Sustainable Alternative Wastewater Treatment for Beneficial Reuse of Industrial Wastewater

Major Qualifying Project completed in partial fulfillment
Of the Bachelor of Science Degree at
Worcester Polytechnic Institute, Worcester, MA

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Abstract

EMD Millipore, a large manufacturing facility, is considering approaches for recycling wastewater from its manufacturing processes for re-use as process water. EMD Millipore currently owns and operates a wastewater treatment plant (WWTP) at their Jaffrey, NH facility in order to treat organic contaminants in the wastewater from the facility. Optimizing the current WWTP will reduce cost, as well as wastewater flowrate from the facility. In addition, reusing the treated wastewater as a water source for processes at the facility will reduce demand on other water sources. Wastewater chemistries from EMD Millipore's operations were analyzed and assessed for the potential for reclamation. Ozone oxidation and activated carbon adsorption technologies were identified for the removal of the constituents. Bench-scale experimental results suggested that ozone and ozone-hydrogen peroxide oxidation is a feasible treatment option for EMD Millipore's wastewater, however further research should be conducted. A pilot-scale ozone system for wastewater reclamation at the facility was designed and selected for implementation at the Jaffrey, NH facility.

Design Statement

This Major Qualifying Project fulfills the capstone engineering design requirements of WPI's Civil and Environmental Engineering Department. This project addressed these design constraints as recommended by the Accreditation Board for Engineering and Technology (ABET). As stated in the ABET General Criterion 3(b) "[Engineering programs must demonstrate that students have attained] an ability to design and conduct experiments, as well as to analyze and interpret data" (ABET, 2014). Furthermore, ABET General Criterion 3(c) states "[Engineering programs must demonstrate that students have attained] an ability to design a system, component, or process to meet desired needs within realistic constraints such as economic, environmental, social, political, ethical, health and safety, manufacturability, and sustainability" (ABET, 2014). Experiments were designed for activated carbon adsorption, ozonation, and ozonation with the addition of hydrogen peroxide for the treatment of EMD Millipore's industrial wastewater. Furthermore, major design considerations for a pilot-scale system were researched, and design parameters selected based on the conditions and requirements of EMD Millipore's Jaffrey, NH facility. The following considerations were taken into account during the design of this pilot-scale system: treatability, financial feasibility, and environmental constraints.

PE Licensure Statement

Professional engineering (PE) licensure is the highest level of competence in the engineering profession. Licensure is especially important in civil and environmental engineering profession for maintaining the high standard of work and designs completed. Whether designing a wastewater treatment plant or constructing a bridge, by nature these industries provide work for public entities and PE licensure aids in protecting public health, safety and welfare. PE licensure provides qualifications or standards for competency in specialized skills, high ethical standards and quality assurance. PE licensing authority and requirements are under the jurisdiction of the state, district, or country in which an engineer practices (NSPE, 2015). The National Council of Examiners of Engineering and Surveying (NCEES) represent the state boards as a national organization. To earn such licensure, an engineer must complete a four-year college degree in engineering, at least four years of work under the supervision of a Professional Engineer, and pass two competency exams. These intensive exams include the Fundamentals of Engineering (FE) exam and the Principles and Practice of Engineering (PE) exam.

There are many reasons and benefits to becoming a licensed engineer. Licensed professional engineers can prepare, sign and seal engineering work for public and private clients. They can also submit engineering plans and drawings to a public authority for approval (NSPE, 2015). Many states require professors teaching engineering to also be licensed professional engineers. Furthermore, licensure is a legal requirement for consulting engineers, whether they are principals or employees. Specific governmental engineering positions in federal, state, and municipal agencies require licensed engineers. PE licensure helps insure public safety, ethics, and overall industry standards.

Acknowledgments

Our team would like to thank Worcester Polytechnic Institute (WPI) Departments of Civil and Environmental Engineering and Chemical Engineering for allowing the research to be done in order to fulfill our graduation requirements. Along with WPI, we would like to thank EMD Millipore for sponsoring our project. Throughout this research, Millipore provided wastewater samples and guidance in order to continue our research on a daily basis. Professors John Bergendahl and Robert Thompson provided countless amounts of advice and expertise throughout the entire project and we could not have completed this research or project on time without them. We would also like to thank Donald Pellegrino for his assistance in supplying our team with every item needed to complete our experiments in the lab such as syringe filters, compressed air and COD test vials. Once again we would like to thank WPI and everyone who helped us complete this project, for without them this great opportunity to complete our undergraduate degrees would not have happened.

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Introduction

According to the United States Geological Survey, only 2.5% of the water on Earth is freshwater. Out of that 2.5% of freshwater, only 30% is accessible as groundwater or surface water. This means that only 1% of the water on Earth is fit for human use (EPA, 2014). Water is an important aspect of survival and with so much of the water on Earth being saltwater or ice, the resources that are available are limited. Water reclamation, or water recycling, helps to alleviate the need for more freshwater.

The Environmental Protection Agency (EPA, 2014) defines water reclamation as "reusing treated wastewater for beneficial purposes." Water can be reclaimed from many sources, including domestic sources, municipal waste, and industrial processes. There are regulations in place to determine the necessary treatment level, depending on the intended use. Reclaimed water is mostly used as nonpotable, or non-drinking water, but with enhanced treatment and stricter regulations, reclaimed water is sometimes used as potable water as well. Some more common uses are landscaping, agriculture, golf course irrigation, industrial processes, and construction activities (EPA, 2014).

The use of reclaimed water can have many environmental benefits. It can be used to recharge underground aquifers or supplement reservoirs, which decreases the strain on these resources. With a more dependable water supply available through use of reclaimed water, the amount of water taken from sensitive ecosystems can be decreased, allowing the ecosystems to flourish (EPA, 2014). Water reclamation is also beneficial for the environment because more water is treated instead of being discharged as wastewater; reusing water can help to decrease the amount of water pollution over time.

Reusing water is not only environmentally friendly, but can also be cost effective. With water demand increasing, it becomes more expensive to acquire water for various purposes, and to pump and transport water to where it is needed. The energy needed to pump and transport water may be more than that needed to treat water for reuse. Also, if water reclamation is used for nonpotable uses, then the amount of treatment needed may be significantly less. By reducing treatment requirements, energy and money is saved. A 2005 study conducted by the California Energy Commission (CEC) stated that recycled water was the least energy-intensive water source in the state, and therefore the most economical (Klein, 2005).

Water reclamation can also be used internally on a smaller scale in industrial or commercial facilities to reduce costs and overall water use for commercial and industrial companies. According to national water use data, industrial processes accounted for 4% of the water used daily in the United States (USGS, 2010). In 2005, industrial processes accounted for approximately 16% of national water use. This decrease can be attributed to more efficient processes, stricter environmental regulations, and a push to reclaim industrial wastewater (USGS, 2010). Reclaiming water is becoming a popular solution for industrial companies and there are many ways for them to accomplish this. One way for companies to reuse water is to redirect their own municipal water from faucets and sinks to be process water. Companies could also redirect water used for cooling or a boiler feed as it will have very little waste. Another popular solution is for the company to treat wastewater on site for reuse. One company that wishes to implement this solution is EMD Millipore.

EMD Millipore is a life science company involved in providing the tools and technologies to aid research, development and production of biotechnology and pharmaceutical drug therapies. As a division of Merck KGaA of Germany, EMD Millipore is a top tier supplier in the life science industry to Good Manufacturing Process (GMP) operations worldwide. The Device

Manufacturing Center of Excellence, located in Jaffrey, New Hampshire is a global source for devices and is responsible for high-volume manufacturing and new product introduction. EMD Millipore's BioProcess Solutions products include normal-flow filtration and tangential-flow filtration devices, all manufactured at the Jaffrey facility.

In the production of these devices, a number of organics and chemical compounds are used. Millipore currently owns and operates its own wastewater treatment plant (WWTP) at the Jaffrey, NH facility in order to treat these constituents before the wastewater is sent to the Town of Jaffrey's municipal WWTP. Millipore's WWTP currently operates with a dual flow sequence batch reactor, handing approximately 10,000-20,000 gallons of wastewater per day.

By implementing a treatment process for the wastewater prior to entering the WWTP, EMD Millipore in Jaffrey NH aims to treat its wastewater for reuse in the manufacturing process and optimize its current wastewater treatment process. The following objectives were developed for this project:

1. To analyze and assess process wastewater chemistries at Millipore's Jaffrey NH facility and to assess the potential for reclamation.
2. To identify technology to re-use the wastewater effluent as a source of process water.
3. Design a pilot-scale wastewater reclamation process for implementation at the Jaffrey facility.

The project tasks included characterizing the wastewater, evaluating reclamation treatment options experimentally, and producing a pilot-scale design. Each product produced involves the manufacturing of different components, and the use of a variety of chemicals for manufacturing. This creates variation in the wastewater composition. Millipore has implemented a storage tank in which the individual flow streams from the manufacturing processes are homogenized and the solution pH adjusted. Thus, reclamation options of wastewater collected from the effluent of this tank were evaluated. This location provided a homogenous and therefore consistent solution.

Environmental sustainability through alternative wastewater treatment and beneficial reuse of process wastewater was EMD Millipore's goal through this project. Optimizing the current WWPT will reduce cost, as well as water input to and output from the facility. Ultimately, this will benefit both EDM Millipore and the Town of Jaffrey.

Background

This chapter provides background information for this project. It covers topics such as different wastewater treatment options and the specific contaminants in Millipore's wastewater stream.

Potential Wastewater Treatment Options for Millipore's Wastewater

This section describes the treatment options investigated for the removal of contaminants from Millipore's wastewater. Information is provided on chemical oxidation, membrane separation, adsorption, and distillation. These four treatment processes were chosen because they are mature technologies accepted by practitioners and industry. Aspects covered include a basic definition of each process, how it is used in general wastewater treatment, and different variations of each treatment.

Chemical Oxidation

Chemical oxidation reactions are important reactions that cannot exist without chemical reduction reactions; reduction and oxidation are coupled. Together, these two types of reactions are called redox reactions. These are energy-producing reactions that are used in industry and biological processes. In redox reactions, one or more electrons are transferred from one species to another. In these coupled reactions, the species that loses electrons is oxidized and the species that gains electrons is reduced. Therefore, oxidation and reduction reactions happen simultaneously. An example of a redox reaction involving sodium chloride is shown below in Reaction 1. In this reaction, the chlorine atom loses two electrons and the sodium atom gains two electrons.

Overall Reaction: $2\ NaCl(l) \rightarrow 2\ Na(l) + Cl_2(g)$
Oxidation half-reaction: $2\ Cl^- \rightarrow Cl_2 + 2e_-$
Reduction half-reaction: $2\ Na^+ + 2e^- \rightarrow 2\ Na$

Reaction 1. Example of an Inorganic Redox Reaction (Bishop, 2013).

In some cases, oxidation and reduction are not defined solely by the transfer of electrons but by the transfer of a hydrogen or oxygen molecule from one species to another. The transfer of hydrogen and oxygen that makes up most redox reactions in organic chemistry can be separated into three categories: the removal of hydrogen, the replacement of hydrogen with oxygen, and the addition of oxygen (Herges & Winkler, 2014). Here, oxidation is the process by which a carbon atom gains bonds to more electronegative elements, most commonly oxygen (Cortes, 2009). An example of a reaction that depicts organic oxidation is shown in the figure below.

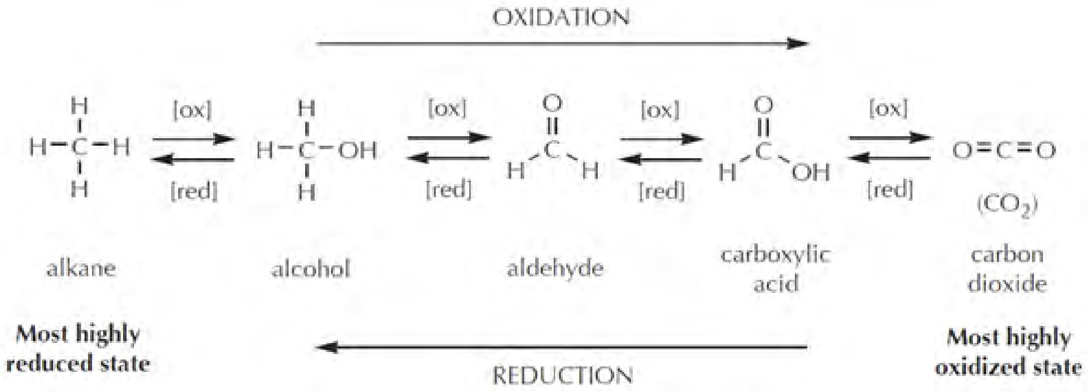

Figure 1. Series of oxidation and reduction reactions (Cortes, 2009).

The process of chemical oxidation for the purpose of wastewater treatment is important because it is used to chemically convert hazardous contaminants to non-hazardous compounds, or recalcitrant compounds to biodegradable compounds. However, some compounds can only be chemically converted into a less toxic compound. Although these compounds may still be toxic, they are preferred to the parent compounds because they are typically more stable, less mobile, and sometimes inert (Deuren et al., 2002).

Chemical oxidation can also be used for other purposes within treatment systems; to control algae and other biological growth, to act as a disinfectant, to remove color and odors, and to precipitate metals (American Water Works Association, 1991).

There are different types of oxidants and methods that can be used to perform oxidation treatment in wastewater. The types of oxidation and oxidants discussed in this paper include ultra violet (UV) oxidation, ozonation, and hydrogen peroxide addition. UV oxidation uses light radiation to break apart molecules and to form reactive radicals. Ozonation is the process of treating the wastewater with ozone in order to oxidize the organics. Ozone is particularly favored in industry because of its recognizable odor, thus leaks can be identified quickly. Ozone can also be used as a disinfectant instead of chlorine which is more toxic and has no odor (Droste, 1997). Finally, peroxides are used to promote the formation of hydroxyl radicals in wastewater, which then oxidize the organic molecules. Several of these processes are used in conjunction with each other to increase their effectiveness in what is now called advanced oxidation.

