ABSTRACT

INVESTIGATING PERACETIC ACID AS AN ALTERNATIVE TO SODIUM HYPOCHLORITE DISINFECTION

by Georgia Brook Fuerst

Chlorine is a commonly used wastewater disinfectant in the United States. Despite the effectiveness of chlorine as a disinfectant, a major disadvantage associated with it is the formation of hazardous disinfection byproducts (DBPs). Peracetic acid has been gaining much attention as an alternative to chlorine because it is not known to form hazardous DBPs associated with chlorine disinfection and it has potential cost savings. This bench-scale research took place at the Mill Creek Treatment Plant in Cincinnati, Ohio and investigates peracetic acid as an alternative to sodium hypochlorite. The results of this study show peracetic acid to be a comparable disinfectant against target organisms, E. coli and fecal coliforms. A pilot study has been initiated at the Little Miami Treatment Plant because of these results.
INVESTIGATING PERACETIC ACID AS AN ALTERNATIVE TO SODIUM HYPOCHLORITE DISINFECTION

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Introduction

Importance of Wastewater Treatment

Wastewater treatment is the treatment of effluent from municipal or industrial sources before they re-enter our natural waterways. Proper treatment is necessary in maintaining the state of our rivers and lakes for additional use. Healthy surface water is essential because it is the influent for most potable (drinkable) water treatment plants. Aquatic life and certain recreation activities also rely on healthy surface waters. Therefore, the need for wastewater treatment to not only remove pollutants, but to also have a minimal effect on the environment is crucial. To aid in protecting the quality of surface waters, government regulations, like the Clean Water Act (CWA), have been created to regulate the discharge of pollutants [1]. As a result of the CWA, the Environmental Protection Agency (EPA) has set wastewater industry standards and water quality standards for contaminants present in surface waters [1]. Additionally, the CWA has made it unlawful without a permit to discharge pollutants from a point source into surface waters [1]. Permits are regulated through the EPA’s National Pollutant Discharge Elimination System (NPDES).

How Wastewater Treatment Works

A typical wastewater treatment plant (WWTP) consists of the following stages: bar screens, primary clarifier, aeration, secondary clarifier, and disinfection. Bar screens are used to remove any large debris present in the influent wastewater to the WWTP. The primary clarifier reduces the amount of fine particles and suspended solids. The aeration tank and the secondary clarifier remove Biochemical Oxygen Demand (BOD). Biochemical Oxygen Demand is the amount of dissolved oxygen needed by organisms to break down organic matter that is present in water; therefore measuring the BOD is an indirect measurement of the amount of organic material. When there are large amounts of organic matter, bacteria need large amounts of dissolved oxygen to break it down. Decreased levels of dissolved
oxygen in the water can be detrimental to aquatic life. To remove BOD, air is bubbled through the aeration basin to provide food for microorganisms (activated sludge) to break down organic matter. In the secondary clarifier the sludge is allowed to settle to the bottom in order to be recycled. All of these steps work to clean the water and remove as much organic matter as possible prior to disinfection. Disinfection occurs after secondary treatment and before the water is released into the environment. In some cases, an additional step is taken after disinfection to remove residual chlorine if chlorination disinfection is used. A typical WWTP schematic is shown in the Figure 1.

![Figure 1. General Wastewater Treatment Plant Schematic](image)

**The Mill Creek Treatment Plant**

This research takes place at the Mill Creek Treatment Plant (MCTP) located in Cincinnati, OH. The MCTP is the Metropolitan Sewer District of Greater Cincinnati’s largest treatment plant. This plant has a design flow of 130 million gallons per day (MGD), but can take 430 MGD through preliminary and primary treatment and 240 MGD through secondary treatment under wet weather conditions [5]. The service area of this plant covers 88,572 acres [5]. About 39% of Mill Creek’s collection is combined sewer and the remaining is separate sanitary sewers [5]. Of the total flow, approximately 11.39 MGD comes from industrial users [5]. There are two outfall points used at this treatment plant, one located on the Ohio River and one located on Mill Creek. The locations of these outfall points are shown in Figure 2. The primary outfall is the Ohio River location, but when the river reaches 41 feet the Mill Creek outfall is used [5].
The water treatment process at the MCTP includes coarse screening, grit removal and fine screening, pre-aeration, primary settling, conventional activated sludge aeration, secondary clarification, and chlorination before discharge (shown in Figure 3) [5]. Sodium hypochlorite (NaOCl), or more commonly known as bleach, is the form of chlorine disinfection used at this plant.
Chlorine Disinfection

History
Well before it was known to be a disinfectant, chlorine was used as a deodorant. It was once believed that disease spread through odor, and controlling odor would stop the spread of diseases [2]. Following the discovery of bacteria and the understanding that bacteria could cause disease, it was found that chlorine could destroy these bacteria [2]. Now, chlorine is among the most commonly used wastewater disinfectants. Widespread use of chlorine disinfection of wastewater in the United States began around 1945 [2]. Due to this long history, there is extensive knowledge available on chlorine disinfection. Chlorine is available in many forms, including liquid and gaseous chlorine. Again, sodium hypochlorite is the form of primary concern in this paper.
Advantages and Disadvantages

Chlorine has many advantages associated with it, mainly its effectiveness against killing a wide range of pathogenic organisms [3]. Since it is so widely used, it is very a well-established technology [3]. It is cost effective when compared to methods such as UV or ozone [3]. Chlorine residual persists in the environment, which actually prolongs disinfection [3]. This can be an advantage or a disadvantage depending on the use. In potable water, chlorine residual is an advantage because it is necessary to ensure that the water is still clean from the time it leaves the treatment plant to the time it reaches a household. In wastewater treatment, persisting chlorine residual is not desirable because it is harmful to the environment and aquatic life.

