THESIS

EVALUATION OF OXIDATION AND ADSORPTION TECHNIQUES FOR TASTE AND ODOR AND TOXIN REMOVAL

Submitted by

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ABSTRACT

EVALUATION OF OXIDATION AND ADSORPTION TECHNIQUES FOR TASTE AND ODOR AND TOXIN REMOVAL

The cyanobacteria, also known as blue-green algae, owe their name to the presence of photosynthetic pigments. Cyanobacteria are a major group of bacteria that occur throughout the world. Freshwater cyanobacteria may accumulate in surface water supplies as "blooms" posing as an environmental hazard because of the release of water soluble toxic compounds, called cyanotoxins. Especially massive blooms of blue–green algae in the surface waters used as drinking water resources may lead to taste and odor problems during the summer and fall, they may also produce cyanotoxins. Since the taste and odor compounds, Geosmin (GSM) and 2-Methylisoborneol (2-MIB) can be easily detected by the human nose at low concentrations of 2-5 ng/L, the surveillance of harmful toxins such as microcystin-LR may be easily performed by sensory analyses due to the likely co-occurrences of the two types of metabolites. This research focused on removal of taste and odor compounds (GSM, 2-MIB) and microcystin-LR with five oxidants: chlorine, chlorine dioxide, potassium permanganate, ozone, mixed oxidants (MiOX) and powdered activated carbon (PAC) using Ralston Reservoir water as reagent water collected in early April, 2014. The objective of the study was to develop a bench scale treatment process efficacy information that Denver Water can utilize to decide on a treatment technique for taste and odor control. The Design Expert software was used to determine the optimum dose of the oxidants for an acceptable treatment level.

ACKNOWLEDGEMENTS

I would like to thank all the people who contributed in some way to the work described in this thesis.

First and foremost, I would first like to thank my thesis advisor Professor Pinar Omur-Ozbek of the Civil & Environmental Engineering department at Colorado State University. The door to Prof. Ozbek's office was always open whenever I ran into a trouble spot or had a question about my research or writing. During my tenure, she contributed to a rewarding graduate school experience by giving me intellectual freedom in my work, engaging me in new ideas, and demanding a high quality of work in all my endeavors and steered me in the right the direction whenever she thought I needed it.

Additionally, I would like to thank my committee members Professor Kenneth Carlson and Professor Greg Dooley for their interest in my work. Every result described in this thesis was accomplished with the help and support of fellow labmates and collaborators. Without their passionate participation and input, the lab analysis could not have been successfully conducted. This research was supported/partially supported by Denver Water. We thank our colleagues from Denver Water who provided insight and expertise that greatly assisted the research.

Finally, I must express my very profound gratitude to my dear parents and friends for providing me with unfailing support and continuous encouragement throughout my years of study and through the process of researching and writing this thesis. This accomplishment would not have been possible without them. Thank you.

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Over the last few decades, water scarcity and quality of water have become issues of major concern. Major source waters are deteriorating in quality, especially in the developed countries. Eutrophication has accelerated in reservoirs used for drinking water supply and has often lead to cyanobacteria (blue-green algae) and actinomycetes (bacteria) blooms. Sustained loading of nutrients to surface waters leads to eutrophication (Correll, 1999). Some of the issues related to eutrophication include increased algal biomass, low dissolved oxygen (DO), increased fish mortality, reduced water transparency and frequent incidences of toxic phytoplankton (Burkholder et al., 1992; Carpenter et al., 1998; Smith, 1998). Most of the aquatic systems have very low concentration of nutrients and small shifts can result in dramatic changes in the ecosystem (Dodds and Welch, 2000; Rabalais, 2002, Miltner and Rankin, 1998;). Increases in algal biomass can disturb the natural ecosystem and cause severe environmental degradation through means other than oxygen depletion, such as toxic blooms associated with certain species and concentrations of algae (Smith et al., 1999). Toxic algal blooms can also disrupt tourism due to foul odors, unsightly views, and fish mortality events (Howarth et al.,2000). Release of algal metabolites cause great concern for drinking water authorities. In addition to taste and odor compounds, some cyanobacteria produce toxic compounds called cyanotoxins. The occurrence of these compounds in water bodies, has a strong impact towards the quality and safety of drinking water. Reducing the non-point discharge of phosphorus helps to control eutrophication which in turn minimizes the algal blooms and hence the occurrence of algal metabolites.

2 : LITERATURE REVIEW

Taste-and-odor (T&O) is a concern for any water treatment plant (WTP) using a surface water source. The odors are predominantly caused by the presence of 2-MIB and Geosmin. Both 2-MIB and Geosmin are algal byproducts and typically come in brief, but potent, T&O events. Geosmin, which accounts for "earthy" odor complaints, while the "musty" odor caused by 2-MIB and they usually occur during the late summer or early fall. Each compound is difficult to treat due to their low thresholds of odor detection. Historically, T&O events have become a persistent and ongoing challenge. Consumers do not want their water smelling and tasting like dirt and hence utilities spend billions of dollars to treat them. Detrimental economic side effects of algal blooms are also seen in expensive water treatment, habitat restoration and human health costs at a national scale (EPA, 2015). The production and release of geosmin and 2-MIB are shown in Figure 2-1.