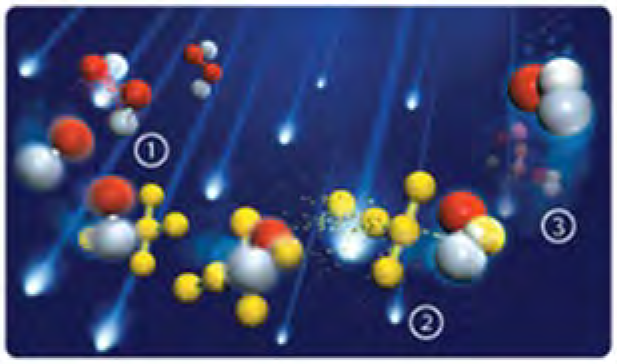

Figure 2. Combined hydrogen peroxide and UV oxidation destruction reaction. (Trojanuv, n.d.).

Ultraviolet light oxidation is a destructive chemical process that oxidizes organic constituents in contaminated water by breaking down molecules into more reactive radicals and molecules that will bond with those radicals. The oxidation reactions are achieved through the high intensity UV light irradiation alone or in conjunction with other treatment methods such as ozone (O_3) and/or hydrogen peroxide (H_2O_2). This process generates hydroxyl radicals (OH•) that then react with most organic chemical compounds. If complete mineralization is achieved in the reaction, carbon dioxide, water and salts are formed. The reaction can break down a wide variety of organic contaminants and has the main advantage of producing no toxic by-products. Another advantage to UV oxidation is that it can be performed in batch or continuous flow operations, depending on the flow rate (Trach, 1996).

Ozonation or ozonolysis is the process of using ozone gas as an oxidizing agent, and contacting it with contaminated water to transform the contaminants through oxidation. Molecules of ozone are very unstable and have a short half-life in water (Sraehelin & Hoigne, 1985). The generation and decay happens according to the following equilibrium reaction.

$$2O_3 \leftrightarrow 3O_2$$

Reaction 2. Equilibrium reaction of oxygen and ozone (Sraehelin & Hoigne, 1985).

This equilibrium reaction favors the decay of ozone in water, and ozone is only produced (the reverse direction of reaction 2) in certain circumstances such as direct contact with strong UV light, during thunderstorms, in waterfalls, or in ozone generators. Due to the spontaneous decomposition of the molecule, ozone has to be generated on site with an ozone generator in order to be used as an oxidant in wastewater treatment.

That being said, ozone is a strong oxidation agent that can oxidize most organic material. When looking at the strengths of different oxidants, it is important to look at the standard electrode potentials of the oxidants. This potential is a measure of the energy per unit charge which is available from the oxidation and reduction reactions that acts as the driving force of the reaction. The standard electrode potential for ozone is 2.07 V. This means that it has a very high potential for oxidizing other molecules and for being reduced. There are only a few other oxidants with standard electrode potential values that are greater than 2 (EPA, 1999). When ozone oxidation occurs, an extra oxygen atom releases from the ozone molecule and binds with the other molecule.

In order to achieve maximum ozonation effectiveness, the ozone concentration dissolved in water has to be maximized. Achieving maximum effectiveness can be difficult to determine because of the limit of solubility of ozone in water. Ozone solubility is dependent on properties of water such as temperature, pH, and concentrations of other dissolved matter.

The effect of pH on ozonation reactions can be seen in the reactions written below for an acidic solution and a basic solution (American Water Works Association, 1990).

$$O_3 + 2H^+ + 2e^- \rightarrow O_2 + H_2O \text{ (Acidic)}$$
$$O_3 + H_2O \rightarrow O_2 + 2HO\bullet \text{ (Basic)}$$

Reaction 3. Ozonation reactions based on pH (American Water Works Association, 1990).

From looking at these reactions, it can be concluded that this oxidation process favors a basic pH because the reaction produces radicals in the basic pH range (American Water Works Association, 1990). The radicals can rapidly and non-specifically react with the organic material that is in the wastewater. These hydroxyl radicals are important because they are one of the most powerful chemical agents known that is capable of reacting with the organics, and they also react with ozone to form oxygen radicals that can also react with the organic material. The reactions that occur between the hydroxyl (and other) radicals and ozone can be seen below (Sraehelin & Hoigne, 1985).

$$
\begin{gathered}
O_3 + OH^- \rightarrow O_2\bullet - + HO_2\bullet \\
HO_2\bullet \rightarrow O_2\bullet^- + H^+ \\
O_3 + O_2\bullet^- \rightarrow O_3\bullet^- + O_2 \\
O_3\bullet^- + H^+ \rightarrow HO_3\bullet \\
OH\bullet + O_3 \rightarrow HO_4\bullet \\
HO_4\bullet \rightarrow O_2 + HO_2\bullet
\end{gathered}
$$

Reaction 4. Reaction mechanism involving hydroxyl radicals and ozone (Sraehelin & Hoigne, 1985)

The final oxidant discussed in this background is hydrogen peroxide. This oxidant is used in many oxidation studies and is often in combination with other oxidants in order to improve the degradation of the organic molecules within the wastewater. When hydrogen peroxide reacts with water, it produces hydrogen peroxide radicals and hydroxyl radicals with the following reactions (Sraehelin & Hoigne, 1985).

$$
\begin{gathered}
H_2O_2 \rightarrow HO_2^- + H^+ \\
HO\bullet_2 \leftrightarrow H^+ + O\bullet_2^- \\
HO\bullet_2 + HO\bullet_2 \rightarrow H_2O_2 + O_2 \\
OH\bullet + HO\bullet_2 \rightarrow H_2O + O_2 \\
OH\bullet + O\bullet_2^- \rightarrow OH^- + O_2 \\
HO\bullet_2 + O\bullet_2^- + H_2O \rightarrow H_2O_2 + O_2 + OH^- \\
OH\bullet + OH\bullet \rightarrow H_2O_2 \\
OH\bullet + H_2O_2 \rightarrow HO\bullet_2 + H_2O
\end{gathered}
$$

Reaction 5. Reaction mechanism involving hydrogen peroxide and water to produce radicals (Sraehelin & Hoigne, 1985).

Sometimes, multiple oxidants are combined to perform advanced oxidation reactions. When hydrogen peroxide is added to wastewater containing ozone, the HO_2^- ions react with the ozone to produce more radicals, as shown below.

$$2\ O3 + H2O2 \rightarrow 2\ OH\bullet + 3\ O2$$

Reaction 6. Reaction between ozone and hydrogen peroxide (Sraehelin & Hoigne, 1985).

The hydroxyl radicals have a very high electrode potential. It is in fact one of the strongest oxidizers available for wastewater treatment. Due to the high potential, more of the organic material in the wastewater will be oxidized and be degraded into non-toxic materials.

These oxidation processes are available in the Environmental Lab in Kaven Hall at WPI. Since ozone is commonly used and a well-established technology, the team decided to pursue the use of ozonation for treating Millipore's wastewater. There is also the potential to use ozone combined with hydrogen peroxide in order to achieve better results for the organic content removal in what is known as advanced oxidation technology.

Membrane Separation

Membrane treatment processes are used to remove dissolved and suspended constituents from water. During membrane treatment, wastewater is pressure driven through a membrane and constituents are concentrated on one side of the membrane due to size exclusion among other separation mechanisms. Membrane treatment is used for removal of suspended solids, microorganisms, hardness, volatile organics and other soluble organics (Droste, 1997). Membrane filtration can range from microfiltration to remove large contaminants (e.g. suspended solids), to reverse osmosis, which can remove dissolved organic compounds and dissolved ionic species. The use of membrane filtration is becoming increasingly more common as stricter water quality regulations are implemented.

Three methods considered for reclamation of Millipore's wastewater were reverse osmosis (RO), ultrafiltration (UF), and nanofiltration (NF) due to their removal capabilities for dissolved and smaller-sized constituents. In nano or ultrafiltration, pressure is used to push water through a membrane that is adsorptive to different constituents (Droste, 1997). Reverse osmosis also filters out dissolved solids from the wastewater by forcing the water through a membrane by applying pressure in excess of the osmotic pressure of the dissolved constituents in the wastewater. Operating pressures decrease as the pore opening size of the membrane increases. Operating pressures for RO systems range from 225-460 psig, from 70-140 psig for nanofiltration systems and from 45-75 psig for ultrafiltration (Droste, 1997). For all three systems, the wastewater must go through multiple pre-treatment steps to remove large suspended solids to prevent membrane fouling.

Based on the criteria of this project, both nanofiltration and reverse osmosis were considered. Both of these membranes have the potential to remove various organic compounds and salts. In a study by Kenneth Agenson in 2003, the removal of multiple organic pollutants through NF and RO membranes was evaluated. Most of the constituents found in the Millipore wastewater are volatile which makes the retention rate of the membranes inefficient with about a 20% removal rate (Agenson, 2003). Higher retention rates can be achieved with more hydrophobic molecules with larger widths and lengths (Agenson, 2003). Nanofiltration and reverse osmosis are also both mature technologies which could easily be implemented into the wastewater treatment system at Millipore. Due to time restrictions and limited lab equipment, experiments using these processes were not feasible.

Adsorption

Adsorption is a physical process in which solutes transfer from a gaseous or liquid phase and accumulate on the surface of a solid matrix. This transfer is not to be confused with absorption, in which a material is transferred to a liquid phase (Armenante, 1999). Adsorbents have adhesive qualities that outweigh their cohesive energy. The molecular bonding effect during physical adsorption is weak and reversible, which allows for adsorbent regeneration and adsorbate extraction. Once saturated with contaminants, the adsorbent surfaces have a reduced ability for additional transfer to the surfaces, and therefore decreased capability for additional adsorption. This accumulation at the interface of two phases is associated with van der Waals forces, hydrogen bonds, steric interaction, hydrophobicity and polarity.

Adsorption can be classified into two basic categories: physical adsorption and chemisorption (Chiou, 2002). Physical adsorption can generate multilayer accumulation by not requiring functional sites for adsorption on a surface. On the other hand, chemisorption entails chemical bonds, generating single layer accumulation through requiring bonding at specific sites with functional groups. The temperature at which adsorption occurs and the pH of the solution are two environmental factors that also affect the type of bonding. For the purpose of this project, physical adsorption is expected to be the primary adsorptive mechanism.

Polarity, molecular size, solvent characteristics and functionality of adsorbate are properties considered when determining proper adsorbents. Surface polarity corresponds to affinity for polar substances, such as water or alcohols (Armenante, 1999). Polar adsorbents are generally referred to as hydrophilic, and include some zeolites, porous alumina, silica gel, and silica-alumina. Non-polar adsorbents are typically hydrophobic and have more affinity for oil or hydrocarbons than water. Surface area is one of the properties that adsorption is most dependent on, as large surface areas linearly correlate to adsorption capacity. Increase in surface area in a limited volume results in the formation of smaller pores between adsorption surfaces. Pore size distribution of micro-pores impacts adsorption in determining adsorbate molecules accessibility to internal surfaces. Furthermore, the adsorbate is characterized by the pKa value and solubility.

Adsorption is a useful tool for purification and separation of contaminants in water sources. This process is operative in most natural physical, chemical, and biological systems. Adsorption consists of three steps involving macro-transport, micro-transport, and sorption (Lenntech, 2014). Macro-transport is the movement of the contaminant in the water through a macro-pore system (macro pore > 50 nm). The second is micro-transport, in which a contaminant diffuses in the interface or liquid layer next to the adsorbent. This would be through a meso-pore or micro-pore system (meso-pore 2-50 nm; micro-pore < 2 nm). Lastly, sorption is the process in which physical attachment of a contaminant to the surface of the adsorbent occurs. There are many different adsorbents that can be used in the adsorption process.

Most adsorbents can be classified into the following three categories: oxygen-containing adsorbents, carbon-based adsorbents, and polymer-based adsorbents (Bart, 2005). Oxygen-containing adsorbents include silica gel, activated alumina, zeolites, clay, and others. They are typically hydrophilic and are used to adsorb polar compounds. Polymer-based absorbants include polystyrene and other patented polymers. These adsorbents are used to remove organic compounds from wastewater, as they have large surface areas, rigidity, and pore size distribution that make them ideal for this situation (Pan, 2009).

The third classification of adsorbents and the type that were used in this project were carbon-based adsorbents. These include activated carbon, activated coke, carbon nanotubes, and other carbon-based compounds. They are produced from organic materials, such as coal, peat, or wood. Carbon-based adsorbents have graphite lattice structures which provide many sites for constituents to bond with. They also normally have high surface areas. Due to these characteristics, carbon adsorbents are frequently used to remove organic and nonpolar compounds from wastewater (Uhríková, 2007).

During this project, experiments were conducted using activated carbon as an adsorbent. Activated carbon has the largest surface area of all absorbants, ranging from 300-4000 m^2/g. It also has widespread application in wastewater treatment. Activated carbon can be classified as powdered activated carbon (PAC) or granular activated carbon (GAC) dependent on size. The difference in which can be seen in Figure 3 below.

Figure 3. Difference between granulated and powdered carbon (Aquatreat Systems and Engineers, 2012).

The left side of the figure shows PAC, an activated carbon with a smaller particle size, typically smaller than 1 mm in diameter. The right side of the figure portrays GAC, which has a larger particle size, typically ranging from 1.2 to 1.6 mm in diameter (EPA, 2015). GAC was used in the experiments for this project, as it can be effectively implemented in fixed bed contactors in wastewater streams.

Distillation

Distillation is a separation process which relies on the differences in volatilities of two (binary) or more liquid components. The two main types of distillation are flash distillation and distillation with reflux. In flash distillation, the liquid mixture is boiled; vapor is produced and is allowed to condense at the top of the column, where it is then collected. In order for flash distillation to be effective, it is assumed that the components present in the mixture boil at a wide range of temperatures. This means that components with similar boiling points cannot be separated using flash distillation. Due to this, it is used mainly in processes such as petroleum refining. If components with similar boiling points need to be separated, distillation with reflux may be used. In distillation with reflux, part of the condensate produced is fed back to the column so that it comes directly in contact with the vapor moving up the column. This allows for an increase in the purity of the distillate, as the liquid flowing down the column enriches the vapor flowing up the column with the most volatile component.