Despite the effectiveness of chlorine as a disinfectant, a major disadvantage associated with it is the formation of hazardous disinfection byproducts (DBPs). As the quality of water becomes increasingly important due to population and industry growth, alternatives to chlorine disinfection have become a widely studied topic due to this formation of DBPs. DBP limits become more strict as more attention is paid to water quality. The primary DBP associated with chlorine disinfection are trihalomethanes (THMs), which are known carcinogens [2]. THMs are formed when chlorine oxidizes organic matter present in the wastewater. The Safe Drinking Water Act (SDWA) calls for the regulation of four THMs, which include chloroform, bromodichloromethane, and dibromochloromethane [2].

Another disadvantage is the possibility of a dechlorination step, which is needed when the chlorine residual is at a concentration that would be harmful to aquatic life if released into the environment. The EPA’s required daily limit of chlorine residual present in wastewater effluent is very low (0.33 mg/L at the Mill Creek Treatment Plant [5]), making dechlorination a necessity in some cases. Sulfur dioxide is the most commonly used method to remove chlorine residual. When sulfur dioxide is added to water it forms sulfurous acid which reacts with chlorine residual species [2]. This adds an acid to the water, which lowers the pH. However, this is not seen as a problem due to wastewaters having a sufficient amount of alkalinity [2]. Dechlorination is mainly a disadvantage because it is an
added cost to wastewater treatment that would not be necessary if not for the presence of residual chlorine.

*Disinfection Mechanism*

Chlorine disinfects wastewater by penetrating cell walls and oxidizing harmful bacteria and viruses. When chlorine is added to water, it hydrolyzes into hypochlorous acid (HOCl).

$$\text{Cl}_2 + \text{H}_2\text{O} \leftrightarrow \text{HOCl}$$

Additionally, hypochlorous acid dissociates into hypochlorite ions and hydrogen ions. Hypochlorous acid and hypochlorite ions both serve as disinfectants for wastewater, but hypochlorous acid is much more effective [2].

$$\text{HOCl} \leftrightarrow \text{H}^+ + \text{OCl}^-$$

The hypochlorite ion is not as effective as HOCl because of the negative charge. Cell walls are also negatively charged, which cause OCl\(^-\) to be repelled [2]. Additionally, it is larger in size than HOCl and diffuses through cell walls much slower [2]. Studies have shown HOCl to be 80 times more effective than OCl\(^-\) in killing *Escherichia Coli* [4]. The presence of HOCl relative to OCl\(^-\) is largely affected by the pH of the water, more so than the temperature. This is shown in Figure 4.
Figure 4. Percent of HOCl present as a function of pH at 20º C [2].

The $K_a$ value used in the above graph was $2.62 \times 10^{-8}$, which is the dissociation constant at 20ºC [2].

\[
K_a = [H^+] [OCl^-] / [HOCl]
\]

\[
[HOCl] + [OCl^-] = 1
\]

\[
[H^+] = 10^{-pH}
\]

By plugging these three equations together, [HOCl] can be solved for. The daily limits for wastewater effluent is 6-9 pH. At a pH of 9, we see that [HOCl] is very low but this value of pH is not typical of effluent and normally has characteristics of pH around 7, where the amount of HOCl dominates over OCl⁻.
The Mill Creek Treatment Plant disinfects its effluent with sodium hypochlorite (NaOCl) before releasing it to the Ohio River. Sodium hypochlorite is preferable over gaseous chlorine because it is much safer to handle [2]. Before sodium hypochlorite was discovered, potassium hypochlorite was used as a bleaching agent for textiles. In the early 1800s, Labarraque developed a method to produce sodium hypochlorite thus replacing potassium hypochlorite, which was more expensive [2]. The first known use of a hypochlorite solution for disinfection of water was as early as 1850 in order to control an outbreak of cholera that was caused by sewage contamination [2]. A variation of Labarraque’s method is still used to manufacture sodium hypochlorite today, shown in the following reaction [2].

\[2\text{NaOH} + \text{Cl}_2 \rightarrow \text{NaOCl} + \text{NaCl} + \text{H}_2\text{O} + \text{Heat}\]

Sodium hypochlorite is a mixture and cannot exist without water. It is not found in nature and must be manufactured. It is a clear or yellowish mixture that has a strong chlorine smell.
In order to form the hypochlorous acid and hypochlorite ions as described previously in the disinfection mechanism section, the following reaction occurs when sodium hypochlorite is added to water:

\[
\text{NaOCl} \rightarrow \text{Na}^+ + \cdot \text{OCl}
\]

The hypochlorite ions then associate with protons to form hypochlorous acid.

\[
\text{OCl}^- + \text{H}^+ \leftrightarrow \text{HOCl}
\]

**Peracetic Acid**

*Overview*

Peracetic Acid (PAA), also known as peroxyacetic acid, has the chemical formula \( \text{CH}_3\text{CO}_3\text{H} \). It is typically commercially available at 5-15 wt% in an equilibrium mixture with acetic acid (vinegar), hydrogen peroxide, and water.