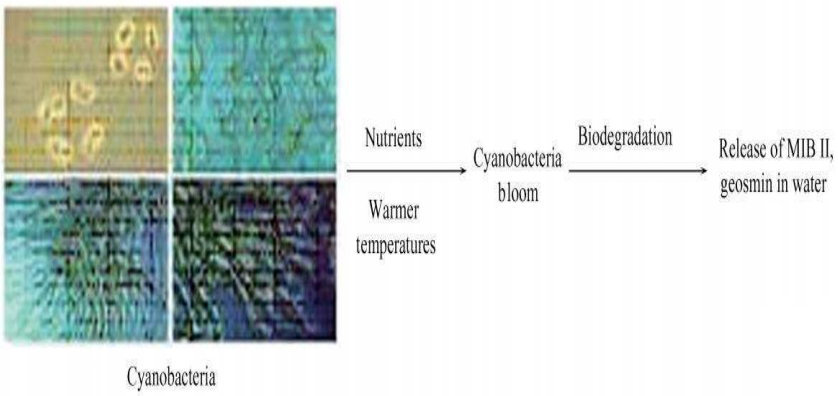


Figure 2-1: Simplified Pathway of MIB/GSM Formation (Srinivasan et al. 2011)

2.1 TASTE AND ODOR COMPOUNDS

2.1.1 GEOSMIN

Geosmin, chemically known as 1,2,7,7-tetramethyl-2-norborneol, is an organic compound that is responsible for the earthy smell that causes the unpleasant flavor in drinking water which is often associated with fresh-turned dirt. Geosmin is a tertiary alcohol, fairly water soluble and has a Henry's law constant (at 20°C) of 0.0023; molecular weight of 182.305 g/mol; and water solubility of 150.2 mg/L (at 20 °C) (Bruce et al., 2002; Omur-Ozbek and Dietrich, 2005). The production of GSM by cyanobacteria is considered to be a secondary metabolite of cellular growth. GSM is detectable by the human nose at a concentration of as low as 4ng/L in water (David et al. 2008), therefore the removal of GSM from drinking water is critical for water providers globally.

2.1.2 2-METHYLISOBORNEOL

2-Methylisoborneol (MIB) is a derivate of borneol. 2-MIB has a musty odor that can be defined as a damp basement (Gerber et al. 1965) and has a Henry's law constant (at 20°C) of 0.0027; molecular weight of 154.25 g/mol; and water solubility of 194.5 mg/L (at 20 °C) (Omur-Ozbek and Dietrich, 2005). Its odor detection threshold is almost 7-15 ng/L (David et al. 2008), and it is one of the chemicals (also GSM) with major influence on the quality of drinking water. The molecular structure of geosmin and 2-MIB are shown in Figure 2-2.

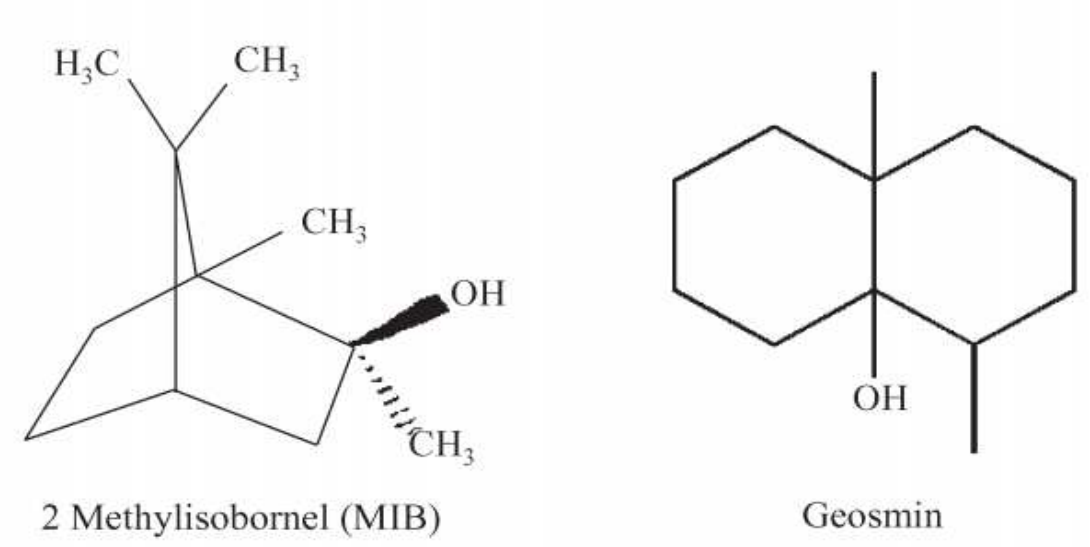


Figure 2-2: Molecular Structure of GSM AND 2-MIB (Srinivasan et al. 2011)

2.2 CYANOTOXINS

The widespread occurrence of cyanotoxins in the available water resources and finished drinking waters around the globe has not only led to livestock deaths but also several cases of human hepatoenteritis and even deaths (Byth, 1980; Francis, 1878; Gugger et al., 2005; Jochimsen et al., 1998). The hepatotoxic microcystins (MC), the most widespread cyanotoxin group, are known to be produced by the members of several cyanobacterial genera including Microcystis, Anabaena, Planktothrix, Anabaenopsis, Nostoc, and Hapalosiphon (Skulberg et al., 1993; Sivonen and Jones, 1999). Typical dissolved microcystin concentrations in surface waters rich in toxic cyanobacteria are 0.1-10 µg L-1, but the concentration can be much higher if a major bloom is breaking down (Sivonen Jones, 1999). Toxic algal blooms in Lake Erie, 2014 have left the residents in Toledo, Ohio without drinking water for days (Ecowatch, 2014). Utah

Lake was closed due to huge toxic bloom which caused big problems for people who used the lake for swimming, fishing and agriculture (The Guardian, 2016).