Distillation with reflux can either be performed as batch distillation, or as continuous distillation. Batch distillation is generally used for products which require higher quality control, as this process is more costly than continuous distillation. Continuous distillation is much more common for large-scale-production, as the process is less costly. For this project, distillation was not considered because of the high energy consumption and cost. This is because the effluent from their production is relatively low in concentration of ethanol and isopropyl alcohol and other volatile components (Wankat, 1944). This means that there would need to be more equilibrium stages to achieve complete or near complete removal from the wastewater stream. The process of distillation would produce a product high in concentration of the volatile organics. This product would be a liquid waste that would be expensive to have taken away and properly disposed of. Distillation would not be economically feasible option for Millipore at this scale.

Advantages and Disadvantages of Treatment Options

The advantages and disadvantages of each treatment option were evaluated for application to EMD Millipore's wastewater stream. The following table outlines the advantages and disadvantages of each treatment option discussed above.

Table 1. Advantages and Disadvantages of Treatment Options Identified for Millipore's Wastewater

Treatment Type	Advantages	Disadvantages
Chemical Oxidation	- Degrades organics into non-harmful byproducts -Most organics can be degraded through oxidation	- Oxidation favors extreme operating conditions such as extreme pHs, high pressures, and high temperatures which would raise operating costs due to pH adjust and reinforced equipment.
Membrane Separation	- Effective for a wide range of constituents based on different pore sizes available -Can treat high flow rates of wastewater -Filters can be added in parallel or series for greater flexibility	-Smaller pore sizes create an energy intensive pumping system to remove contaminants - Each filter is only effective for a specific range of pore sizes
Adsorption	- Applicable to a wide variety of organic compounds - Wide range of activated carbons available	- Not effective for highly soluble constituents - Unable to remove high concentrations of contaminants - Disposal or regeneration of contaminated carbon is costly
Distillation	-Can be used to separate the more volatile species out of the water -Can use one distillation column for all contaminants that have a lower boiling temperature than water-high efficiencies - Could potentially reuse the highly concentrated organics water for energy production	- High energy consumption - High cost - If not reused, disposal of high concentration organic liquid that would be costly

Based on the information provided in the sections above, as well as summarized in Table 1, chemical oxidation and adsorption were chosen for further evaluation. Distillation was not considered because of the large energetic costs. Membrane separation was not considered because resources to conduct these experiments were not readily available. Chemical oxidation and adsorption were considered to be potentially feasible technologies to implement at EMD Millipore's facility.

Millipore Wastewater Constituents

The production process at EMD Millipore involves using multiple chemicals. These chemicals include acetone, n-methyl-2-pyrrolidone, glycerol, polyethylene glycol (PEG), triethylene glycol, ethanol, and isopropyl alcohol. These chemicals all contribute, in varying concentrations, to the organic load in the wastewater stream. Properties for these chemicals are summarized in Table 2.

Table 2. Chemical Properties (Dow, n.d.; CDC, 1988; EMD Millipore, 2015)

Chemical	**Molecular Weight** (g/mol)	**Solubility** (% in water)	**Polarity**	**Vapor Pressure at 20 °C** (kPa)
Acetone	58.08	100%	polar	23.99
n-methyl-2-pyrrolidone	99.13	100%	polar	0.0316
Glycerol	92.09	100%	polar	1.06×10^{-5} (at 25 °C)
PEG & Triethylene Glycol	150	100%	polar	< 0.001
Ethanol	46.07	100%	polar	5.95
Isopropyl alcohol	60.1	100%	polar	4.1

Acetone

Acetone is a clear, colorless, low-boiling and flammable liquid with rapid evaporation characteristics. The organic compound is one of the most widely used industrial solvents, with chemical production, surface coatings, films and adhesives to cleaning fluids, as well as other commercial and pharmaceutical applications (Dow Chemical, 2014). The compound is increasingly being used as a chemical intermediate and commonly used for cleaning purposes in laboratory settings. The chemical is often a component of pharmaceutical and biomedical filtration device production (Dow Chemical, 2014). The chemical's structure is shown below.

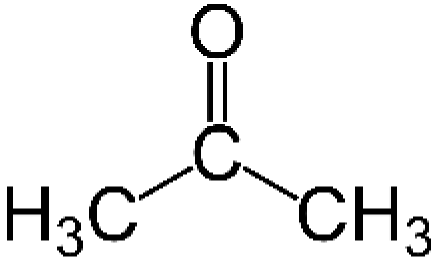

Figure 4. Structure of Acetone ("Acetone," 2015).

Due to acetone's high solubility, adsorption with activated carbon is not a highly effective method of removal. A study conducted through the Desert Research Institute and University of Illinois at Urbana-Champaign studied the removal of volatile organic compounds (VOCs) from humidified gas streams using activated carbon cloth. The use of relative humidity and adsorption of acetone with activated carbon yielded poor results for acetone removal by adsorption to activated carbon (Cal, 1996). Adjustments in relative humidity and concentrations had little effect on the adsorption capacity of acetone due to its solubility in water and binding characteristics with AC.

A removal study performed in 2002 by the USAE Engineering Research and Development Center-Waterways Experiment Station (WES) analyzed three advanced oxidation processes (AOPs) for the treatment of acetone contaminated water. The purpose of the study was to yield comparative data in order to optimize the oxidation processes and determine the most effective technique. Examples of methods that have proven to work included UV photolysis of hydrogen peroxide, UV photolysis with ozone, and peroxone reaction with hydrogen peroxide and ozone. The AOPs conducted rely on the formation of hydroxyl radicals to further oxidize organic contaminants such as acetone (Hernandez, 2002).

Oxidation was tested at various concentrations of H_2O_2 and within one hour of contact time, more than 90 percent of acetone had degraded. The figure below indicates that concentrations of 98 mg/L and 612.5 mg/L of H_2O_2 resulted in the highest level of acetone decomposition. It was observed that higher concentrations of H_2O_2, 785 mg/L, had an adverse effect on the degradation of acetone due to the production of hydroxyl radicals. The scavenging effect of excess hydrogen peroxide was observed with the higher concentration dosages, 612.5 mg/L and 785 mg/L. It was determined that approximately 100 ppm was the optimal concentration because it yielded almost the same results as the 612.5 mg/L dose and used only a fraction of the H_2O_2 (Hernandez, 2002).

Oxidation was tested at various concentration of O_3, as a weight percent in feed gas input. The figure below indicates a correlation between high O_3 concentrations and an increased rate of acetone degradation. However, within the hour, all three ozone concentrations reduced the same fraction of acetone, a level of acetone that was below analytical method detection. It was determined that the range (1-2.25% O_3) had little to no effect on acetone degradation beyond a time of 45 minutes, only the rate of removal prior to that time (Hernandez, 2002).

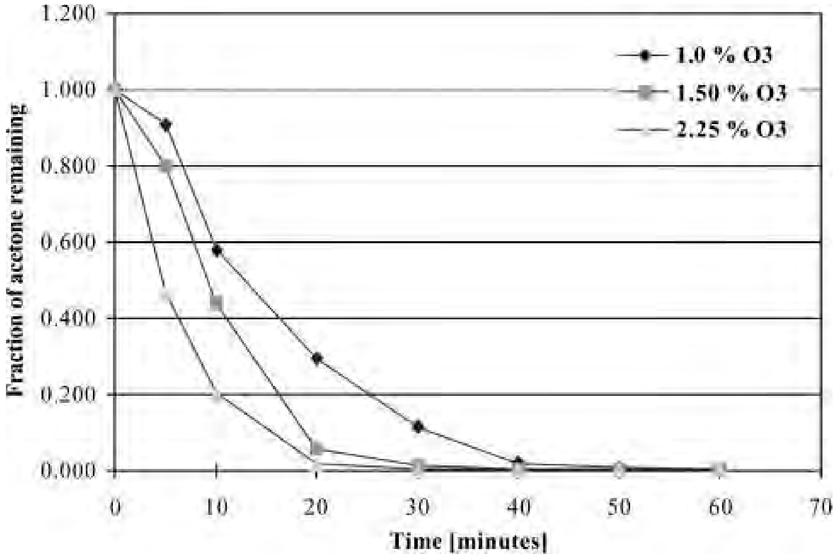

Figure 5. Effect of ozone concentration of the sparged air strem on acetone degradation (LPUV/oxone) (Hernandez, 2002).

For the peroxone reaction, different methods were evaluated using various H_2O_2 and O_3 concentrations. Using O_3 concentration of 2.25% and 2.0% in a sparged stream, the effect of H_2O_2 concentration was analyzed for the acetone degradation. This process removed significantly less acetone, with approximately 20-60% of acetone remaining.

The most effective of the peroxone methods was the addition of 10 mg/L of H_2O_2 and 2.0% O_3 concentrations. This combination resulted in the removal of about 99% of acetone within 1 hour. These data implied that hydrogen peroxide concentrations of 100 ppm also had a scavenging effect; this adversely affected the initial rate of acetone degradation. However, this technique displayed slower kinetics than the two UV-based methods; Figure 5 shows almost complete removal in approximately 20 minutes.

It was concluded that of the three AOPs examined, the most effective process for acetone decomposition was low-pressure UV/O_3. This technique removed approximately 99% of the acetone in 30 minutes and by increasing the concentration of ozone, the rate of degradation could also be increased. These results indicate the potential for advanced oxidation processes for the removal of acetone from EMD Millipore's wastewater stream.

N-methyl-2-pyrrolidone (NMP)

N-methyl-2-pyrrolidone (NMP) is pictured below in Figure 6. The chemical has a high boiling point and polarity, but a low melting point, volatility, viscosity, and low toxicity. The chemical is also thermally resistant. Because of these properties, it is typically used in industrial processes as an inert medium. It can be found in many processes, including chemicals processing, coatings, engineering plastics, electronic engineering, paint stripping, and agricultural chemicals (Usula, 2014).

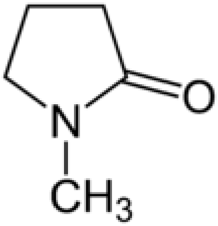

Figure 6. Structure of n-methyl-2-pyrrolidone (Usula, 2014).

Due to NMP's low toxicity and relatively low potential to harm the environment, little research has been done to determine treatment options for removing NMP from wastewater. All of the studies found on the topic dealt with activated carbon adsorption. One study compared the efficiency of multiple types and forms of activated carbon for removing NMP from wastewater. This study concluded that non-impregnated activated carbon worked with an efficiency of approximately 99% removal. The study also concluded that activated carbon impregnated with either citric acid or a strong acid resin did not produce the same results (Dallas, 2014). From this study, it is speculated that activated carbon adsorption will be an efficient treatment process for the removal of n-methyl-2-pyrrolidone from EMD Millipore's wastewater. There was no material found that commented on the removal of NMP by chemical oxidation.

Glycerol

Glycerol is used in many solids, both organic and inorganic, which are important in the preparation of pharmaceuticals. Glycerol is completely soluble in both water and alcohol, but insoluble in hydrocarbons. A figure of its structure can be found below in Figure 8.

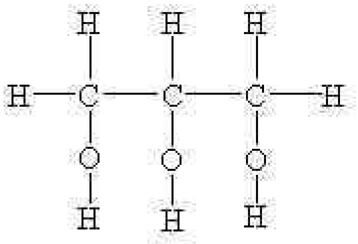

Figure 7. Structure of glycerol (Eggling, 2003).

One study focuses on activated carbon as a treatment option for glycerol. Both granular, in fixed-bed adsorbers/filters and powdered grades, in a batch process, can be used depending on the requirements and specifications. Activated carbons can purify glycerin to a colorless and odorless standard (Reay, n.d.).

Since glycerol is an organic compound it can be destroyed by ozone. Samples that are exposed to pretreatment can see up to 44% COD removal and 25% COD reduction in untreated wastewater (Satyawali, 2008). Adding UV radiation or hydrogen peroxide to the ozone process can also help with the removal of glycerol in wastewater. When UV radiation is added, COD removal can be expected to increase at least 10% compared to just treating with ozone (Beltran, 1997). Therefore, it is speculated that both activated carbon and oxidation are viable treatment options for removing glycerol from EMD Millipore's wastewater stream.

Polyethylene Glycol (PEG) & Triethylene Glycol (TEG)

Polyethylene glycol (PEG) is a polymer that is made up of many ethylene glycol units. Varying amounts of ethylene glycol units can react in water in order to form the polymer chain. The structure of ethylene glycol can be seen below.

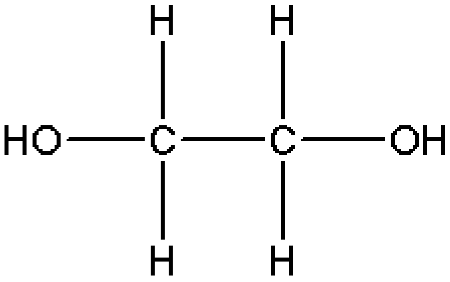

Figure 8. Ethylene Glycol structure (Ethers, 2010).

Low molecular weight PEGs with 2-4 ethylene glycol units are clear, watery liquids. When up to 700 ethylene glycol units are present, the PEG is a clear thick liquid. PEGs containing 1,000 or more ethylene glycol units appear to be waxy solids. PEGs are non-toxic, odorless, colorless and do not evaporate easily.

TEG is a form of PEG with three repeating ethylene glycol units. TEG is a colorless, odorless liquid with high viscosity and boiling point. It is soluble in many liquids such as ethanol, acetone, acetic acid and glycerin; but insoluble in oil, fats and hydrocarbons. The uses of TEG include a plasticizer for safety glass, separation membranes and gas dehydration. The structure of TEG is pictured below.