![Figure 6. Chemical structure of PAA.](image)
This paper examines PAA as an alternative to sodium hypochlorite disinfection of wastewater. In this study, VigorOx WWT II manufactured by PeroxyChem was used. This solution of peracetic acid is designed specifically for wastewater use. PeroxyChem has been marketing peracetic acid as a disinfectant since the 1980s for a variety of uses, including a biocide for medical devices and disinfection of Listeria, Salmonella, and E. coli in food processing facilities [7]. VigorOx WWT II peracetic acid is produced by combining acetic acid (CH₃COOH), hydrogen peroxide (H₂O₂), and water [7].

This equilibrium solution is 15% PAA, 23% hydrogen peroxide, 16% acetic acid, and 46% water by weight [7]. It is commercially available with stabilizers, and has a guaranteed shelf life of one year, which is important for on-site storage [6,7]. The freezing temperature is -49°C which results in the ability to use it in winter months without any concern of freezing [7]. Although the solution contains hydrogen peroxide, PAA has been found to be the primary disinfectant with hydrogen peroxide not having a significant role [19].

*Why Peracetic Acid?*

Peracetic acid has been gaining attention as a wastewater disinfectant as chlorine disinfection comes under scrutiny. The main reason for this attention is it is not known to form hazardous DBPs associated with chlorine disinfection. When PAA is added to water it decomposes into less harmful acetic acid, oxygen, and water [2]. Three reactions occur regarding the decomposition of peracetic acid: spontaneous decomposition, hydrolysis, and transition metal catalyzed decomposition [8].
Spontaneous Decomposition  
\[2\text{CH}_3\text{CO}_3\text{H} \rightarrow 2\text{CH}_3\text{CO}_2\text{H} + \text{O}_2\]

Hydrolysis  
\[\text{CH}_3\text{CO}_3\text{H} + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{CO}_2\text{H} + \text{H}_2\text{O}_2\]

Catalyzed Decomposition  
\[\text{CH}_3\text{CO}_3\text{H} + \text{M} \rightarrow \text{O}_2 + \text{other products}\]

Although slower than the decomposition of PAA, the hydrogen peroxide from the hydrolysis reaction will further decompose to water and oxygen [9].

\[2\text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{O}_2\]

Another advantage of PAA is its potential to save money because it would eliminate the need for any subsequent processes (i.e., dechlorination) that are sometimes needed when chlorine disinfection is used.

Additionally, as far as alternative disinfection methods go, PAA is easily implemented. The same equipment can be utilized if a liquid chlorine disinfection system is already in place. Other methods, including UV and chlorine dioxide gas, are known to be much better for the environment than sodium hypochlorite, but the equipment needed for these methods are expensive and would take a long time to implement. Chlorine dioxide requires on-site production and there are many safety concerns associated with this process, putting workers at risk. UV requires completely new and expensive equipment and could raise electricity costs. With PAA, minor changes can be made to already in-place equipment, keeping transition and implementation costs low.

Peracetic acid is considered to have a lower toxicity to aquatic life than chlorine disinfection. During a full-scale trial of peracetic acid disinfection, a wastewater treatment plant in St. Augustine found aquatic life to have a higher survival rate in the PAA effluent than the chlorination/dechlorination effluent [14].

As organic wastes break down, they form large amounts of ammonia. Nitrification is a process that occurs during wastewater treatment that converts ammonia to nitrate through nitrifying bacteria. As temperature drops, the efficiency of nitrification is
decreased because the activated sludge that promote nitrification are temperature sensitive and not as active when the water is cold [15]. This leads to higher amounts of ammonia present in the wastewater. Chlorine reacts with ammonia rapidly to form chloramines, which increases chlorine demand and decreases disinfection efficiency. Peracetic acid does not react with ammonia; therefore the disinfection efficiency is unchanged as nitrification fluctuates [16].

Disinfection Mechanism
Like sodium hypochlorite, peracetic acid uses oxidation to disinfect wastewater. It is effective as a bactericidal, virucidal, fungicidal, and sporicidal [20]. The exact disinfection mechanism is not well understood, but it does function as an oxidizing agent [20]. It is believed that bacteria are destroyed by protoplasmic oxidation, which results in cell lysis, the breaking down of a cell membrane [6]. For enzymes and proteins, PAA oxidizes the sulfur and sulfhydryl bonds [20]. It has also been shown to act on the base of DNA molecules [20].

The disinfection capability of PAA decreases with an increasing pH because the undissociated (CH$_3$COOOH) acid is the more effective disinfectant [20]. As pH increases, the concentration of dissociated PAA (CH$_3$COO$^-$) also increases, shown in Figure 8 below.

\[
\text{CH}_3\text{COOOH} \leftrightarrow \text{H}^+ + \text{CH}_3\text{COO}^-
\]
Figure 8. Percent of $\text{C}_3\text{H}_6\text{COOOH}$ present as a function of pH compared to HOCl (Figure 4).

The pKₐ of PAA is 8.2, which was used to create the above plot. Figure 8 shows the percent of PAA in the undissociated form as a function of pH. Two observations can be taken from this graph. The first is that under typical effluent conditions (pH=7), the primary form of PAA is the undissociated form, which is the more effective over the dissociated form. The second is by plotting the percent of chlorine present as HOCl on the same graph, it can be shown that PAA stays in the undissociated form longer and therefore may be a more effective disinfectant at higher pH conditions.