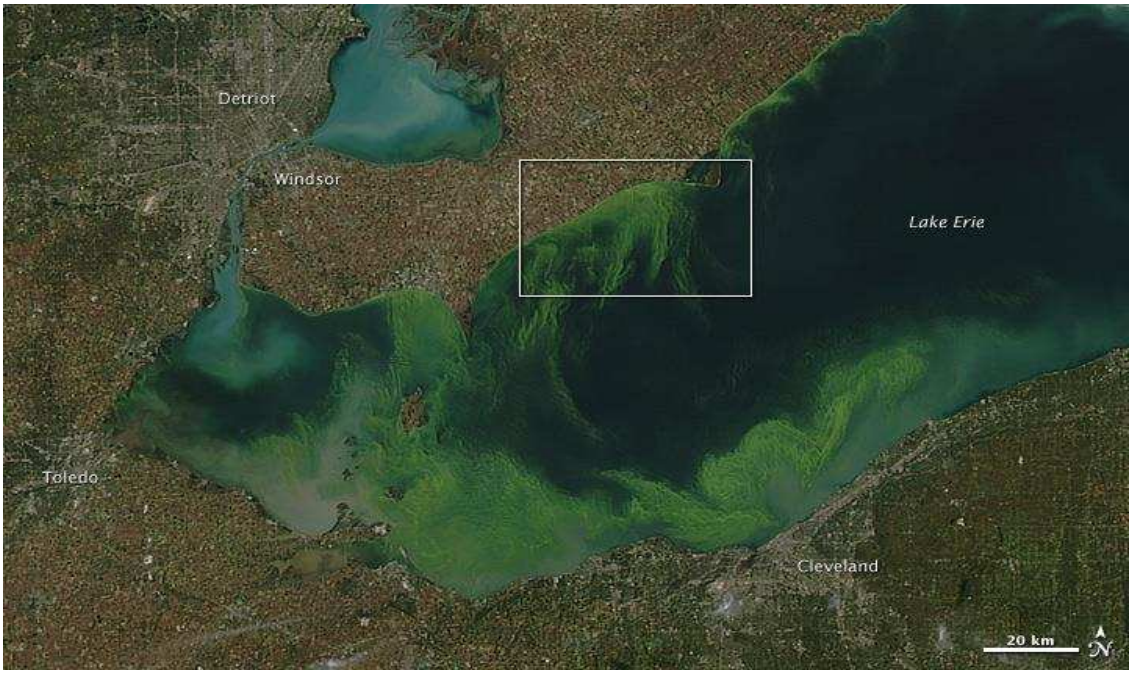


Figure 2-3: Bloom of the Microcystis aeruginosa in Lake Erie in Oct 2011 (NASA,2011)

The occurrence of MCs in natural water bodies become a major concern for production of drinking water due to their severe acute and sublethal toxicities. Although over 80 microcystin variants are known, the most common is microcystin LR (MC-LR), which has been identified together with other commonly found MC variants such as MC-LA, MC-RR and MC-YR in natural water samples (Falconer et al., 1999; Spoof et al., 2003). Microcystin-LR (MC-LR) is one of the most toxic variants, with a mouse LD50 of 50 $mgkg^{-1}$ (Chorus and Bartram, 1999). The molecular structure of Microcystin-LR is show below in the figure 2-3.

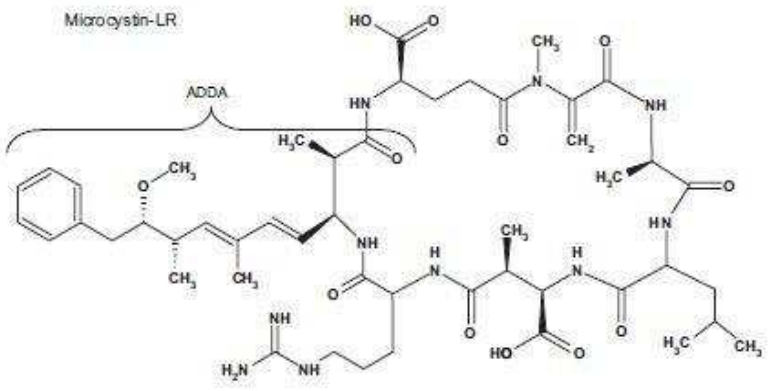


Figure 2-4: Structure of Microcystin-LR (Rodriguez et al. 2007)

For this reason, the Environmental Protection Agency (EPA) has set a provisional drinking water guideline of 0.3 µg/L for microcystins for bottlefed infants and young children of preschool age. For school-age children through adults, the health advisory (HA) value for drinking water is 1.6 µg/L. The HA values are based on exposure for ten days (EPA, 2015).

2.3 TREATMENT OPTIONS

For control of T&O compounds as well as toxins in drinking water treatment plants, the application of conventional water treatment technologies like coagulation flocculation/sedimentation, filtration have been reported to be effective for removal of cyanobacterial cells but ineffective for removal of extracellular metabolites (Himberg et al., 1989; Chow et al., 1999; Hrudey et al., 1999). Thus, alternative treatment options such as use of adsorbents like activated carbon (both powdered and granular) and oxidants such as ozone, chlorine-dioxide, potassium permanganate and MIOX (Rodriguez et al, 2007, 2008, Dixon et al., 2010) need to be incorporated into the water treatment processes to remove these compounds. With respect to oxidation rate, the following general trend is typically observed: O_3> H_2O_2> HOCl>ClO_2>$KMnO_4$>Cl_2. However, discrepancies have been observed depending on the type of

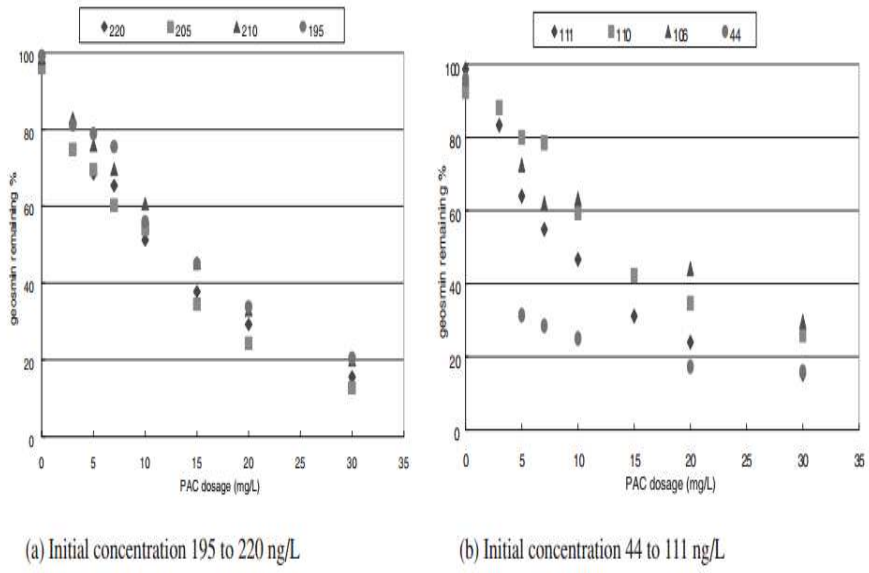
compound that is oxidized. The oxidants are usually added at the beginning (e.g., peroxidation) or at the end (e.g., disinfection) of the water treatment process, while they can also be added at various intermediate points, depending on the treatment objectives (Sharma et. al 2012). Previous studies have demonstrated the efficiency of different oxidants potassium permanganate (Rodriguez et al., 2007a) and ozone (Onstad et al., 2007), as well as advanced oxidation processes (Cornish et al., 2000; Qiao et al., 2005) to oxidize extracellular MC.

