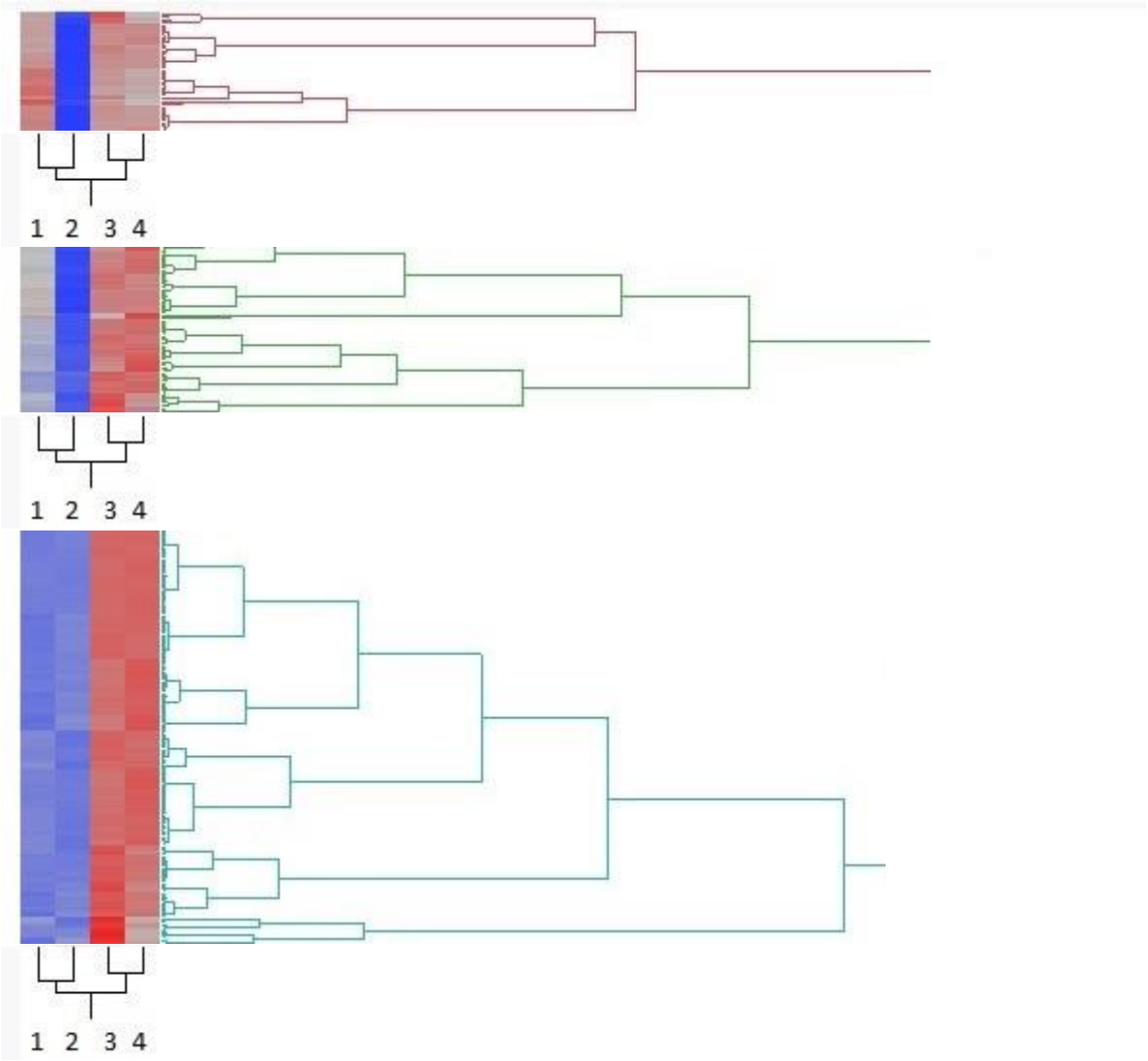

Figure 4.12 Hierarchical clustering of volatile compounds that were not removed (top figure), partially removed (middle figure), and completely removed (bottom figure) by carbon treatment (16 g/100 ml)

[1]Carbon treated brines
[2]Internal Standard Blanks
[3]Filtered brines
[4]Unfiltered brines

Chapter 5

Conclusions

The use of crossflow filtration and activated carbon in the treatment of spent brine has the potential to reduce operational costs and the amount of waste produced. The crossflow filtration of spent brine in conjunction with activated carbon treatment is a novel procedure. The work done in this study was focused on the qualitative characteristics of the spent brine through this process. The equipment and procedures used were too small for accurate, scalable results relating to flowrates and filter/carbon efficiency.

The next step for crossflow filtration will be to determine the efficiency of a pilot scale filtration system utilizing the same pore size (0.8 µm) filters used in this study. A pilot scale unit would be needed on-site at the fermentation yard or somewhere close where the spent brine after fermentation can easily be transported. The purpose of this unit would be to test higher flowrates and larger filter housings than the crossflow system used in this study. The numbers attained from the pilot scale unit would be used to determine if a full-scale unit would be economically possible. The implementation of sequential membranes is another aspect of the pilot scale system to investigate. Starting the process with filters of larger pore sizes would remove larger particles. A possible set-up could include a course filter to remove larger, visible particles such as stems, seeds, and other debris followed by filters with pore sizes of 4, 3, and 2 µm before the final 0.8 µm pore size. According to the particle size data, a majority of the particles are below the 5 µm size. Using filters with pore sizes of 4, 3, and 2 µm would allow for particles to be retained by each filter to reduce overloading on one specific filter. Once the filter pore sizes are reduced to the 0.8 µm size, the larger particles will have been removed allowing for a clearer solution and a higher flowrate through the 0.8 µm pore size.

The next step towards implementing an activated carbon system on-site at a pickle processing company would be to conduct a pilot study. This would include the treatment of the filtered brine through use of activated carbon in columns. The objective of that would be to determine the most effective operating conditions that allow the carbon to be used most efficiently. The data analyzed from that study would make it possible to determine if a full scale carbon process would be economically possible.