**Decomposition**

One aspect of the environmental impact of PAA is how long it persists in the environment [9]. It is necessary to have an understanding of the decomposition kinetics of PAA in wastewater to understand how long PAA residual will persist in the environment. When added to wastewater, PAA has been found to have an initial rapid consumption from an
oxidant demand followed by a slow consumption [17,18]. This decomposition is best modeled by a modified first-order kinetics that includes a term, D, that represents the initial disinfectant demand [17,18]. This is shown in the following model [9,17,18]:

\[ C(t) = (C_o - D)e^{-kt} \]

- \( C(t) \) = concentration of PAA at time \( t \) (mg/L)
- \( C_o \) = initial concentration of PAA (mg/L)
- \( D \) = initial demand of PAA (mg/L)
- \( k \) = rate constant (1/min)
- \( t \) = time (min)

The rate constant (\( k \)) and initial demand (\( D \)) will vary between WWTPs due to different water conditions. A PeroxyChem study collected secondary effluent prior to disinfection sample from various wastewater treatment plants, shown in Table 1.

**Table 1. Location of samples used in PAA decomposition study by PeroxyChem [9].**

<table>
<thead>
<tr>
<th>State</th>
<th>Number of Utilities</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alabama</td>
<td>1</td>
</tr>
<tr>
<td>Arkansas</td>
<td>1</td>
</tr>
<tr>
<td>Florida</td>
<td>1</td>
</tr>
<tr>
<td>Georgia</td>
<td>1</td>
</tr>
<tr>
<td>Louisiana</td>
<td>1</td>
</tr>
<tr>
<td>New York</td>
<td>2</td>
</tr>
<tr>
<td>Oregon</td>
<td>2</td>
</tr>
<tr>
<td>Tennessee</td>
<td>4</td>
</tr>
<tr>
<td>Washington</td>
<td>2</td>
</tr>
</tbody>
</table>

Each sample was treated with varying concentrations of PAA. After treatment, multiple PAA concentration measurements were taken between 1 and 45 minutes [9]. This data was then fitted to the first-order kinetics model to determine values for \( k \) and \( D \). In some studies, the initial demand (\( D \)) is assumed to be a constant and not dependent on the initial concentration of PAA added [17,18]. PeroxyChem fit their experimental data under the
assumption that \( D \) is constant as well as the assumption that it is a function of the initial PAA concentration. The second assumption is shown below.

\[
C(t) = C_0 (1 - x)e^{-kt}
\]

All of the variables are the same as the previous model except for \( x \), which is \( D/C_0 \) [9]. The initial consumption term was calculated and then divided by the concentration of PAA added to account for differences in disinfection dose. To determine how each assumption affects the data, the two models can be plotted together.

Figure 9. Decomposition model comparison [9].

Figure 9 shows the comparison between the two decomposition models with the results from three different WWTPs. The legend identifies the state the sample came from and the sample number. Model 1 is the assumption that the initial demand is a constant and Model 2 is the assumption that it is a function of the initial concentration of PAA. An initial dose of
5 ppm VigorOx WWT II was used. Time zero on the above figure is not at the initial concentration of PAA because the initial disinfection demand has been taking into account, so time zero is right after the initial demand takes place. The variation between models is different for each plant. Some of the plants show a close relation between models while others show a larger difference. These results make it difficult to make a conclusion on which model is better. As time increases, the difference between each model decreases. This makes sense because each model assumes a different initial condition, but the same decomposition rate, so they will be closer together with an increasing time. Therefore, when only looking at how long it will take for PAA to decompose in wastewater, it is not necessarily important on which decomposition model is chosen. It is also apparent in this graph that the qualities of wastewater have a large impact on the decomposition of PAA, shown by the variation between plants. The decomposition rate of PAA is location specific and to determine values for k and D, individual bench-scale studies must be conducted.

Figure 10. PAA decomposition kinetics of multiple WWTPs [9].
Figure 10 shows the comparison of PAA decomposition kinetics from multiple samples collected by PeroxyChem, modeled by the assumption that the initial disinfection demand is a constant. As in the previous graph, a dose of 5 ppm VigorOx WWT II was used. Similar to the above graph, it is clear to see how the variation in wastewater qualities largely dictates the decomposition of PAA. Although the kinetics vary, the concentration of PAA was under 0.1 mg/L by 200 minutes (3.33 hours) for each WWTP. This shows that PAA residual decomposes quickly once added to wastewater and does not persist. The measurements taken in this study were from a jar test procedure, so the concentration of PAA residual would actually be a lot less at this time because of dilution upon effluent discharge. From these decomposition results, PAA residual from disinfection should not be a concern.

**Concerns with PAA**

Unlike sodium hypochlorite, PAA is an organic compound. A major concern associated with using PAA as a disinfectant is the increase in organic content in the water. Microorganisms in the water use dissolved oxygen to break down organic matter, so a higher amount of organic content in wastewater effluent can possibly lead to a decrease in dissolved oxygen in the water. A large decrease in dissolved oxygen can be detrimental to aquatic life. PAA generates biochemical oxygen demand (BOD) from the biological oxidation of acetic acid [10].

\[ \text{CH}_3\text{COOH} + 2\text{O}_2 \rightarrow 2\text{CO}_2 + 2\text{H}_2\text{O} \]

Combining the biological oxidation of acetic acid with the decomposition of peracetic acid, the theoretical oxygen demand can be calculated. If it assumed that the wastewater is treated with 5 ppm of VigorOx WWT II (15% PAA, 16% acetic acid, 23% hydrogen peroxide by weight) the following theoretical oxygen demand (ThOD) calculations are shown below.

\[
15 \text{ wt\% PAA} \times \frac{5 \text{ mg}}{76.0513 \text{ g}} \times \frac{1 \text{ mol PAA}}{2 \text{ mol PAA}} \times \frac{2 \text{ mol acetic acid}}{1 \text{ mol acetic acid}} \times \frac{32 \text{ g}}{1 \text{ mol O}_2} = 0.631 \text{ mg O}_2 \text{ L}^{-1}
\]
The above calculation is the oxygen demand of the decomposition of peracetic acid, but there is also 16 wt% acetic acid already present in the VigorOx WWT II mixture that contributes to the addition of BOD.