2.3.1 POWDERED ACTIVATED CARBON (PAC)

Among the treatment options listed, PAC is the most commonly utilized technique for control of taste and odor compounds as it has a lower cost and can be used in existing water treatment plants without any major adaptations and additional capital costs. Depending on the season, the PAC can be applied intermittently and at varying doses for the control of odorants and microcystins. For an initial MIB concentration of 250 ng/l and PAC dosage of 40 mg/l, the MIB removal efficiency was reported as 70% (Seckler et al. 2013), which means that the odorant levels were still above the human detection levels. Most of the studies pertaining to PAC adsorption of cyanotoxins have been conducted on the microcystins, in particular, MC-LR (Falconer et al., 1989; Donati et al., 1994; Pendleton et al., 2001; Cook and Newcombe, 2002, 2008; Campinas and Rosa, 2010a, b). Experiments carried out by Cook and Newcombe (2002) for PAC adsorption on four variants of microcystin showed the differences in the adsorption of each variant with the ease of removal following the order: MC-RR>MC-YR>MC-LR>MC-LA. It was concluded by Campinas et al. (2010) that for low concentrations of microcystins (5 µg/L), 10mg/L of PAC effectively controlled the microcystins in a model water with M. aeruginosa culture whereas a PAC dose of 15 mg/L was necessary when the NOM surrogate concentration doubled. For high concentrations of microcystins (20 µg/L),15 mg/L of PAC were unable to

achieve the WHO guideline-value. GAC filtration and PAC with conventional treatment in full scale application were both generally observed to reduce raw water microcystins by more than 80% except when raw water levels dropped below 0.5 µg/L (Lambert et. al 1996).

Results from Ho et. al (2011) demonstrated that PAC could be an effective treatment option for the removal of the cyanotoxins from the studied waters under WTP conditions. No difference was observed in the removal of the cyanotoxins using contact times of 30, 45 and 60 mins. The study carried out by Jung et al. (2014), as shown in Figure 2-4 & 2-5, showed that removal efficiencies of geosmin and 2-MIB for a given dosage was almost constant regardless of initial concentration except geosmin of 44 ng/L, which was lowest beyond the range of most initial concentrations. The study also shows that adsorption efficiency of geosmin by PAC was superior to that of 2-MIB.



(a) Initial concentration 195 to 220 ng/L (b) Initial concentration 44 to 111 ng/L

Figure 2-5: % GSM conc. as a function of PAC dosage (Jung et al. 2004)

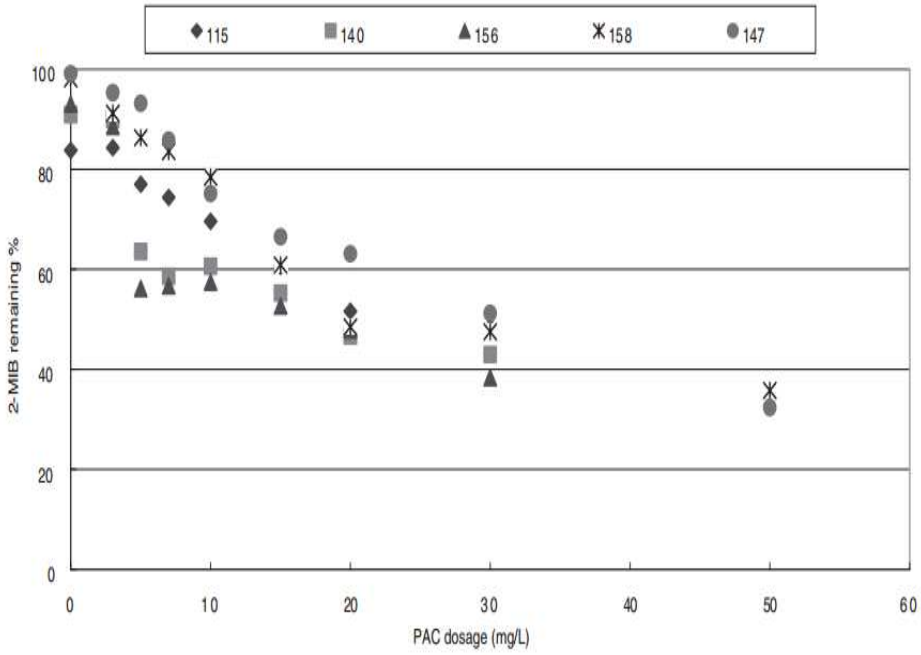


Figure 2-6: % 2-MIB conc. as a function of PAC dosage (Jung et al. 2004)

2.3.2 OZONE (O_3)

Ozone has been used to control taste and odor, remove color, and control biological growth in treatments plants. AOPs have great potential for oxidation of double bonds and amines found in toxins, and that makes them useful in microcystin degradation (Brooke et.al 2006, Onstad et. al 2007). The ozonation process is favored for the treatment of drinking water because of its high oxidation efficiency by a direct pathway (O_3 direct reaction) and an indirect pathway (OH radical reaction).