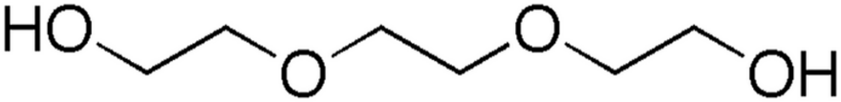

Figure 9. Structure of TEG (Figoli, 2014).

TEG is an organic compound and can be removed using activated carbon. The activated carbon adsorbs organic material because the attractive forces between the carbon surface, non-polar, and the contaminant, polar, are stronger than the forces keeping the contaminant dissolved in the water (DeSilva, 2000). In a study where multiple molecular weights of PEG's (30, 70, 110, 150, 200 and 300 $\frac{mg}{dm^3}$) were tested using commercial grade activated carbon. The primary factor in adsorbant performance is the initial concentration of PEG and particle size (Chang, 2002). According to the Freundlich model ($q_e = K_F C_e^{1/n}$), where 1/n represents the intercept and slope, the value of n=3.7 presents favorable adsorption (Chang, 2002).

The ozonation of PEG is an effective way to reduce the chemical oxygen demand (COD) and total organic carbon (TOC) of the wastewater. Ozone can directly react with pollutants, "direct ozonation," and also react indirectly with pollutants. In a study by Junzo Suzuki, wastewater treatment with ozone was tested and found to decrease TOC from 800 ppm to 200 ppm (75%) in 5 days. In another study by C.Y. Chang combining ozone and UV radiation, the decomposition of PEG can be increased when UV radiation is added to the process. Ozonation combined with UV radiation is deemed as a more effective process to remove organics because UV radiation is used to enhance the ozone decomposition, yielding more free radicals and resulting in higher ozonation rate. Activated carbon and oxidation are the two treatment processes being evaluated in this project. Research shows that both are feasible options for removing PEG and TEG from wastewater.

Ethanol

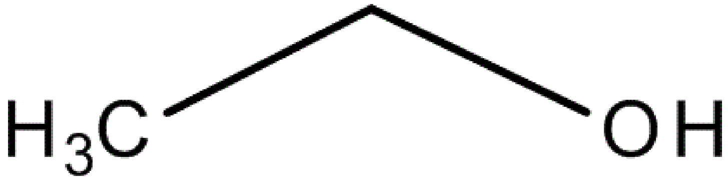

Figure 10. Structure of ethanol (EDM Millipore, 2015).

Ethanol, also known as ethyl alcohol, has the chemical formula of C_3H_8O. It is known to be acutely toxic at high doses. This chemical is also known to be a skin and eye irritant, and is a human ingestion hazard. Also, long periods of exposure cause damage to the internal organs (ScienceLab.com, 2013). It also causes harm to the environment and aquatic life and the disposal of this chemical is regulated by the EPA. Ethanol is used in many industrial processes, in wines and liqueurs, and also as a component of some fuels. Because of its role in their industrial processes, it contributes a significant portion to the COD levels in EMD Millipore's wastewater stream.

Ethanol can be degraded by the process of chemical oxidation, as shown by many case studies. In one such case study, the ethanol was oxidized according to the following reaction equation (Kaksonen et al., 2003).

$$2CH_3CH_2OH \ + \ SO_4^{2-} \rightarrow 2CH_3COO^- + HS^- + H^+ + 2H_2O$$

Reaction 7: Chemical oxidation of ethanol

This oxidation reaction worked well to degrade the concentration of ethanol in water over time. The concentration of the ethanol decreased over time when the oxidation reaction is left alone to react in batch. At lower initial concentrations of ethanol, between 2-10 mg/L, the reaction takes from 2-10 minutes to go to completion and remove all of the ethanol from the solution. When there is a greater concentration of ethanol, 20-110 mg/L, the reaction takes from 20-60 minutes to degrade all of the ethanol. Although there are variations in the time it takes to degrade the ethanol using this chemical oxidation reaction, the case study shows clearly that chemical oxidation is effective for the removal and degradation of ethanol in water.

The removal of ethanol from water using a series of different activated carbons has been studied at standard temperature (298 K). These experiments provided breakthrough results that show that the development of porosity and surface area increases the adsorption capacity for ethanol. However, the total amount of ethanol adsorbed (g/100 g AC) reaches a maximum for the sample at total micro pore volume of approximately 0.55 cm^3/g before decreasing. This decrease in adsorption, after reaching a critical point for optimum packing of the adsorbed molecules, is observed for alcohol solvents with low boiling points such as ethanol. After this critical point, further broadening of the porosity is detrimental because of decreased overlapping adsorption potential inside the micro pores (Silvestre-Albero et al., 2008). These results are depicted in the figure below and similar results are observed for isopropyl alcohol due to similar characteristics.

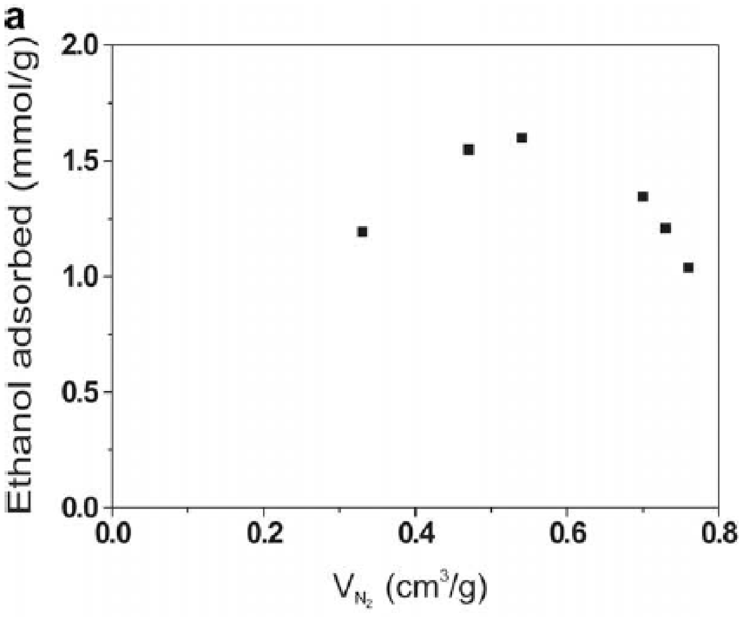

Figure 11. Total amount of ethanol absorbed as a function of total micropore volume (Silvestre-Albero et al., 2008).

These results and the results of other case studies show that ethanol can be absorbed by activated carbon. Ethanol adsorption favors activated carbon with larger pore sizes so that a pore can accommodate two adsorbed layers of ethanol. Also, these activated carbons can be easily regenerated by passing an air flow through them at room temperature which results in a recovery of more than 98%. This process also enhances the adsorption capacity for a polar molecule such as ethanol. Although ethanol can be adsorbed by the activated carbon, the maximum loading achieved was only 7.4 grams of ethanol to 100 grams of the activated carbon. This is a low adsorption capacity that would not be very cost effective (Silvestre-Albero et al., 2008).

Isopropyl Alcohol

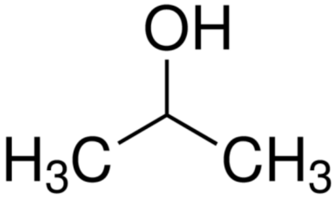

Figure 12. Molecular structure of isopropyl alcohol (MP Biomedicals, 2014).

Isopropyl alcohol, also known as 2-propanol, has the chemical formula of C_3H_8O. This chemical has been observed to be acutely toxic to animals (mice) if ingested in liquid form at 3600 mg/kg. Like ethanol, this chemical is known to be a skin and eye irritant, and is a hazard if ingested. More importantly, also like ethanol, causes damage to the internal organs when a person is exposed to it for long periods of time. (ScienceLab.com, 2013).

There are many studies that show that chemical oxidation reactions are effective for degrading isopropyl alcohol. The results from one such study that investigated hydrogen peroxide addition and UV irradiation are shown in the figures below.

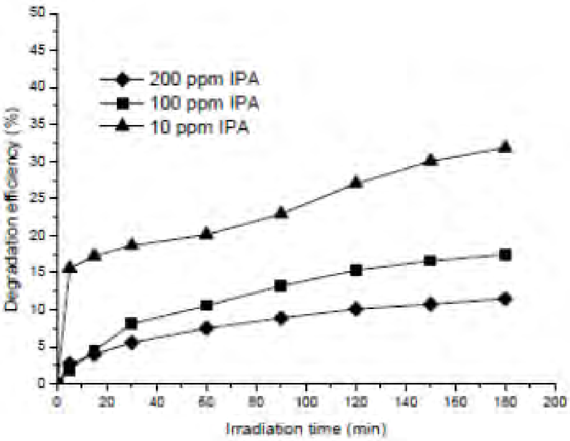

Figure 13. Percent removal of COD when isopropyl alcohol is oxidized with difference doses of hydrogen peroxide (Cheng, 2010).

The hydrogen peroxide addition without the UV light achieved approximately 35 percent COD removal. In Cheng's experiment, three concentrations of isopropyl alcohol (200, 100, and 10 ppm) were placed in brown glass bottles, where 2.5, 10, and 20 ppm of H_2O_2 were added and were left to react for 180 minutes. The results for the highest does of hydrogen peroxide, 20 ppm, are shown in Figure 14 for three different starting concentrations of isopropyl alcohol.

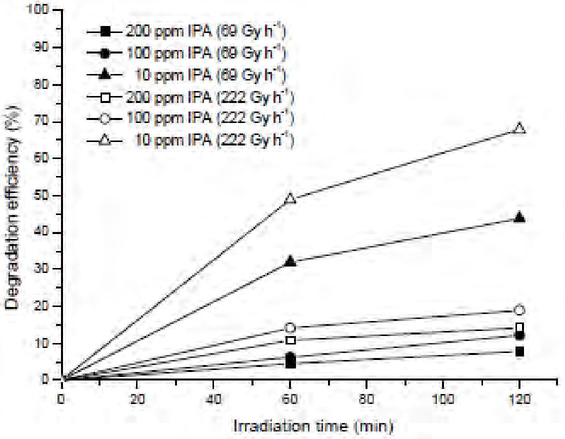

Figure 14. Percent removal of COD when isopropyl alcohol is oxidized with different doses of UV radiation (Cheng, 2010).

In Figure 15, three concentrations of isopropyl alcohol, 200, 100, and 10 ppm, were placed in sample bottles and irradiated using 69, 111, 138, and 222 Gy h $^{-1}$or γ-rays generated using Co-60 without H_2O_2 (Cheng, 2010). The UV light experiments show that increasing the dosage of UV light achieved up to a 65 percent removal of the organics. These figures show the effectiveness of oxidation treatment methods for the removal of isopropyl alcohol.

When treating organics with activated carbon, several factors have to be considered in order to gauge the effectiveness. This is because some chemicals can be adsorbed readily by activated carbon when they are in a gas phase but will not be absorbed very effectively when it is a solvent in aqueous solution. Isopropyl alcohol is one such molecule. According to a performance index for activated carbon in water, isopropyl alcohol is unlikely to be absorbed by activated carbon (Tchobanoglous & Burton, 1991). However, activated carbon has a high adsorption capacity for isopropyl alcohol in the vapor phase than in water due to decreased overlapping adsorption potential inside the micropores similar to ethanol (Island Clean Air, 2008).

Review of Contaminants Present in Millipore's Wastewater

As discussed in the studies noted above, both activated carbon adsorption and chemical oxidation are well-established technologies for the removal of contaminants from wastewater streams. These options were investigated further in WPI's Environmental laboratory for application to Millipore's wastewater. Table 3 summarizes the potential of these treatment options for each specific contaminant.

Table 3. Review of chemicals present in Millipore's wastewater and potential treatment options

Chemical	Chemical Oxidation	Activated Carbon Adsorption
Acetone	Best results are achieved when ozone is combined with UV radiation.	No material to support efficient treatment, not speculated to work due to high solubility.
N-methyl-2-pyrrolidone	No material to support efficient treatment.	Shown to be efficient treatment with non-impregnated carbon.
Glycerol	Shown to be efficient treatment, but can be improved with the addition of UV radiation or hydrogen peroxide.	Shown to be efficient treatment with both granular and powdered AC.
PEG and TEG	Shown to be efficient treatment when ozone is combined with UV radiation.	Shown to be efficient treatment, dependent on the initial concentration.
Ethanol	Shown to be efficient treatment.	Material to support non-efficient treatment
Isopropyl Alcohol	Shown to be efficient treatment.	Material to support non-efficient treatment except in very low concentrations.

Experimental Methodology

This chapter outlines the general laboratory procedures that were used in the treatment experiments and chemical analysis conducted to evaluate the removal of specific contaminants in EMD Millipore's wastewater stream.

Chemical Oxygen Demand Analyses

In order to test the samples for COD, the team created a standard curve using multiple concentrations of potassium hydrogen phthalate (KHP) concentrations in purified water. Once the KHP and purified water were added to a large beaker, the solution was mixed with a stir bar and stirring plate for two hours to allow for adequate mixing. Once completely mixed, 5 solutions were made with KHP concentrations of 0, 200, 400, 600 and 800 mg/l respectively. These solutions were made by placing specific amounts of KHP solutions and purified water into the COD test vials. Specific concentrations are shown in Table 4.

Table 4. Concentrations for KHP Standard Curve

Sample	Final Concentration of KHP solution (mg/l)	Amount of KHP solution (ml)	Amount of Purified water (ml)
1	0	0	2.50
2	200	0.60	1.85
3	400	1.25	1.25
4	600	1.90	0.60
5	800	2.50	0

Standards were added to the COD vials, incubated for 2 hours, and light absorbance measured using a Varian spectrophotometer (600 nm). These data can be found in Appendix A. The standard curve is shown in Figure 16.