\[
16 \text{ wt} \% \text{ Acetic Acid} \times \frac{5 \text{ mg}}{\text{L}} \times \frac{1 \text{ mol acetic acid}}{60.05 \text{ g}} \times \frac{2 \text{ mol } \text{O}_2}{1 \text{ mol acetic acid}} \times \frac{32 \text{ g}}{1 \text{ mol } \text{O}_2} = 0.8526 \text{ mg } \text{O}_2 \text{ L}^{-1}
\]

Therefore, the total ThOD is 1.484 mg O₂ / L if treated with 5 ppm of VigorOx WWT II. Some of this oxygen demand is offset by the dissolved oxygen that is formed from the decomposition of hydrogen peroxide and peracetic acid to acetic acid.

\[
15 \text{ wt} \% \text{ PAA} \times \frac{5 \text{ mg}}{\text{L}} \times \frac{1 \text{ mol PAA}}{76.0513 \text{ g}} \times \frac{1 \text{ mol } \text{O}_2}{2 \text{ mol PAA}} \times \frac{32 \text{ g}}{1 \text{ mol } \text{O}_2} = 0.15778 \text{ mg } \text{O}_2 \text{ L}^{-1}
\]

\[
23 \text{ wt} \% \text{ H}_2\text{O}_2 \times \frac{5 \text{ mg}}{\text{L}} \times \frac{1 \text{ mol H}_2\text{O}_2}{34.0147 \text{ g}} \times \frac{1 \text{ mol } \text{O}_2}{2 \text{ mol H}_2\text{O}_2} \times \frac{32 \text{ g}}{1 \text{ mol } \text{O}_2} = 0.5409 \text{ mg } \text{O}_2 \text{ L}^{-1}
\]

The ThOD is now only 0.785 mg O₂ / L when the dissolved oxygen that is formed is accounted for. The EPA requires reporting of the Carbonaceous Biochemical Oxygen Demand (CBOD₅), which is the oxygen required to oxidize only carbon compounds while excluding nitrogenous compounds. The NPDES 30-day average CBOD₅ limit of the MCTP is 25 mg/L year-round [5]. The 50th percentile of CBOD₅ reported by the MCTP was 8 mg/L during the summer and 12 mg/L during the winter [5]. Therefore, the use of PAA will likely allow WWTPs with already low organic matter to stay well within their permit limits. If a WWTP is operating under a high organic load and is having trouble reaching CBOD₅ permit limits, PAA may not be a desirable alternative disinfectant.

As mentioned earlier, PAA is gaining attention because it is not known to form any of the hazardous DBPs associated with chlorine. Dell ‘Erba has studied the DBPs associated with PAA. It was found that no chlorinated or brominated phenols were formed, but the formation of aldehydes did occur [13]. Although aldehydes did form, they were minimal.
and excess PAA oxidates them to carboxylic acids and eventually carbon dioxide [13]. The aldehyde formation measured was well under the allowable limit [13]. This study shows that the formation of DBPs from PAA disinfection is not likely to be a concern. Many WWTPs are having difficulties reaching DBP limits [14], so PAA could potentially resolve this problem.
Research

Objective

The objective of this research is to assess if peracetic acid is a feasible alternative to sodium hypochlorite disinfection. Although there are many studies supporting the use of PAA and it is currently being used at select treatment plants, applicability of PAA must be explored on a case-by-case basis because of variation in wastewater conditions and effluent limits. Peracetic acid was assessed on its ability to disinfect wastewater with respect to target organisms, *Escherichia Coli (E. Coli)* and fecal coliforms, compared to sodium hypochlorite. Temperature, amount of total suspended solids, dose and contact time were examined to determine their effect on PAA disinfection.

Membrane Filtration

Membrane filtration was used for a majority of this research to determine the amount of colony-forming units (cfu/100 mL) present in a sample. In this technique, daily samples were taken in 100 mL sterile bottles from either primary or secondary effluent. The number of samples varied daily. Samples were tested on the same day that they were collected.

Each sample was either untreated or treated with a disinfectant (PAA or sodium hypochlorite). A membrane filter was placed at the bottom of a funnel using sterilized forceps. The membrane filter prevented *E. coli* and fecal coliforms from passing through it. The funnel was disinfected with UV light before use. A phosphate buffer was used to wet down the filter before the vacuum was turned on. The sample was then filtered through the apparatus. The goal was to obtain a countable number of colonies (normally 20-60). In order to do this, serial log dilutions were made before filtration.
After filtration, the membrane filter was rinsed with the phosphate buffer a second time, removed with sterile forceps and placed in a petri dish that contains either m-ColiBlue24® or m-FC broth with rosolic acid depending on the test being performed. The m-ColiBlue24® broth allows *E. Coli* to be distinguished from total coliform colonies and the m-FC broth detects fecal coliforms. The petri dish was then placed in a water bath to allow an environment for the colonies to grow. The temperature of the *E. coli* water bath is 34.5±2 °C and for fecal coliforms it is 44.5±2 °C. After a minimum incubation time of 24 hours for *E. coli* and 24±2 hours for fecal coliforms, the petri dishes were removed and the number of colonies was counted. To calculate cfu/100 mL of the original sample, the following equation was used.