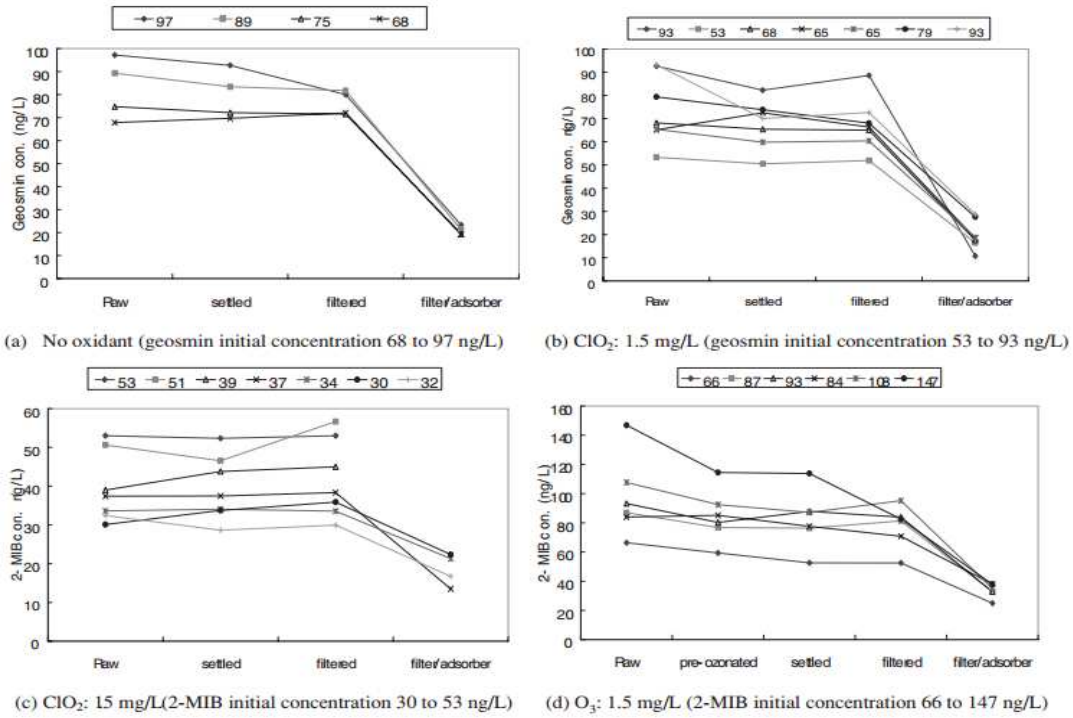


Figure 2-7: Variation of GSM and MIB in each Process (Jung et al. 2004)

When the initial concentrations of MIB and GSM were between 43 and 220 ng/l, the removal efficiency of MIB rapidly increased in proportion to O_3 dosage and removal up to 84.8% for 2- MIB occurred at 3.8 mg/l for 6.4 minutes contact time (Jung et al. 2004).

Figure 2-8: Ozone Generator

Collivignarelli and Sorlini, (2004) reported that a complete removal geosmin and MIB can be obtained only with the combination of ozone (conc. of 1.5–3 mg/l and contact time of 2–3 mins) with UV radiation (dose of 5,000–6,000 J/m^2). Yuan et al. (2013) identified that ozonation can lead to 99.9% of GSM removal rate within 30 min at the ozone dosage of 4.19 mg/l. The ozonation process led to the algae removal of 91.2% within 60 mins under the ozone dosage of 5 mg/l and the algae could not survive the dosage of 3 mg/l (Miao et al. 2004). Suffet et al. (1986) found that ozone is generally the most effective oxidant for use in taste and odor treatment, ozone doses of 2.5 to 2.7 mg/L and 10 minutes of contact time (residual 0.2 mg/L) significantly reduce levels of taste and odors. Momani et. al. (2008) and Rodriguez et. al. (2007) stated that ozone was very efficient for any type of toxin degradation. Total toxin degradation was obtained by an ozone dosage of less than 2 mg/L and a reaction time of 144s (Momani et. al 2010)

2.3.3 CHLORINEDIOXIDE (ClO_2)

Cheng et al. (2011) reported that effective removal of MIB and GSM was observed with just chlorine dioxide (ClO_2) at an optimum dosage of 5 mg/l, in comparison to a mixture of ClO_2 and coagulant (poly. Aluminum chloride). Lalezary et al. (1986) used chlorine, chlorine dioxide, ozone, and permanganate to treat earthy-musty smelling compounds. In that study, chlorine dioxide was found most effective, although none of the oxidants were able to remove geosmin and MIB by more than 40 to 60 percent. Chlorine-based weaker oxidants (and disinfectants) such as chlorine dioxide (ClO2) and chloramines have been used as alternative to chlorine but found ineffective due to their low reaction kinetic constant, k (Rodriquez et. al 2005, 2007, Kull et al. 2006). Oxidants such as chloramines and chlorine dioxide are not plausible options for the removal of MC from natural waters, due to their low reactivity with these oxidants (Acero et al.,

2005; Kull et al., 2004). ClO_2 as an oxidant in drinking water treatment will have only a small or negligible impact on dissolved microcystins if these toxins are present in the raw water (Kull et. al 2006).