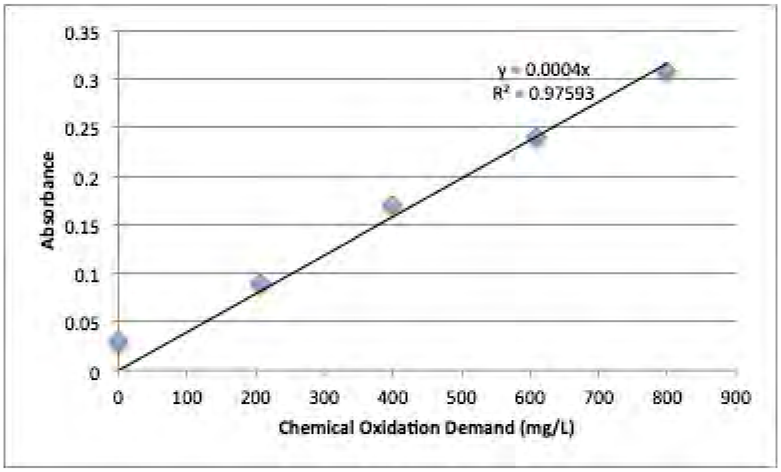

Figure 15. KHP-COD Standard Curve

The next set of vials prepared used wastewater collected from Millipore equalization tank. The wastewater was diluted with purified water by a factor of 40 to within the range of the standard curve. With the high organic content in their wastewater, it was important to dilute the water so the medium range COD test kit could be used to obtain accurate test results. 2.5 ml of solution was added to each COD vial, containing 1.9 ml of purified water along with 60 µl of wastewater. After the solution was added to the COD vial and shaken vigorously, they were placed in the COD incubator for 2 hours. Once incubation was complete, the test vials were cooled and samples removed using a pipette. Sample removed were then placed in the spectrometer, which was set to 600 nm, to determine absorbance. With the recorded absorbance values, the numbers were then compared to the linear regression line formed by the KHP standard curve to determine the unknown concentration of COD in the wastewater.

pH Measurement

Samples pH was measured using an Orion 420A pH meter. Prior to measurements, the instrument was calibrated using three standardized pH buffers with known pH values of 4, 7, and 10. The pH meter probe was immersed in the sample until a stable reading was reached. Before and after immersing the probe in each solution, the probe was rinsed with purified water. The probe was stored in a pH probe storage solution when not in use.

Ozonation Oxidation Experiments

The ozone oxidation experiments were conducted at room temperature (20±0.5 °C) in 1000 mL glass graduated cylinders. This experiment was performed in a lab fume hood with safety glasses, gloves, and a lab coat. First, 300 mL of wastewater was transferred from the main sample bottles to a 600 mL beaker. Then, the pH was determined using a pH probe (Orion pH meter, model 420A) and the pH recorded. The pH of the sample of 300 mL of wastewater was adjusted to values of 7, 7.5, 8, 9, 9.5, 11, and 13 using 10 M of NaOH solution. After the pH was adjusted, the samples were transferred to a 1000 mL glass graduated cylinder.

Ozone was generated using an oxygen-fed L-25 ozone generator from Ozonology Inc. (Northbrook, IL). This ozone generator was set to an airflow of 1 SCFH, 20 psi, and with voltage setting of 100 V. Ozone was passed through a glass dispersion tube (Model 7197-18, Ace Glass, Vineland, New Jersey) and into the sample in the glass graduated cylinder for 4 hours.

Two vials of the sample after oxidation and two vials of the sample before oxidation were analyzed for COD immediately following each ozonolysis experiment, see Chemical Oxygen Demand Analysis section above. The results from each experiment were recorded in an Excel spreadsheet.

Ozonation Oxidation Experiments with Hydrogen Peroxide Addition

The ozone oxidation experiments were conducted at room temperature (20±0.5 °C) in 1000 mL glass graduated cylinder. They were performed in a lab fume hood while wearing safety glasses, gloves, and a lab coat.

First, 300 mL of wastewater was transferred from the main sample bottles to a 600 mL beaker. Then, the pH of the sample was determined using a pH probe (ORION pH meter, model 420A) and the pH recorded. The pH of the sample was then adjusted to pH 7 using 10 M NaOH solution.

Then, 15 mL, 20 mL, and 30 mL of 30 % hydrogen peroxide solution were transferred to 300 mL samples of wastewater for the first set of experiments. For the second set of experiments, 1, 2, 5, 7, 13, and 15 mL of 30 % hydrogen peroxide solution was transferred to 300 mL samples of wastewater. The samples were then mixed for 5 minutes.

Following mixing, the samples were transferred to 1000 mL glass graduated cylinders and placed inside a fume hood. Next, ozone was generated using an oxygen fed L-25 ozone generator from Ozonology Inc. (Northbrook, IL). The ozone generator was set at an airflow of 1 SCFH, 20 psi, and with voltage setting of 100 V. During the experiment, ozone passed through a glass dispersion tube (Model 7197-18, Ace Glass, Vineland, New Jersey) and into the sample in the glass graduated cylinder for a duration of 4 hours.

Finally, two vials of the sample after oxidation and two vials of the sample before oxidation were analyzed for COD immediately following each ozonolysis experiment, see COD Analysis Procedure section above. After the analysis, the results were recorded in an Excel spreadsheet.

In a separate experiment, 6 beakers containing 300 mL of purified water were set on magnetic mixers. Then, doses of 1, 2, 5, 7, 13, and 15 mL of hydrogen peroxide were added to the beakers so that each sample of purified water contained a separate dose of hydrogen peroxide. The samples were allowed 5 minutes of mixing time. Then, a COD analysis was performed on each sample, using 2 COD vials per dose of hydrogen peroxide. After the analysis, the results were recorded in an Excel spreadsheet. This procedure was performed again using 300 mL of wastewater in place of the purified water.

Ozone Dosage Determination

Immediately after the ozone treatment was complete, the 1000 ml graduated cylinder was removed from the fume hood. Two 50 ml beakers were obtained and 40 ml of treated purified water was transferred to one of the beakers and 40 mL of un-treated purified water was transferred to the other. Once both beakers were filled, the Hach DR 900 was turned on and the Hach Ozone HR AV program under "Stored Programs" was selected. One of the Ozone AccuVac Ampuls from the container was placed upside down in the un-treated purified water beaker. Once submerged, the tip of the Ampul was broken to allow the water to flow into the Ampul. The Ampul was kept submerged until completely filled. Once filled, a cap was placed on the Ampul and then was quickly inverted several times to allow for adequate mixing. After mixing was complete, the lid to the Hach DR 900 was opened and the Ampul was placed inside. The lid was closed and the "zero" button on the screen was selected. The Ampul was removed once the machine was zeroed.

After the zeroing of the machine was complete, another AccuVac Ampul was submerged in the treated purified water beaker. While completely submerged, the tip to the Ampul was broken and allowed to fill completely before it was removed from the beaker. Then, the cap was put on and it was quickly inverted several times. The Ampul was placed in the Hach DR 900 and the lid was closed. The "read" button on the screen was selected and the number was recorded.

Activated Carbon Adsorption Experiments

Each activated carbon sample was evaluated for adsorption efficiency by using the same carbon to wastewater ratio for each sample. A 200 mL dilution of sample was prepared in a 1000 mL Erlenmeyer flasks. 5 mL of the sample was diluted with 195 mL of purified water and allowed to mix for 24 hours. Approximately 0.1 g of each activated carbon was measured and each placed into 40 mL amber, glass vials. All vials were labeled accordingly. The VOA vials were placed in an end-over-end mixer and allowed liquid-solid contact for 24 hours. Approximately 10 mL were filtered using a 20 mL NORM-JECT Luer syringe with a disposable nylon filter. Using a micropipette, 2.5 mL were transferred into COD Standard Range vials. Each sample was analyzed for final COD content, see Chemical Oxygen Demand section above.

Three granular carbons were selected to proceed with for further treatment study. The previous procedure was repeated, only altering the dosage of activated carbon. A range of 0.025 – 2.0 g was used to evaluate the adsorption efficiency of each carbon at the different dosages. Each sample was analyzed for final COD content, see Chemical Oxygen Demand section above.

Results

This chapter presents the results that were obtained from the treatability experiments conducted on Millipore's wastewater. Multiple experimental approaches were used to evaluate removal of organic contaminants from EMD Millipore's wastewater stream.

Activated Carbon Adsorption Experiments

Seven activated carbon samples were tested in 24-hour adsorption experiments, following the procedure outlined in the Methodology section above. A carbon dose of approximately 0.1 g was used to assess the adsorption efficiency of each activated carbon. By using the same ratio of activated carbon to wastewater for each sample, the activated carbons resulted in the best treatment effectiveness were identified. Both granular and powdered carbons were tested, but the granular carbons proved more efficient. Data for these experiments can be found in Appendix B. Based on these experiments, the three granular carbons that yielded the best results were used in further experiments. These three carbons were Norit GAC 300, Calgon FILTRASORB 300, and Calgon OLC 12x40.

Various dosages of these three activated carbons were used to further assess adsorption capabilities. Results of varying carbon doses can be seen in the table below.

Table 5. Activated Carbon Adsorption Results

Carbon Dose (mg)	**% Removal over 24 hours**		
	Norit GAC 300	**Calgon FILTRASORB 300**	**Calgon OLC 12x40**
25	4	8	-
50	8	8	24
75	9	10	29
100	10	12	41
250	11	15	50
500	21	19	55
750	-	-	60
1000	-	-	65
2000	-	-	68

As seen in Table 5 above, Calgon OLC 12x40 activated carbon showed significantly higher removal effectiveness. It was noticed that wastewater samples gathered on different days showed some variability in COD concentrations, as expected. This caused some variability in the results obtained for adsorption effectiveness. Even after noting this variability, the Calgon OLC 12x40 carbon still proved significantly more effective than the Norit GAC 300 and Calgon

FILTRASORB 300 carbons for this wastewater. Therefore, further experiments and analysis were conducted using only Calgon OLC 12x40.

After another set of experiments with Calgon OLC 12x40 was conducted to confirm the results above, the data were analyzed to determine which isotherm model best matches the equilibrium data. The data for this analysis can be found in Appendix C. The Langmuir, Freundlich, and linear models were considered as shown in the figures below.

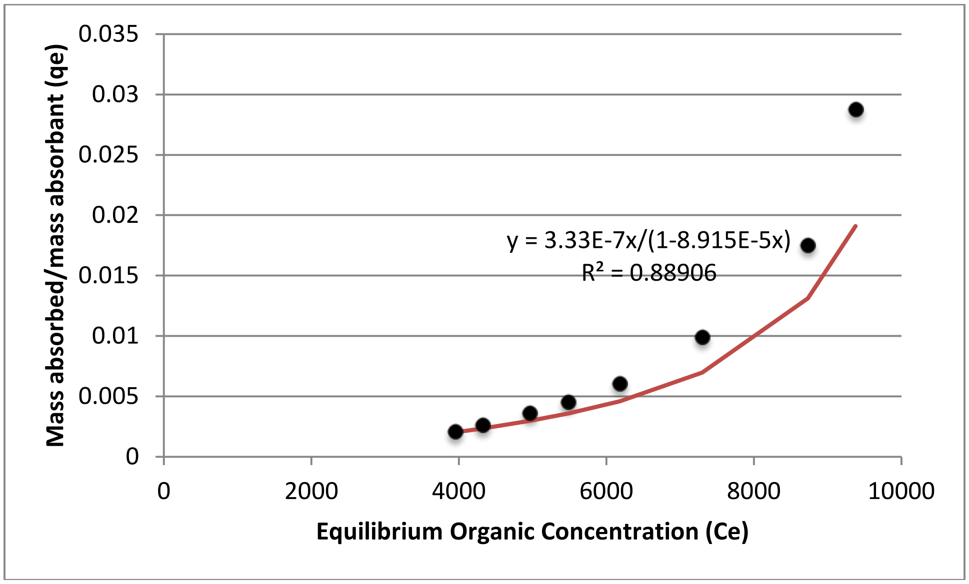

Figure 16. Plot of Langmuir isotherm with Calgon OLC 12x40 carbon. Initial COD = 12270 mg/L, pH = 5.5, temperature = 25 degrees C, contact time = 24 hours.

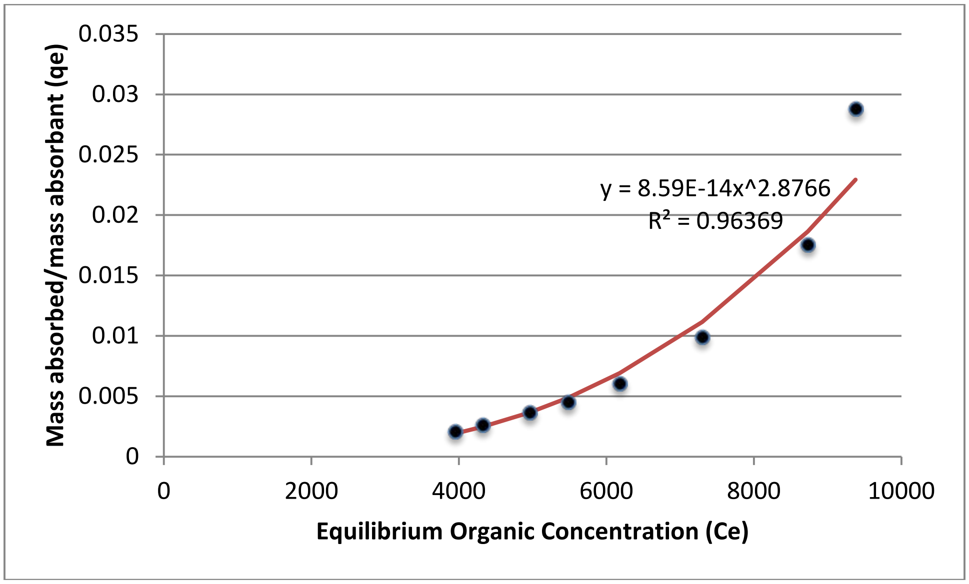

Figure 17. Plot of Freundlich isotherm with Calgon OLC 12x40 carbon. Initial COD = 12270 mg/L, pH = 5.5, temperature = 25 degrees C, contact time = 24 hours.