\[
\text{cfu/100 mL} = \frac{\text{colony count} \times 100 \times \text{dilution factor}}{\text{volume filtered (mL)}}
\]

If a 1:10 dilution is made, the dilution factor is ten. An example calculation is as follows when a 1:10 dilution was made, 10 mL of the dilution was filtered, and 39 colonies were counted.

\[
\frac{39 \text{ colonies} \times 100 \times 10}{10 \text{ mL}} = 3900 \text{ cfu/100 mL}
\]

Because the characteristics of wastewater changes day to day, many serial dilutions were needed to ensure a countable number of colonies would be obtained. The weather was also an indicator of how many dilutions were needed. If it had recently rained, the water would be dilute and fewer dilutions were needed and vice versa if it hadn’t rained. Additionally, the location where the sample was taken from was an indicator. In primary effluent, many dilutions are needed to get a countable number. In secondary effluent, only one or two dilutions were needed.

For quality control, a blank was run daily to ensure clean equipment. If any colonies were present on the blank membrane, the data was not used. Samples were run in duplicates for reproducibility. A major source of error in this procedure is incorrect plate count and improper mixing of serial dilutions. For example, if a 3-log dilution is made and a plate was
read wrong by 1 colony, an error of 1,000 cfu/100 mL would be made. Most WWTPs do not use the method in this research and instead use a more accurate procedure.

Again, m-ColiBlue24® broth measures total coliforms while distinguishing *E. coli* colonies. A blue colony represented a positive result of *E. coli*. Any non-blue colony is a negative *E. coli* result. Red or blue colonies represents total coliforms and any clear or white colonies represent a negative result. When measuring fecal coliforms with the m-FC broth, a blue colony represents a positive result. A negative result is shown by any non-blue colony.

![Image of plate readings](image)

*Figure 11. Example of E. coli (left) and fecal coliform (right) plate readings [21].*

**Disinfection Comparison**

This study took place in July 2015. Peracetic acid and sodium hypochlorite were compared on their ability to kill *Escherichia coli (E. coli)* and fecal coliform colonies. Testing for *E. coli* and fecal coliforms is important because they are indicator organisms, representing the presence of other pathogenic, meaning disease causing, organisms. Daily samples were collected from the WWTP primary effluent. Although secondary effluent is where disinfection occurs, primary effluent was used for means of comparison due to the higher amounts of *E. Coli* and fecal coliforms present at this stage of the process. A control sample was filtered before treatment to determine the amount of *E. coli* or fecal coliforms present in the water before treatment. Duplicate samples were then treated with PAA and sodium.
hypochlorite and left in contact for ten minutes. In this study, a 15 trade% sodium hypochlorite solution and a 15 wt% peracetic acid solution (VigorOX WWT II) were used. Trade percent is the percent of available chlorine available for disinfection expressed as Cl₂. The molar concentrations of these solutions are shown below.

\[
15 \text{ trade } \% \text{ Cl}_2 = \frac{150 \text{ g Cl}_2}{L} \cdot \frac{1 \text{ mol Cl}_2}{70.096 \text{ g}} = 2.12 \text{ mol Cl}_2/L
\]

\[
15 \text{ wt } \% \text{ PAA} = \frac{150 \text{ g PAA}}{L} \cdot \frac{1 \text{ mol PAA}}{76.051 \text{ g}} = 1.97 \text{ mol PAA/L}
\]

The molar concentration of peracetic acid used in this study is a little bit lower than the sodium hypochlorite solution that was used.

Contact Time

This study took place in August 2015. In the disinfection comparison study, a treatment contact time of ten minutes was assumed. To confirm this was an appropriate selection, a contact time study was conducted. It was expected that after 10 minutes, disinfection would slow down significantly. This was expected because of the rapid decomposition of PAA residual in water. In this study, the daily sample from primary effluent was treated with PAA for 30 minutes. During the 30 minutes, a sample was taken every ten minutes and tested for E. coli colonies using membrane filtration to observe how disinfection changed over time.

NPDES Permit Limits

To confirm that PAA would be able to meet the permit limits specific to the Mill Creek Treatment Plant, samples of secondary effluent were treated with PAA at a dose varying from 1-4 ppm and a contact time of ten minutes. This was done for E. coli and fecal coliforms, although the NPDES permit for MCTP only includes a limit for fecal coliforms. Permit limits require fecal coliforms to have a monthly average of 200 cfu/100 mL during the summer months and 1000 cfu/100 mL during the winter months [5]. Although the Mill
Creek Treatment Plant does not have a permit limit for *E. coli*, other plants within the Metropolitan Sewer District of Greater Cincinnati do. The Sycamore Creek Wastewater Treatment Plant requires a monthly *E. coli* average of 126 cfu/100mL and a weekly average of 284 cfu/100mL [11]. This study took place in January 2016 and allowed the dose needed to reach permit limits of fecal coliforms and *E. coli* on a bench-scale to be estimated.

**Temperature**

The temperature study took place during January-February 2016. The goal of this study was to see the effect temperature has on PAA disinfection efficiency. One of two things was expected to occur during this study: (1) the disinfection efficiency would increase with a higher temperature as observed in other studies [20] or (2) disinfection efficiency would decrease possibly because of bacteria in the water being more active and reproducing faster in warmer conditions.

For this study duplicate samples of secondary effluent were collected. Half of the sample was placed in an ice bath at 2±2 °C and the other half was allowed to reach room temperature. The membrane filtration technique was then used to test each sample for fecal coliforms and *E. coli*.