2.3.4 POTASSIUM PERMANGANATE ($KMnO_4$)

Permanganate ($KMnO_4$) is a strong oxidizing agent that has been used to control taste and odor, remove color, control biological growth in treatment plants and remove iron and manganese. Typical dosages of $KMnO_4$ vary from 0.25 to 20 mg/l for oxidation of grassy odors, however, it does a poor job of removing GSM and 2-MIB (Crittenden, 2012). $KMnO_4$ ($\leq$3 mg/l) may be used for pre-oxidation in the presence of cyanobacteria without impacting cell membranes which is a benefit over other oxidants (Fan et al. 2013). Studies indicate that the application of permanganate was found to be effective for the removal of dissolved MC-LR, although with live intact cells toxin removal was much poorer, suggesting that permanganate was unable to effectively penetrate or lyse the cells (Rositano, 1996). Hall et al. (2000) reported that permanganate is a possible treatment for dissolved MC-LR in waters with low oxidant demand and must be applied before sedimentation/filtration of treatment train in order to control final manganese concentrations. However, the dose of permanganate must be controlled since the high doses might cause cell lysis and toxin release in raw water containing algal cells (Knappe et al., 2004; Pietsch et al., 2002). Around 1–1.25 mg/L of permanganate was enough to reduce the concentration of MCs below the WHO guideline value of 1 µg/L in the experiments performed with surface water. Therefore, permanganate is a feasible option for the oxidation of MCs in natural waters prior to coagulation-sedimentation steps (Rodriquez et. al 2007).

2.3.5 CHLORINE (Cl_2)

Chorine is a very effective method for taste and odor control, but its use must be evaluated carefully due to the formation of carcinogenic disinfection by-products when organics are present. Reactivity of chlorine with toxins is influenced by pH of the water and by the presence of NOM. Contact time (CT) values required for destruction of microcystins with free chlorine may be many times higher than required for the surface water treatment rule depending on specific water quality conditions (Ohio EPA, AWWA, 2011). Even though chlorine is effective at removing odorants, it is ineffective at removing microcystins. One study showed that even a 5 mg/L was ineffective for destroying the algal toxin extracts (Hoffman, 1976). A second study demonstrated that combined treatment processes which included chlorination at 0.5 mg/L were also ineffective (Keijola et al., 1988; Himberg et al., 1989). A third study showed chlorination achieved negligible reduction in microcystin levels of 0.3-0.5 μg/L in treated water (Lambert et al., 1996). However, chlorination was very effective at destroying microcystin-LR and nodularin with free chlorine residual of 0.5 mg/L after 30 minutes contact time with pH < 8 (Nicholson et al., 1994). Dissolved microcystin-LR and anatoxin-a concentrations in the range 5-10 μg/L, using a chlorine residual of 0.7 mg/L at pH 5, yielded a removal of more than 93 % within 30 minutes but at pH 7 removal reached only 88 % after 22 hours (Carlile, 1994; Croll and Hart, 1996; Hart et al., 1997).

2.3.6 MIXED OXIDANTS (MIOX)

The mixed-oxidants (MIOX) disinfection system appears to provide a reasonable alternative for small distribution systems as a safe, reliable, and cost effective technology that is easy to operate and is readily compatible with other treatment systems. However, it hasn't been used to treat odorants or toxins.

Figure 2-9: MIOX Equipment Setup

2.4 DATA ANALYSIS

Response Surface Methodology (RSM) is a statistical method for heuristic optimization, which is basically a combination of design of experiments (DOE), regression analysis and statistical inferences. It is a very useful technique for modeling and analysis of problems in which a response of interest is influenced by several variables. Factorial design is particularly used in the early stages of experimental work, when there are likely to be many factors to be investigated.

Stat-Ease makes it easy to perform statistical design of experiments (DOE) with Design Expert software. Design Expert helps to design, run, and analyze a few real experiments in a short amount of time. Design Expert offers multilevel factorial screening designs to help find the critical factors that lead to breakthrough improvements. Using response surface methodology, it helps to optimize the process and display optimum performance with 3D plots (Figure.5.2). The software is being used in wide fields of research as well as industries to help in reducing the

chemicals consumption, cost and the time spent in carrying out numerous experiments (conventional practice) to optimize the results.

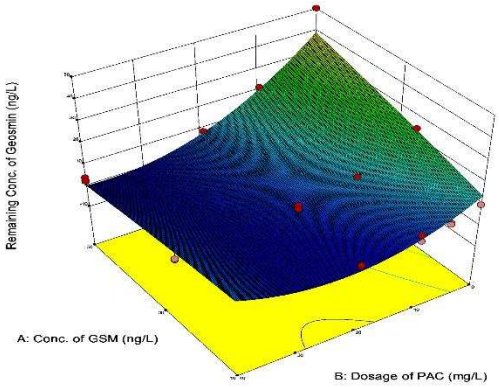


Figure 2-10: A view of graph plotted in Design Expert

Design Expert identifies the breakthrough factors for process or product improvement and helps to set up and analyze general factorial, two-level factorial, fractional factorial (up to 31 variables) and Plackett-Burman designs (up to 31 variables). The software can also carry out numerical optimization and with these designs; the critical factors and their interactions can be easily screened (Figure.5-3).

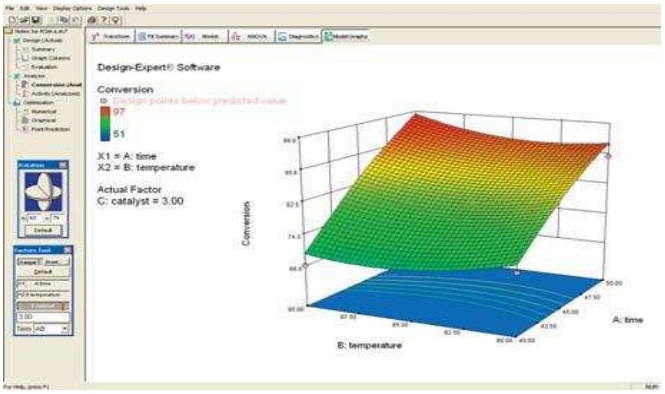


Figure 2-11: A view of graph plotted in Design Expert

Design-Expert offers rotatable 3D plots to aid in visualizing the response surface and explore the 2D contours, setting flags along the way to identify coordinates and predict responses. The sweet spot where all your requirements are met can be found via the program's numerical optimization function, which finds the most desirable factor settings for multiple responses simultaneously.