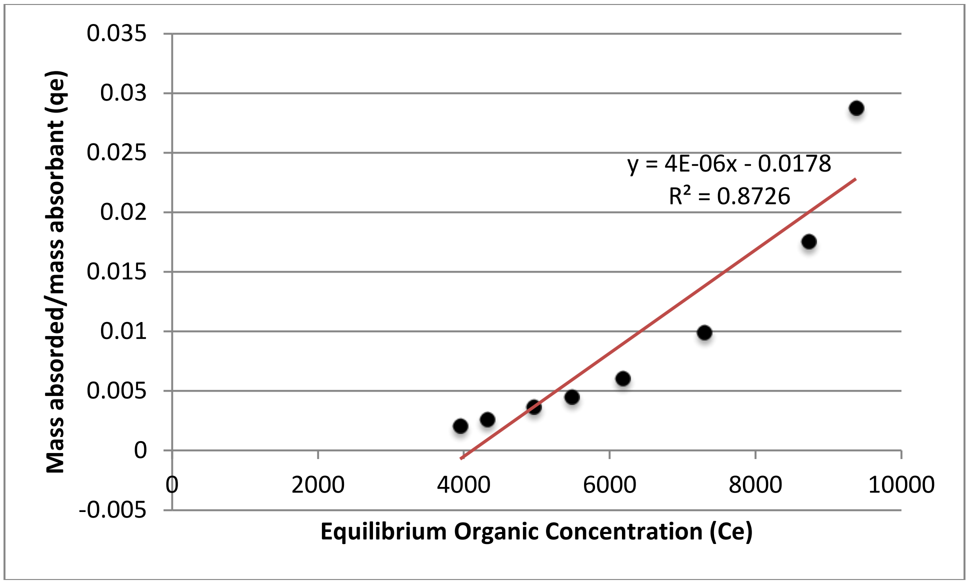

Figure 18. Plot of Linear isotherm with Calgon OLC 12x40 carbon. Initial COD = 12270 mg/L, pH = 5.5, temperature = 25 degrees C, contact time = 24 hours.

Of the three isotherm models analyzed, it was determined that the Freundlich isotherm represented the data the best. The linear isotherm does not match the trend of the data and the Langmuir only matches the trend until the equilibrium organic concentration reaches approximately 7000 mg/L. The Freundlich isotherm follows the data trends quite accurately and has a high correlation with a R^2 value of 0.9637.

Using the Freundlich model, a cost analysis was then conducted. The bed life design approach was used, which employs the following equation:

$$m_{GAC} = q_e \cdot V_{GAC} \cdot \rho_{GAC}$$

This equation can then be rearranged to calculate the amount of activated carbon that is required to treat a volume of wastewater:

$$\frac{m_{GAC}}{V_{WW}} = \frac{C_0}{q_e}$$

The C_0 value, 12270 mg/L, represents the initial COD of the wastewater. The q_e value, 0.0496, was obtained from the linearized Freundlich model. The values are then substituted into the equation above.

$$\frac{m_{GAC}}{V_{ww}} = \frac{12270 \frac{mg}{L}}{0.0496}$$

$$\frac{m_{GAC}}{V_{ww}} = 247104.77 \frac{mg}{L}$$

$$\frac{m_{GAC}}{V_{ww}} = 936 \frac{g}{gal}$$

As shown by the calculation above, 936 g of carbon is needed for every gallon of wastewater treated. The cost of Calgon OLC 12x40 carbon is 0.0055 \$/g resulting in a cost of \$5.16 for treating every gallon of wastewater.

With the Calgon OLC 12x40 carbon, experiments yielded a 68% removal. Even though this removal may be considered an acceptable level of treatment, it is an expensive treatment option. Any financial gain that would result from treating wastewater with this activated carbon would be negating by the cost of carbon needed to treat it. An additional cost for activated carbon treatment of this wastewater would be disposal or regeneration costs of the activated carbon after its use. At this point, it was determined that activated carbon is not a feasible treatment option for EMD Millipore's wastewater stream.

Ozone Oxidation Experiments

Initial experiments were performed without adjusting pH to determine if ozone oxidation was an effective treatment options. Data from these experiments can be found in Appendix D. Further experiments proved that pH played a role in the effectiveness of the treatment; data showing differences in pH can be found in Appendix E. The effect of pH on the removal of organics in the wastewater is shown in Figure 20 below. Two separate wastewater samples were evaluated, as indicated by the two data series in Figure 20 shown with blue diamonds and orange squares.

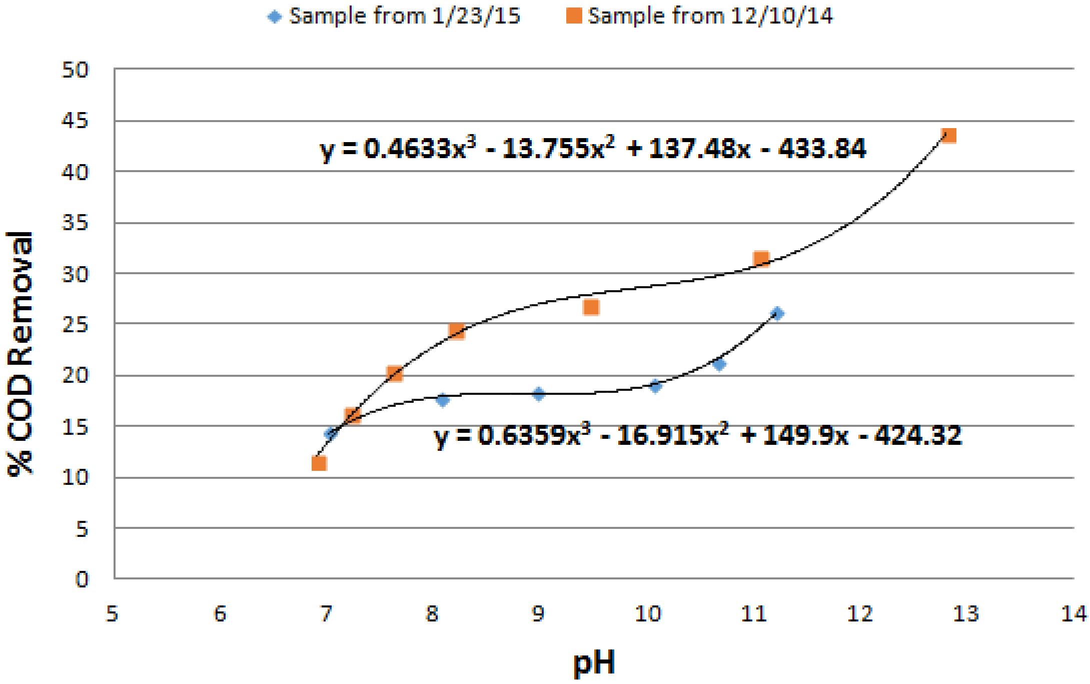

Figure 19. Percent COD removal on wastewater after ozonation. Temperature = 20 degrees C, contact time = 4 hours.

As depicted in Figure 20, both samples of wastewater responded in a very similar manner to ozone oxidation, in that an increase in pH resulted in greater percent removal of COD. The results were fit to a third degree polynomial. The data sets exhibited the same trends, but were of somewhat different magnitudes. This difference can be explained by the fluctuating composition of the samples based on the processes that Millipore is performing on the day that the samples were collected. Oxidation effectiveness varies with the properties of the wastewater, such as pH, temperature, and constituents present. In this experiment, the temperature and contact time were held constant for the two samples and the pH was the variable controlled.

Results show that the optimal pH value to perform the oxidation is approximately 8. These data sets show that increasing pH above 8 produces only small increases in the percent removal of COD.

Ozone Oxidation with Hydrogen Peroxide Addition

Experiments were performed to determine the most effective hydrogen peroxide dose to aid in removing contaminant from the wastewater. The data from these experiments can be found in Appendix F. Testing revealed that the hydrogen peroxide negatively affected the COD analysis results, as shown in the figure below. These results were the opposite of what was expected based on previous research referred to in the oxidation chapter in the background of this paper. The addition of hydrogen peroxide to the oxidation reaction produces more hydroxyl radicals, and the presence of these radicals should produce greater decomposition of organics.

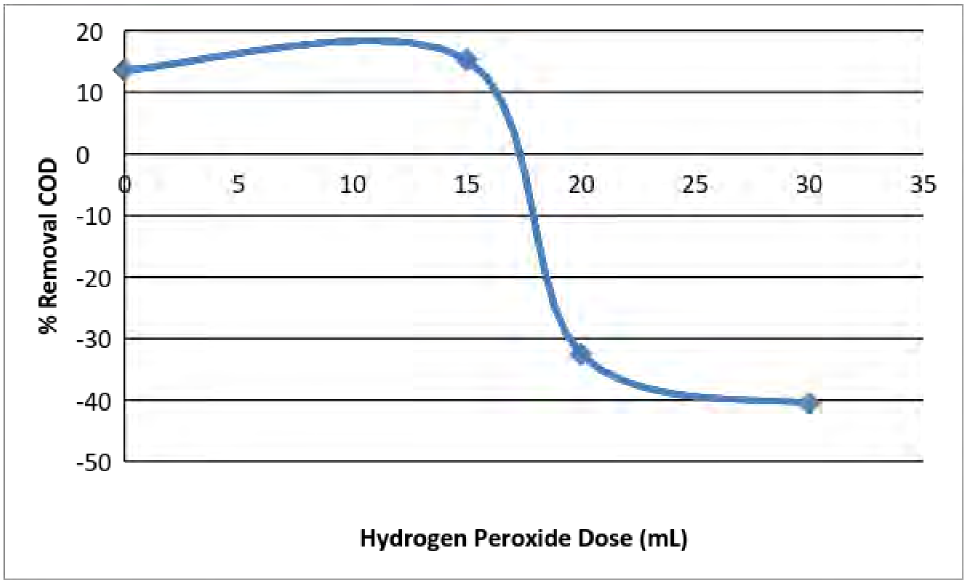

Figure 20. Percent COD removal results from the initial testing of ozonation treatment with the addition of hydrogen peroxide. Initial COD= 13670 mg/L, pH = 7±0.04, temperature =20±0.5°C, contact time = 4 hours.

These results can be explained by the nature of hydrogen peroxide as both an oxidizing and reducing agent during oxidation reactions. It was hypothesized that the hydrogen peroxide that remained unreacted in the wastewater after ozone treatment reduced the dichromate present in the COD vials. The observed behavior prompted a study of the effects of hydrogen peroxide on the COD analysis. In order to adjust our final COD readings to more accurate results, the COD of the doses of hydrogen peroxide in purified water were measured. Once the COD values after treatment were adjusted accordingly by subtracting the COD due to the hydrogen peroxide demand, the values were plotted in the bar graph shown below. Additional data and analysis on the effects of hydrogen peroxide on COD can be found in Appendix G.

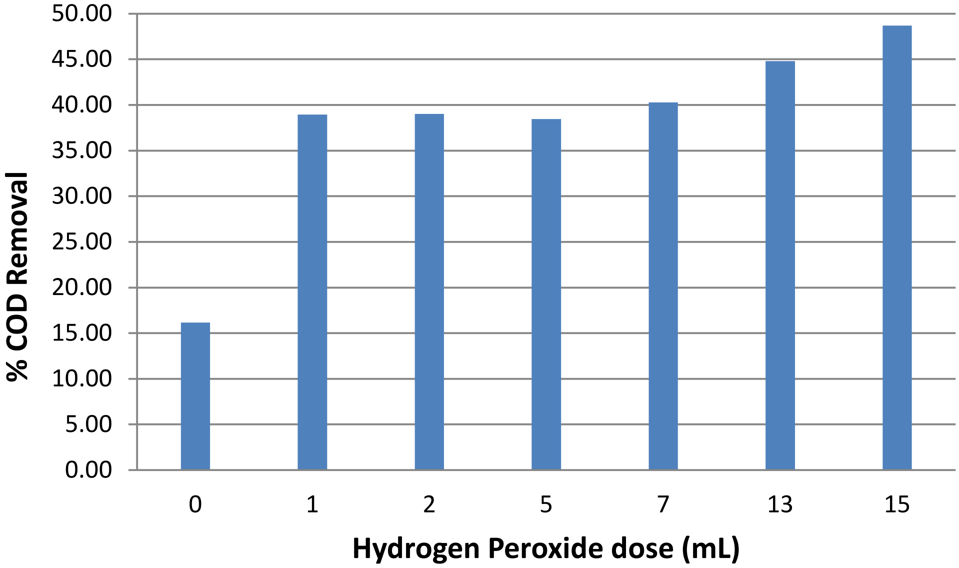

Figure 21. Percent COD removal results from the final testing of ozonation treatment with the addition of hydrogen peroxide. pH = 7±0.04 and temperature = 20±0.5˚C, contact time = 4 hours.

The maximum percent removal of COD that was achieved was determined to be approximately 50% at a dose of 15 mL of hydrogen peroxide per 300 mL of wastewater.

Ozone Oxidation Pilot Scale Design

After the completion and success of many ozone experiments, it is clear to suggest that EMD Millipore investigate using an ozone pilot scale system to remove constituents from their wastewater. To develop this pilot scale system, EMD Millipore must consider many factors. These factors include the pH of wastewater, location of the ozone system, amount of water treated, dosage of ozone and contact time. Along with purchasing the ozone pilot system, Millipore must also provide piping, fittings and power to the system. In order to avoid a need for air permits, adding an ozone destroyer for excess gas is recommended. Adding an ozone destroying unit can make this system completely self-sufficient and avoiding any fees for ozone discharge into the atmosphere. All of the parameters needed can be found below.

Through the experiments conducted, it was found that the preferred pH was between 8 and 9. In this pH range, the greatest COD removal was found with reasonable pH adjust. This pH range is consistent with the pH needed to support the existing biological treatment system. Increasing the pH to a higher level would cost Millipore more money on chemicals without significant increase in COD removal. The system would be best implemented after the pH of the wastewater is adjusted, to keep pH values consistent and monitored. As discovered in ozone oxidation experiments, different pH values have an impact on the effectiveness of ozone oxidation, so the ability to keep the pH values between 8 and 9 is very important. The proposed location of the pilot scale system is pictured below.