**Total Suspended Solids**

Total suspended solids are any solids present in wastewater that can be collected on a filter. The goal of this study was to determine how total suspended solids affected PAA disinfection. For this study, duplicate 250 mL samples of secondary effluent were vacuum-filtered through a pre-weighed filter pad with a porosity of 1.5µm. Each filter was then placed in a 104±1°C oven for one hour. After the hour, the filter was taken out, allowed to cool, and then weighed. The sample was then placed back in the oven for a half hour. After the half hour, the sample was taken out and weighed. This practice is known as consistent weights. If the percent difference was greater than 4% (or 0.0005g) the sample was put back in the oven and the process was repeated. For quality control, a blank and a lab control was used. If the blank had a difference of more than 0.0005g and if the lab control
was not within 4% of the expected value, the data was not used. The following equation was used to calculate total suspended solids.

\[
\text{TSS}^{\text{mg/L}} = \frac{\text{Dried(g)} - \text{Tare(g)}}{\text{Volume(mL)}} \times 1,000,000
\]

This study took place January 26-February 1, 2016. For three different days the total suspended solids results were compared with the membrane filtration results that occurred on those days. Some studies have shown there is a slight decrease in PAA disinfection as the amount of suspended solids increases [12].
Results and Discussion

Disinfection Efficiency

*Figure 12. PAA and NaOCl disinfection comparison of fecal coliforms in primary effluent.*
The above graphs show the comparison of sodium hypochlorite and PAA disinfection in primary effluent for fecal coliforms and *E. coli*. The y-axis is the natural log of the amount of colonies after disinfection divided by the control. The control is the number of colonies present in the sample before disinfection occurs. The more negative the \( \ln(N/N_0) \) value is, the better the disinfection. Wastewater conditions change from day to day, so this method accounts for these differences and reduces the amount of error when plotting results. Error on the above graph is the standard deviation between multiple data points. Some points still have relatively large amounts of error, even with taking into account the control group. This could be because of plate reading error as described earlier.

In Figure 12, it can be seen that chlorine and PAA are comparable disinfectants. They follow the same inactivation trend with small differences. In Figure 13, PAA is better than NaOCl.
at every point starting at 4 ppm. This shows that *E. coli* is more sensitive to PAA than it is to NaOCl at high doses. At a low dose (2 ppm), PAA does not appear to be effective against killing *E. coli*. In conclusion, PAA and NaOCl are comparable disinfectants for fecal coliforms, but for *E. coli* PAA performs better than NaOCl.

**Contact Time**

![Graph showing contact time study for E. coli colonies in primary effluent.](image)

*Figure 14. Contact time study for E. coli colonies in primary effluent.*

In the disinfection comparison study, a contact time of 10 minutes was assumed. The above graph confirms that the assumed contact time was appropriate. For 5 ppm, disinfection appeared to stop after 10 minutes and the amount of colonies was almost constant with a very slight decrease. For 3 and 4 ppm, measurements were only taken at 10 and 20 minutes based on the results from 5 ppm and to save lab resources. In the cases of 3 and 4
ppm, disinfection did occur from 10 to 20 minutes, but not as much as in the first 10 minutes. From these results we can assume that although some disinfection does occur after a contact time of 10 minutes, it is not as significant as the disinfection that occurs in the first 10 minutes. Therefore, a contact time of 10 minutes is effective. Additionally, when using PAA for disinfection it makes sense to have a lower contact time over a higher one because of its rapid decomposition. PAA residual begins decomposing as soon as it is added to water, as described in the decomposition section in the introduction, so increasing the contact time is likely to not make a difference during full scale disinfection.

**Comparison with Microbial Inactivation Kinetics**

As described in the introduction, PAA decomposition includes an initial rapid followed by a slower decomposition. Microbial inactivation models do not account for this behavior, so Falsanisi, et al. proposed an equation to model microbial inactivation kinetics when disinfected with PAA.

\[
\ln \left( \frac{N}{N_0} \right) = -k' \ast (C_0 - D)^n t^m \left[ 1 - e^{\frac{-nkt}{m}} \right]^{\frac{m}{nkt}}
\]

\(N\) = number of colonies at time \(t\) (cfu/100mL)
\(N_0\) = number of colonies before disinfection (cfu/100mL)
\(k', n, m\) = empirical parameters
\(C_0\) = initial concentration of PAA (mg/L)
\(D\) = initial demand of PAA (mg/L)
\(k\) = rate constant (1/min)
\(t\) = time (min)

For primary effluent, the following best-fit parameters for *E. coli* are shown below in Table 2.
Table 2. Best fit parameters of Haas and Joffe’s model for E. coli in primary effluent [18].

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>k'</td>
<td>7.93</td>
</tr>
<tr>
<td>n</td>
<td>0.085</td>
</tr>
<tr>
<td>m</td>
<td>0.100</td>
</tr>
</tbody>
</table>

Given these parameters, the experimental results of the contact time study can then be compared with the microbial inactivation kinetics. This research did not include a PAA residual study in primary effluent, but by using this model a value for k and D can be estimated.

Figure 15. Experimental data compared with microbial inactivation model.
In Figure 15, the experimental data from the contact time study is compared with the microbial inactivation kinetics model. This comparison allows the confirmation that the experimental results follow expected inactivation trends. Values for the decomposition rate constant (k) and the initial PAA demand (D) were varied until the model best fit the experimental data. Based on this model, the value for k and D are approximately 0.05 min$^{-1}$ and 0.25 mg/L, respectively.