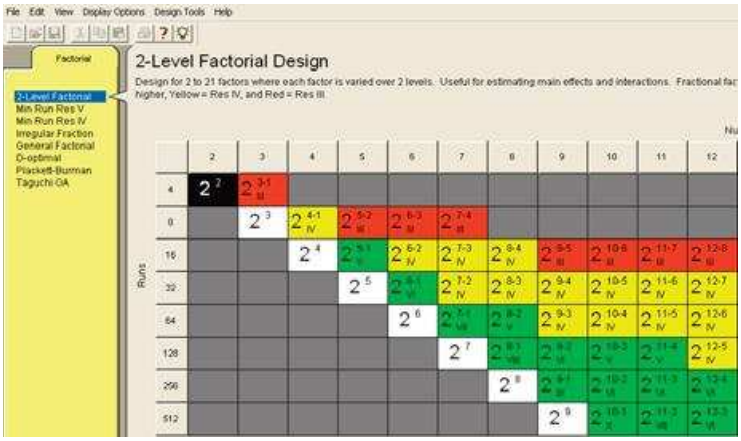


Figure 2-12: A view of factorial design plotted in Design Expert

3 : MODELLING OF TASTE & ODOR AND TOXIN REMOVAL WITH VARIOUS WATER TREATMENT METHODS

3.1 SYNOPSIS

The cyanobacteria, also known as blue-green algae, owe their name to the presence of photosynthetic pigments. Cyanobacteria are a major group of bacteria that occur throughout the world. Freshwater cyanobacteria may accumulate in surface water supplies as "blooms" posing as an environmental hazard because of the release of water soluble toxic compounds, called cyanotoxins. Especially massive blooms of blue–green algae in the surface waters used as drinking water resources may lead to taste and odor problems during the summer and fall, they may also produce cyanotoxins. Since the taste and odor compounds, Geosmin (GSM) and 2-Methylisoborneol (2-MIB) can be easily detected by the human nose at low concentrations of 2-5 ng/L, the surveillance of harmful toxins such as microcystin-LR may be easily performed by sensory analyses due to the likely co-occurrences of the two types of metabolites. This research focused on removal of taste and odor compounds (GSM, 2-MIB) and microcystin-LR with five oxidants: chlorine, chlorine dioxide, potassium permanganate, ozone, mixed oxidants (MiOX) and powdered activated carbon (PAC) using Ralston Reservoir water as reagent water collected in early April, 2014. The objective of the study was to develop a bench scale treatment process efficacy information that Denver Water can utilize to decide on a treatment technique for taste and odor control. The Design Expert software was used to determine the optimum dose of the oxidants for an acceptable treatment level.

3.2 INTRODUCTION

Over the last few decades, water scarcity and quality of water have become issues of major concern. Major source waters are deteriorating in quality, especially in the developed countries. Eutrophication has accelerated in reservoirs used for drinking water supply and has

often lead to cyanobacteria (blue-green algae) and actinomycetes (bacteria) blooms. Sustained loading of nutrients to surface waters leads to eutrophication (Correll, 1999). Some of the issues related to eutrophication include increased algal biomass, low dissolved oxygen (DO), increased fish mortality, reduced water transparency and frequent incidences of toxic phytoplankton (Burkholder et al., 1992; Carpenter et al., 1998; Smith, 1998). Most of the aquatic systems have very low concentration of nutrients and small shifts can result in dramatic changes in the ecosystem (Dodds and Welch, 2000; Rabalais, 2002, Miltner and Rankin, 1998;). Increases in algal biomass can disturb the natural ecosystem and cause severe environmental degradation through means other than oxygen depletion, such as toxic blooms associated with certain species and concentrations of algae (Smith et al., 1999). Toxic algal blooms can also disrupt tourism due to foul odors, unsightly views, and fish mortality events (Howarth et al.,2000). Release of algal metabolites cause great concern for drinking water authorities. In addition to taste and odor compounds, some cyanobacteria produce toxic compounds called cyanotoxins. The occurrence of these compounds in water bodies, has a strong impact towards the quality and safety of drinking water. Reducing the non-point discharge of phosphorus helps to control eutrophication which in turn minimizes the algal blooms and hence the occurrence of algal metabolites.

Taste-and-odor (T&O) is a concern for any water treatment plant (WTP) using a surface water source. The odors are predominantly caused by the presence of 2-MIB and Geosmin. Both 2-MIB and Geosmin are algal byproducts and typically come in brief, but potent, T&O events. Geosmin, which accounts for “earthy” odor complaints, while the “musty” odor caused by 2-MIB and they usually occur during the late summer or early fall. Each compound is difficult to treat due to their low thresholds of odor detection. Historically, T&O events have become a persistent and ongoing challenge. Consumers do not want their water smelling and tasting like dirt and hence utilities spend billions of dollars to treat them. Detrimental economic side effects

of algal blooms are also seen in expensive water treatment, habitat restoration and human health costs at a national scale (EPA, 2015).

Geosmin, chemically known as 1,2,7,7-tetramethyl-2-norborneol, is an organic compound that is responsible for the earthy smell that causes the unpleasant flavor in drinking water which is often associated with fresh-turned dirt. Geosmin is a tertiary alcohol, fairly water soluble and has a Henry's law constant (at 20°C) of 0.0023; molecular weight of 182.305 g/mol; and water solubility of 150.2 mg/L (at 20 °C) (Bruce et al., 2002; Omur-Ozbek and Dietrich, 2005). The production of GSM by cyanobacteria is considered to be a secondary metabolite of cellular growth. GSM is detectable by the human nose at a concentration of as low as 4ng/L in water (David et al. 2008), therefore the removal of GSM from drinking water is critical for water providers globally. 2-Methylisoborneol (MIB) is a derivate of borneol. 2-MIB has a musty odor that can be defined as a damp basement (Gerber et al. 1965) and has a Henry's law constant (at 20°C) of 0.0027; molecular weight of 154.25 g/mol; and water solubility of 194.5 mg/L (at 20 °C) (Omur-Ozbek and Dietrich, 2005). Its odor detection threshold is almost 7-15 ng/L (David et al. 2008), and it is one of the chemicals (also GSM) with major influence on the quality of drinking water.