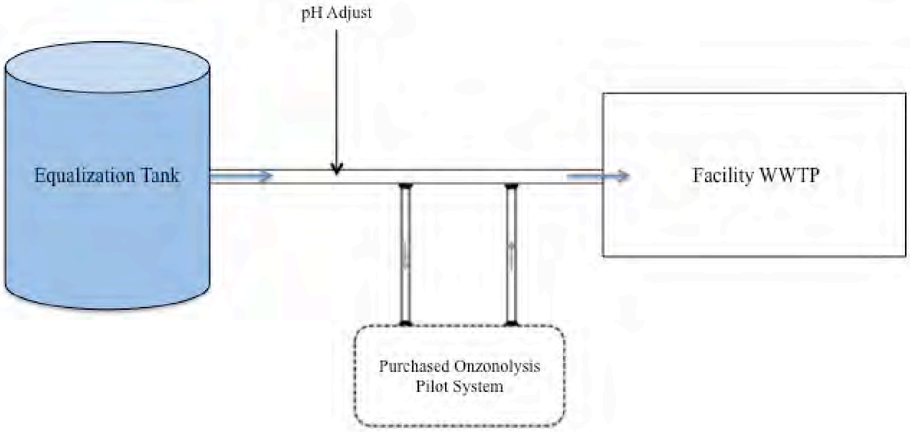

Figure 22. Location of Proposed Ozone Pilot Scale System

After discussing pilot scale systems with companies manufacturing ozone treatment systems, including Spartan Water Treatment, Ozonology and Ozonia, the ideal pilot scale flowrate is between 5-10 gallons per minute (GPM). The pipe diameter chosen for the influent and effluent pipes in this system will be 1.5”. With this diameter of pipe, we can expect to have a flow velocity of 1.81 ft/s. The pilot scale flow rate and pipe diameter can be adjusted depending on Millipore’s specific needs and the type of pilot scale system used. Chlorinated polyvinyl chloride (CPVC) piping is recommended for the piping to the pilot scale system. One of the main features of CPVC that will be beneficial to the ozone system is the resistance to corrosion. The inside surface of CPVC is friction free and won’t breakdown over time due to hard water flowing through it. Shipping will also be less expensive because of how lightweight the material is. Dimensions and proposed materials can be found in Figure 24.

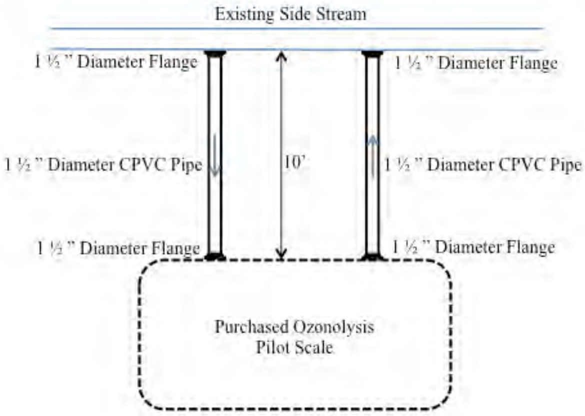

Figure 23. Proposed Connection to Existing Side Stream

To determine the approximate dosage of ozone that was being used in our experiments, purified water was ozonated for four hours, to replicate the amount of time used in previous experiments. The dosage of ozone in the purified water after the treatment was 1.83 mg/l. This number is slightly skewed because ozone was allowed to escape the water through bubbles or was lost in the transfer from the 1000 ml graduated cylinder to the 300 ml beaker. In order to determine the appropriate dose for the pilot scale system, multiple pilot scale studies were read and compared. Pilot scale studies reviewed ranged from textile mills to a winery. Even though the water treated in all studies was different, all the water was similar in that each had high organic content in their water, similar to Millipore's wastewater. Dosage of ozone for these case studies ranged from 2-10 mg/l. In a study to validate the use of ozone for contaminant oxidation and disinfection in water reclamation, the ozone dosage was conducted at 3, 5, and 7 mg/l. 5 mg/l was selected due to the significant oxidation of compounds (Gerrity, 2011). During this experiment, best results were found for contact times between 100-150 minutes. Any amount of time greater than 150 minutes did not result in significant removal of the contamination. Based on compiled research, the suggested pilot scale design parameters are listed in Table 6.

Table 6. Suggested Pilot Scale Design Parameters

Design Parameter	Suggested Value
pH of Wastewater	8.5
Location	After pH adjust
Flow Rate	10 GPM
Ozone Dosage	5 mg/l
Contact Time	150 minutes

Throughout this design process, Spartan Water Treatment was responsive to requests for information. The cost to rent a pilot-scale ozone system provided by Spartan Water Treatment was quoted to be $3,000 per month. Spartan provided multiple documents with various models, which display information regarding ozone output, water flow, estimated pump horsepower and total power. An example of one of Spartan's industrial ozone treatment systems is pictured in Appendix H. Along with the base rental cost, there will also be labor and installation fees, as well as the cost for piping and fittings. Below is a table displaying the cost breakdown per month for a 14 GPM, SPARTOX A20 model with an integrated ozone compressor with a 1.5 HP pump.

Table 7. Estimated Costs of Pilot Scale System

Item	Quantity	Cost Per Unit	Total Cost
Monthly Rental Fee	1 month	$3,000.00/month	$3,000
Installation and Labor	6 hours	$16.50/hour	$93.00
CPVC Piping (1.5")	20 feet	$4.09/foot	$81.80
1.5" flanges (fittings)	4 fittings	$12.65/fitting	$25.00
Total Power	2 kW/h	14.2 cents/kWh	28 cents/kWh ($33.60)
		Cost of Initial Installation	$224.80
		Installation with 1 month of use	$3,033.60
		Total cost after 1 month	**$3,258.40**

In order to power this pilot scale system it will need to be wired by an electrician from an industrial power supply company. The system requires three-phase power and needs to be wired directly into a power distribution panel. These power requirements may affect where the ozone pilot scale system can be installed. Figure 25 below shows the flow in and out of the system along with the water pump and energy requirements.

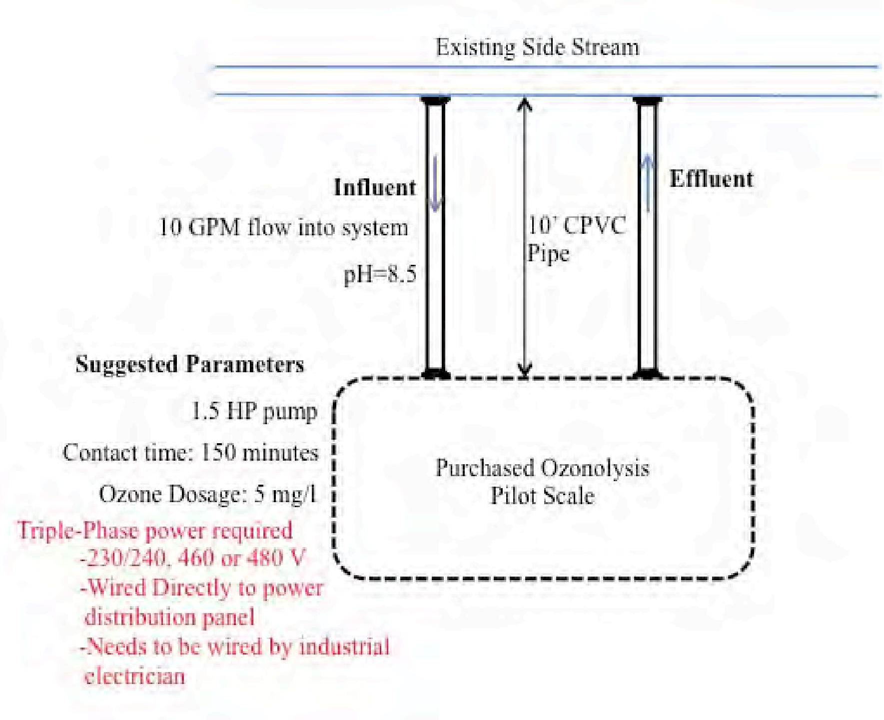

Figure 24. Proposed Energy and Flow Parameters

Another benefit to these ozone systems is the ability to add hydrogen peroxide to the treatment. These systems come prepared to add hydrogen peroxide if Millipore would like to further investigate the benefits of hydrogen peroxide addition to their wastewater treatment system.

Conclusions

The purpose of this project was to research and analyze possible treatment options for the reclamation of process water at EMD Millipore. Experiments were performed using activated carbon adsorption. While results showed that this method of treatment removed up to 68% of organic content from the wastewater, it was determined that this treatment was not a feasible option. The amount of carbon needed to obtain a 68% removal was 4 grams per ml of water treated. This amount of carbon is expensive and would not provide any economic benefit for EMD Millipore. On top of activated carbon costs, there would be an additional cost for activated carbon regeneration or disposal.

From the experiments completed in this project, it is apparent that ozonation in conjunction with hydrogen peroxide is a feasible treatment option. The results showed that approximately 40-50% of organic content was removed from the wastewater using this treatment. The variability in the data was due to uncertainty in the method of quantifying the percent of organic removed. It was also determined through experimentation that the most effective pH range for this treatment is between 8 and 9.

Spartan Water Treatment has been identified as a possible supplier for a pilot scale system, providing a 14GPM, SPARTOX A20 model with an integrated O_2 compressor with a 1.5 HP pump. A monthly operating cost analysis showed that this method of treatment would benefit EMD Millipore. The installation of an ozone treatment system in conjunction with hydrogen peroxide addition for further analysis by EMD Millipore is recommended.

Recommendations

After all experimentation was completed and data were analyzed, it was determined that there are multiple steps that can be taken to further the research. The data showed that ozonation combined with hydrogen peroxide treatment removed approximately 40% of the organic contaminant from the wastewater. A pilot-scale design was done and it was determined that this treatment would prove beneficial for EMD Millipore. It is recommended that a pilot scale system be installed to treat the wastewater with ozonation and hydrogen peroxide. The pilot scale should be run for approximately 3 months and data should be collected during that period. These results will indicate more clearly the advantages and disadvantages of this wastewater treatment process. It will provide more data for a full-scale design, and provide more information for estimating the potential cost savings of an ozonation treatment system for Millipore's wastewater.

The experiments conducted have many potential sources of uncertainty, the greatest of which is most likely the COD testing. The added hydrogen peroxide reacted in such a way that it interfered with the COD analysis and provided artifacts in the COD results. It is recommended that a different way of quantifying organic concentration be used in any further experimentation. It would also be advantageous to perform chemical analyses that would identify the concentrations of specific constituents in the water. This would help identify which treatment targets specific constituents. If the ozonation and activated carbon adsorption targeted different chemicals to greater or lesser extents, it would be feasible to implement ozonation with hydrogen peroxide as a primary treatment with activated carbon adsorption as a polishing step.

Through initial research, reverse osmosis was identified as a possible treatment process, but was eliminated from this study due to a lack of resources. It is recommended that experiments be conducted to determine the feasibility of implementing reverse osmosis to treat the wastewater stream at EMD Millipore. It is speculated that reverse osmosis will target a majority of the contaminants present in the wastewater and prove effective in reducing the organic content.

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Appendices

Appendix A: Potassium Hydrogen Phthalate (KHP) Standard Curve Data

Concentration KHP (mg/L)	Absorbance (nm)
0	0.0309
208	0.0891
400	0.16985
608	0.2414
800	0.3082

Appendix B: Activated Carbon Adsorption Data

November 13, 2014
Initial COD =25101.67 mg/L

Activated Carbon	Dosage (g)	Absorbance (nm)	Concentration Diluted WW Solution (mg/L)	Concentration WW Solution (mg/L)
Norit Hydrodaro 4000 M-1785	0.1005	0.1069	356.33	14253.33
	0.1010	0.1416	472.00	18880.00
Norit GAC 300	0.1005	0.1015	338.33	13533.33
	0.1010	0.1032	344.00	13760.00
Calgon WPH -1000	0.1006	0.1162	387.33	15493.33
	0.1014	0.1078	359.33	14373.33
Calgon WPH - 650	0.1020	0.1077	359.00	14360.00
	0.1000	0.1192	397.33	15893.33
Calgon FILTRASORB 300	0.0990	0.097	323.33	12933.33
	0.1056	0.0974	324.67	12986.67

Activated Carbon	Average Concentration (mg/L)	Change in Concentration (mg/L)	Percent Removed
Norit Hydrodaro 4000 M-1785	16566.67	8535.00	34%
Norit GAC 300	13646.67	11455.00	46%
Calgon WPH -1000	14933.33	10168.34	41%
Calgon WPH - 650	15126.67	9975.00	40%
Calgon FILTRASORB 300	12960.00	12141.67	48%

November 23, 2014
Initial COD =20150 mg/L

Activated Carbon	Dosage (g)	Absorbance (nm)	Concentration Diluted WW Solution (mg/L)	Concentration WW Solution (mg/L)
Norit Hydrodaro 4000 M-1785	0.0999	0.1132	377.33	15093.33
	0.1004	0.1132	377.33	15093.33
Norit GAC 300	0.1005	0.1021	340.33	13613.33
	0.1003	0.1056	352.00	14080.00
Calgon FILTRASORB 300	0.1005	0.1032	344.00	13760.00
	0.1002	0.106	353.33	14133.33
Calgon OLC 12x40	0.1002	0.1167	389.00	15560.00
	0.1005	0.1278	426.00	17040.00

Activated Carbon	Average Concentration (mg/L)	Change in Concentration (mg/L)	Percent Removed
Norit Hydrodaro 4000 M-1785	15093.33	4520.00	23%
Norit GAC 300	13846.67	5766.67	29%
Calgon FILTRASORB 300	13946.67	5666.67	29%
Calgon OLC 12x40	16300.00	3313.33	17%