**NPDES Permit Limits**

*Figure 16. PAA doses needed to reach NPDES permit limits of E. coli in secondary effluent.*
Figures 16 and 17 show the dose of PAA needed to reach NPDES permit limits for *E. coli* and fecal coliforms. The y-axis on these graphs differ from the previous ones because it is the actual number of colonies instead of the ln(N/N₀) term. For both *E. coli* and fecal coliforms, all of the trials treated with 3 and 4 ppm reached permit limits. However, this study only occurred over a range of a few days and wastewater conditions change. Some days may have higher levels of *E. coli* and fecal coliforms present in the water and a dose of 3 or 4 ppm may not allow for permit level inactivation. Therefore, from these bench scale results doses of 3 and 4 ppm were effective, but a pilot study (which is ongoing for many days) will allow determination of a more accurate disinfection dose.
The amount of total suspended solids in secondary effluent can vary from day to day. It is important to know how total suspended solids affects disinfection because the amount of disinfection may need to be varied based on these conditions. For sodium hypochlorite, the chlorine reacts rapidly with suspended solids so a higher dose is needed when there is a high amount of suspended solids present in the wastewater. The above graph shows the amount of total suspended solids on three different days. On each day, *E. coli* and fecal coliforms were treated at a dose of 1, 2, 3, and 4 ppm. These results were then compared with the amount of total suspended solids on that particular day to observe how total suspended solids affect PAA disinfection.
Figure 19. Disinfection of fecal coliforms compared to the amount of total suspended solids present in secondary effluent.
Based off of the results shown in Figures 19 and 20, it is hard to make a conclusion about how the total suspended solids affects disinfection. The \( \ln(N/N_0) \) value stays relatively constant as the amount of total suspended solids changes. Therefore, it can be assumed that TSS has little effect on the disinfection efficiency of PAA. Some results have showed that disinfection decreases as total suspended solids increases, as mentioned previously, but other results have shown that the total suspended solids under 100 mg/L has little effect of PAA disinfection [18]. If this is the case, peracetic acid is advantageous over sodium hypochlorite because the disinfection dose does not need to be increased as TSS increases. This can potentially save money by reducing the amount of disinfectant needed under high TSS conditions.
Figure 21. Effect of temperature on PAA disinfection of E. coli.

The above graph shows the comparison of PAA disinfection for E. coli at two different temperatures. At a low dose (1ppm), PAA is much more effective at a higher temperature. As dose increases, the difference in disinfection decreases, although the warmer temperature still achieves a higher amount of disinfection.
Contrary to Figure 21, the above graph shows that the difference in disinfection of fecal coliforms remains relatively constant. Although the difference is not large, the warmer temperature still achieves better disinfection. One of the two predictions was that disinfection would possibly decrease as temperature increased because of the quicker bacteria reproduction rate but both graphs confirm that disinfection decreases as temperature decreases. Therefore, for both target organisms PAA disinfection increases as temperature increases. For *E. coli*, temperature has a much larger impact on disinfection at a low dose, as shown by the large difference at a dose of 1 ppm. Although temperature does have an impact on disinfection, the difference is not very large and the dose of disinfection is likely not needed to be changed much as temperature changes.

**Figure 22. Effect of temperature on PAA disinfection of fecal coliforms.**
Discussion

The purpose of this research was to assess peracetic acid as an alternative to sodium hypochlorite. From these bench-scale results, peracetic acid has shown to be a feasible alternative to chlorine disinfection. The disinfection efficiency study shows PAA and sodium hypochlorite to be comparable disinfectants at killing the target organisms with a contact time of 10 minutes. PAA has shown to be more effective at inactivating *E. coli* than sodium hypochlorite and comparable at killing fecal coliforms. PAA was able to reach NPDES permit limits for both *E. coli* and fecal coliforms at a dose of 3 ppm. After a disinfectant contact time of 10 minutes, disinfection begins to slow down significantly. This is likely because of the rapid decomposition of PAA once added to water. Results from this research also show temperature and total suspended solids to not have significant impacts on the disinfection efficiency. Because this bench-scale study has proven PAA to be an effective alternative, a pilot study has been initiated.

The pilot study will take place at the Little Miami Treatment Plant. The Little Miami Treatment Plant uses sodium hypochlorite for chlorination and sodium bisulfate for dechlorination. This location was chosen by MSDGC because PAA eliminates the need for the dechlorination step, leading to potential cost savings. PeroxyChem’s Field Pilot Reactor will be used for the pilot study.

*Figure 23. View 1 of pilot test at Little Miami Treatment Plant.*
Figure 24. View 2 of pilot test at Little Miami Treatment Plant.

Figure 25. View 3 of pilot test at Little Miami Treatment Plant.
The reactor is fed with effluent prior to disinfection, and then returned to the process before chlorination, therefore no regulatory approval is needed [22]. It can handle 20 gallons per minute and there are six different sampling points to obtain results at various contact times [22]. PAA is dosed at the beginning of the reactor and then passes through an in-line mixer [22]. The flow rate of the PAA can be varied to test different disinfection concentrations [22]. The location of the sampling points (red valves) can be seen in Figure 24. The goal of the pilot study is to ensure that PAA can reach NPDES limits of various wastewater characteristics. If the pilot study is successful, planning for a full-scale trial will begin.

Healthy surface waters are essential for human life and any steps should be taken to protect and minimize our impact on them. PAA has many environmental advantages over chlorine disinfection, and the concerns associated with it are not as great as the concerns associated with chlorine. The potential cost savings associated with PAA also make it a desirable alternative. This study will hopefully continue the growing interest in PAA and encourage other wastewater treatment plants to explore it as a potential disinfectant.
References