December 8, 2014
Initial COD =17685 mg/L

Activated Carbon	Dosage (g)	Absorbance (nm)	Concentration Diluted WW Solution (mg/L)	Concentration WW Solution (mg/L)	Change in Concentration (mg/L)	Percent Removed
Norit GAC 300	0.0250	0.1496	374.00	14960	2725	15%
	0.0500	0.1445	361.25	14450	3235	18%
	0.0750	0.1369	342.25	13690	3995	23%
	0.1000	0.1374	343.50	13740	3945	22%
	0.2500	0.1380	345.00	13800	3885	22%
	0.5000	0.1396	349.00	13960	3725	21%
Calgon FILTRASORB 300	0.0250	0.1628	407.00	16280	1405	8%
	0.0500	0.1632	408.00	16320	1365	8%
	0.0750	0.1584	396.00	15840	1845	10%
	0.1000	0.1565	391.25	15650	2035	12%
	0.2500	0.1498	374.50	14980	2705	15%
	0.5000	0.1424	356.00	14240	3445	19%

January 29, 2015
Initial COD =12930 mg/L

Dosage (g)	Absorbance (nm)	Concentration Diluted WW Solution (mg/L)	Concentration WW Solution (mg/L)	Change in Concentration (mg/L)	Percent Removed
0.0512	0.0999	249.75	9990	2940	23%
0.1012	0.0972	243.00	9720	3210	25%
0.2499	0.0860	215.00	8600	4330	33%
0.5008	0.0674	168.50	6740	6190	48%
0.7498	0.0598	149.50	5980	6950	54%
1.0007	0.0549	137.25	5490	7440	58%
1.4996	0.0483	120.75	4830	8100	63%
1.9996	0.0444	111.00	4440	8490	66%

Initial COD =12270 mg/L

Dosage (g)	Absorbance (nm)	Concentration Diluted WW Solution (mg/L)	Concentration WW Solution (mg/L)	Change in Concentration (mg/L)	Percent Removed
0.0502	0.0938	234.50	9380	2890	24%
0.1008	0.0873	218.25	8730	3540	29%
0.2505	0.0730	182.50	7300	4970	41%
0.4998	0.0618	154.50	6180	6090	50%
0.7509	0.0548	137.00	5480	6790	55%
1.0005	0.0496	124.00	4960	7310	60%
1.5002	0.0432	108.00	4320	7950	65%
2.0011	0.0395	98.75	3950	8320	68%

Appendix C: Activated Carbon Adsorption Isotherm Data

Dosage (g)	Final COD (mg/L)	Initial COD (mg/L)	Volume WW (L)	Mass Adsorbent (mg)	Equilibrium Organic Concentration (Ce)	Mass Absorbed/ Mass Absorbant (qe)
0.0502	9380	12270	0.0005	50.2	9380	0.028784861
0.1008	8730	12270	0.0005	100.8	8730	0.017559524
0.2505	7300	12270	0.0005	250.5	7300	0.00992016
0.4998	6180	12270	0.0005	499.8	6180	0.006092437
0.7509	5480	12270	0.0005	750.9	5480	0.004521241
1.0005	4960	12270	0.0005	1000.5	4960	0.003653173
1.5002	4320	12270	0.0005	1500.2	4320	0.002649647
2.0011	3950	12270	0.0005	2001.1	3950	0.002078857

Appendix D: Initial Ozonation Oxidation Testing Data

Date	Test Run	Absorbance	COD (mg/L)	Percent Removal	Average Percent Removal
11-13-14	1	0.1350	18000	28.29	29.67
	2	0.1356	18080	27.97	
	3	0.1254	16720	33.39	
11-23-14	1	0.1311	17480	13.25	11.53
	2	0.1363	18173.33	9.81	
12-3-14	1	0.1423	14230	18.78	18.51
	2	0.1415	14150	19.24	
	3	0.1445	14450	17.52	
12-5-14	1	0.1458	14580	27.37	31.81
	2	0.1457	14570	27.46	
	3	0.1316	13160	40.59	
12-7-14	1	0.1497	14970	15.35	16.20
	2	0.1467	14670	17.05	

Appendix E: Ozonation Oxidation with pH Adjust Data

Sample from 12/10/14					
pH	Test Run	Absorbance	COD (mg/L)	Percent Removal	Average Percent Removal
7.21	1	0.1497	14970	15.35	16.20
	2	0.1467	14670	17.05	
7.6	1	0.1458	14580	18.03	20.38
	2	0.1457	14570	18.04	
	3	0.1316	13160	25.06	
8.19	1	0.1541	15410	24.33	24.43
	2	0.1592	15920	21.83	
	3	0.1484	14840	27.13	
9.5	1	0.1458	14580	25.09	26.78
	2	0.1400	14000	28.07	
	3	0.1417	14170	27.19	
11.05	1	0.1373	13730	30.29	31.37
	2	0.1376	13760	30.13	
	3	0.1306	13060	33.69	
12.8	1	0.1105	11050	41.91	43.65
	2	0.1010	10100	46.90	
	3	0.1101	11010	42.14	

Sample from 1/23/15					
pH	Test Run	Absorbance	COD (mg/L)	Percent Removal	Average Percent Removal
7.02	1	0.1208	12080	12.40	14.38
	2	0.1174	11740	14.87	
	3	0.1160	11600	15.88	
8.04	1	0.1134	11340	17.77	17.74
	2	0.1123	11230	18.56	
	3	0.1146	11460	16.90	
8.96	1	0.1171	11710	15.08	18.35
	2	0.1101	11010	20.16	
	3	0.1106	11060	19.80	
10.05	1	0.1170	11700	17.49	19.16
	2	0.1120	11200	21.09	
	3	0.1150	11500	18.90	
10.99	1	0.1200	12000	9.81	21.39
	2	0.0937	9370	29.58	
	3	0.1001	10010	24.77	

Appendix F: Ozonation Oxidation with Hydrogen Peroxide Addition Data

COD Testing of Sample Before Treatment		
Test Run	Absorbance	COD (mg/L)
1	0.1381	13810
2	0.1321	13210
3	0.1437	14370
4	0.1369	13690
5	0.1340	13400
	Average	13696

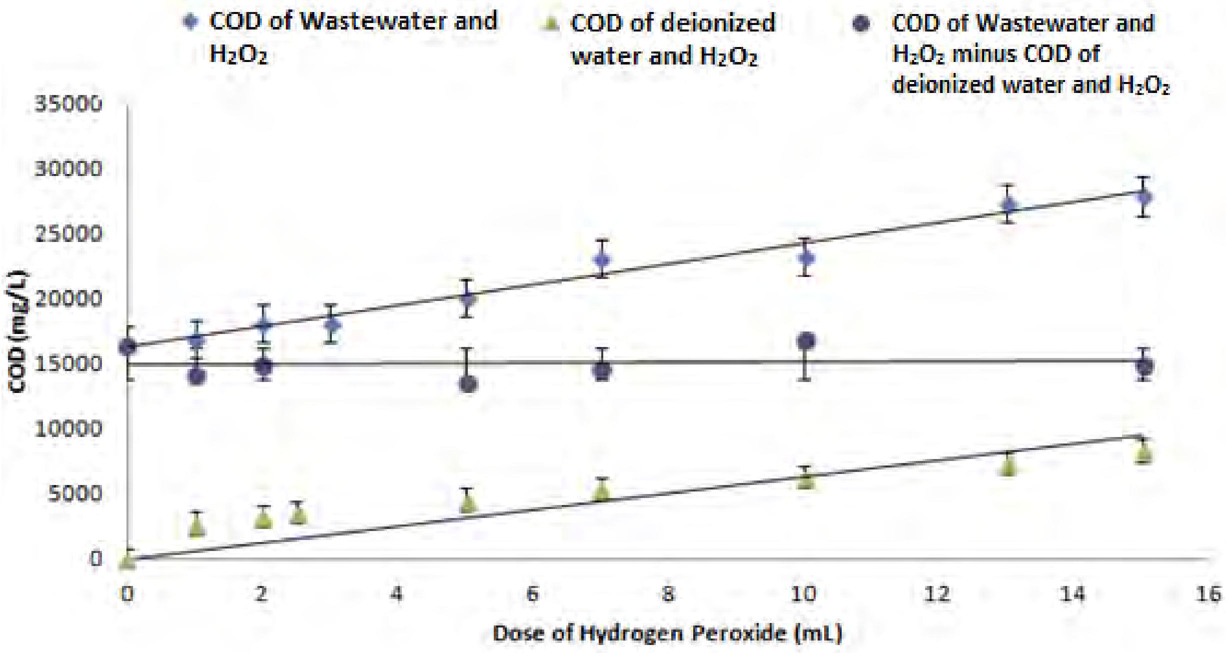
Hydrogen Peroxide Addition Experimental Data for Sample 1				
Hydrogen Peroxide Dose (mL)	Absorbance	COD (mg/L)	Average COD (mg/L)	Percent Removal
0	0.1208	12080	11807	13.61
	0.1174	11740		
	0.1160	11600		
15	0.1171	11710	11577	15.29
	0.1132	11320		
	0.1170	11700		
20	0.1636	16360	17083	-32.58
	0.1733	17330		
	0.1756	17560		
30	0.1947	19470	19217	-40.61
	0.1861	18610		
	0.1957	19570		

Hydrogen Peroxide Addition Experimental Data for Sample 2					
Hydrogen Peroxide Dose (mL)	Absorbance	COD (mg/L)	Average COD (mg/L)	COD of H_2O_2 Dose (mg/L)	Percent Removal
0	0.1388	13880	14103	0	16.18
	0.1414	14140			
	0.1429	14290			
1	0.1339	13390	13053	2780	38.94
	0.1226	12260			
	0.1351	13510			
2	0.1323	13230	13523	3260	39.00
	0.1360	13600			
	0.1374	13740			
5	0.1462	14620	14960	4605	38.45
	0.1480	14800			
	0.1546	15460			
7	0.1554	15540	15463	5415	40.28
	0.1525	15250			
	0.156	15600			
13	0.1691	16910	16670	7380	44.78
	0.1606	16060			
	0.1704	17040			
15	0.1623	16230	17037	8405	48.70
	0.1735	17350			
	0.1753	17530			

Appendix G: Effects of Hydrogen Peroxide on COD of Untreated Wastewater

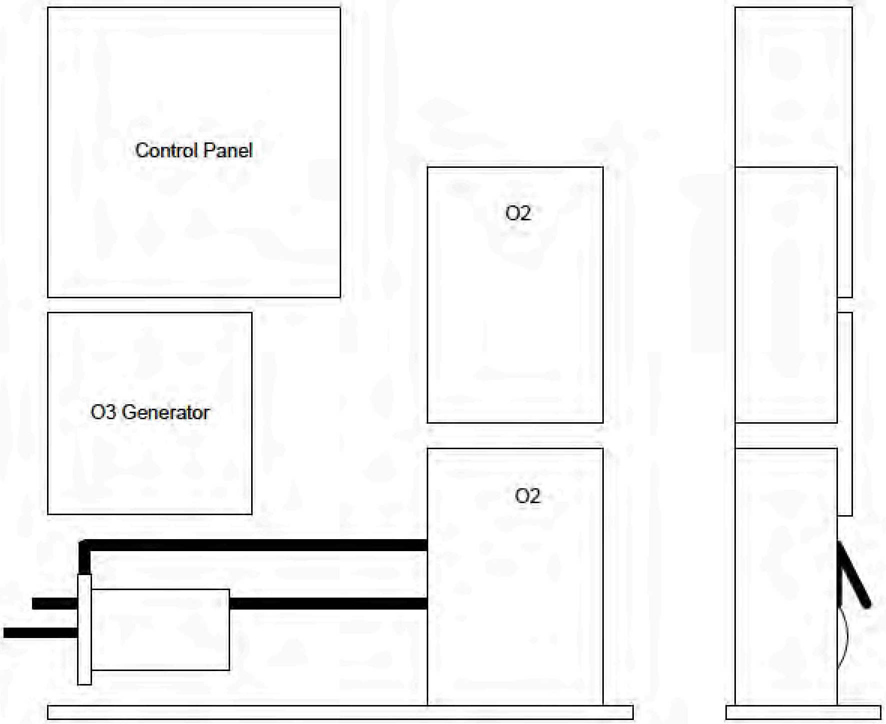
Hydrogen Peroxide Addition to Pure Water			
Hydrogen Peroxide Dose (mL)	Absorbance	COD (mg/L)	Average COD (mg/L)
0	0.0000	0	0
	0.0000	0	
1	0.0277	2770	2780
	0.0279	2790	
2	0.0322	3220	3260
	0.0330	3300	
2.5	0.0348	3480	3600
	0.0372	3720	
5	0.0442	4420	4605
	0.0479	4790	
7	0.0543	5430	5415
	0.0540	5400	
10	0.0636	6360	6355
	0.0635	6350	
15	0.0839	8390	8405
	0.0842	8420	

Hydrogen Peroxide Addition to Wastewater			
Hydrogen Peroxide Dose (mL)	Absorbance	COD (mg/L)	Average COD (mg/L)
0	0.16425	16425	16425
	0.16425	16425	
1	0.16920	16920	16895
	0.16870	16870	
2	0.18140	18140	18170
	0.18200	18200	
3	0.18190	18190	18195
	0.18200	18200	
5	0.20040	20040	20070
	0.20100	20100	
7	0.23230	23230	23155
	0.23080	23080	
10	0.23290	23290	23290
	0.23290	23290	
13	0.27420	27420	27430
	0.27440	27440	
15	0.27600	27600	27925
	0.28250	28250	



The COD of the different hydrogen peroxide doses were determined in pure wastewater and in untreated wastewater. The differentiation between these values resulted in a constant value that is approximately equal to the initial COD of the wastewater. This is represented by the horizontal line on the graph above. Measurements were made within 5 minutes of mixing to assess the initial COD of wastewater solution, and the effect of added H_2O_2.

Appendix H: Spartan Industrial Ozone Treatment System



SPARTOX Skid Concept with Oxygen Concentrators with Internal Compressors