The widespread occurrence of cyanotoxins in the available water resources and finished drinking waters around the globe has not only led to livestock deaths but also several cases of human hepatoenteritis and even deaths (Byth, 1980; Francis, 1878; Gugger et al., 2005; Jochimsen et al., 1998). The hepatotoxic microcystins (MC), the most widespread cyanotoxin group, are known to be produced by the members of several cyanobacterial genera including Microcystis, Anabaena, Planktothrix, Anabaenopsis, Nostoc, and Hapalosiphon (Skulberg et al., 1993; Sivonen and Jones, 1999). Typical dissolved microcystin concentrations in surface waters

rich in toxic cyanobacteria are 0.1-10 µg L-1, but the concentration can be much higher if a major bloom is breaking down (Sivonen Jones, 1999). Toxic algal blooms in Lake Erie, 2014 have left the residents in Toledo, Ohio without drinking water for days (Ecowatch, 2014). Utah Lake was closed due to huge toxic bloom which caused big problems for people who used the lake for swimming, fishing and agriculture (The Guardian, 2016).

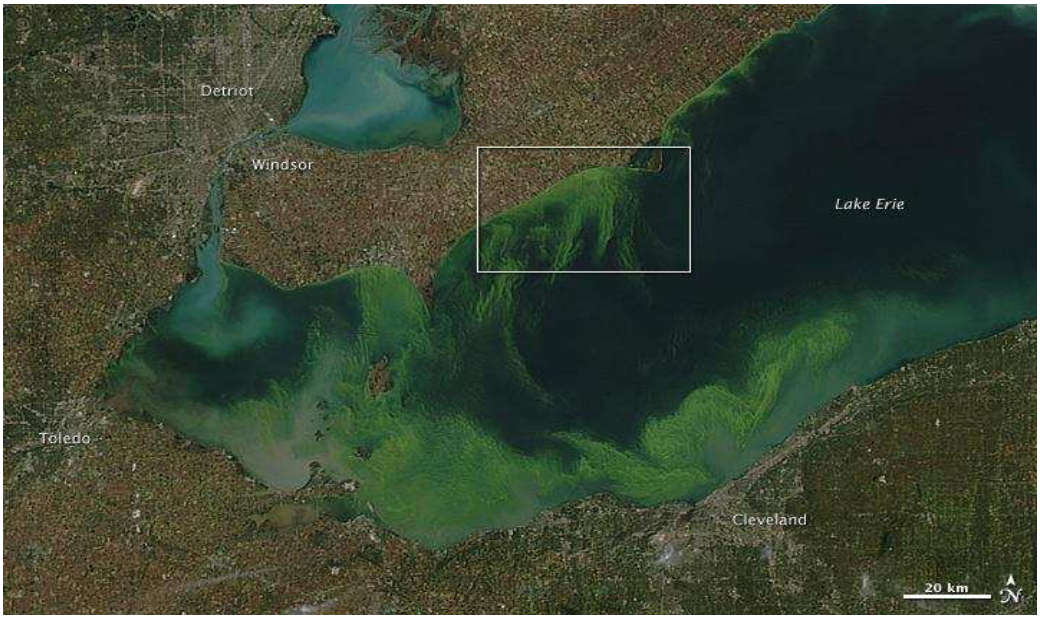


Figure 3-1: Bloom of the Microcystis aeruginosa in Lake Erie in Oct 2011 (NASA,2011)

The occurrence of MCs in natural water bodies become a major concern for production of drinking water due to their severe acute and sublethal toxicities. Although over 80 microcystin variants are known, the most common is microcystin LR (MC-LR), which has been identified together with other commonly found MC variants such as MC-LA, MC-RR and MC-YR in natural water samples (Falconer et al., 1999; Spoof et al., 2003). Microcystin-LR (MC-LR) is one of the most toxic variants, with a mouse LD50 of 50 $mgkg^{-1}$ (Chorus and Bartram, 1999). The molecular structure of Microcystin-LR is show below in the figure 2-3.

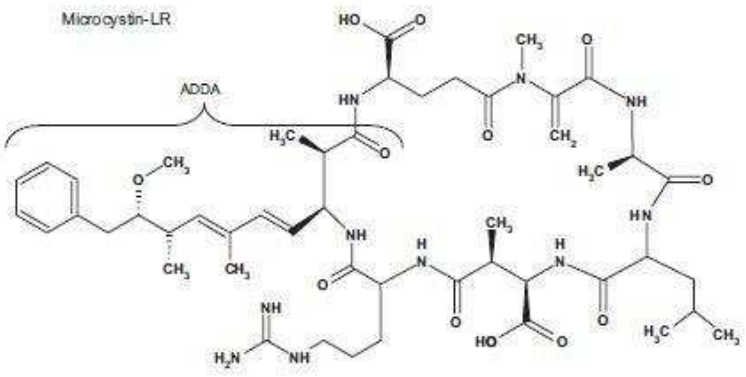


Figure 3-2: Structure of Microcystin-LR (Eva Rodriguez et al. 2007)

For this reason, the Environmental Protection Agency (EPA) has set a provisional drinking water guideline of 0.3 µg/L for microcystins for bottlefed infants and young children of preschool age. For school-age children through adults, the health advisory (HA) value for drinking water is 1.6 µg/L. The HA values are based on exposure for ten days (EPA, 2015).

For control of taste and odor compounds as well as toxins in drinking water treatment plants, the application of conventional water treatment technologies like coagulation flocculation/sedimentation, filtration have been reported to be effective for removal of cyanobacterial cells but ineffective for removal of extracellular MCs (Himberg et al., 1989; Chow et al., 1999; Hrudey et al., 1999). Thus, alternative treatment options such as use of adsorbents like activated carbon (both powdered and granular) and oxidants such as ozone, chlorine-di-oxide, potassium permanganate and MIOX (Rodriguez et al, 2007, 2008, Dixon et al., 2010) need to be incorporated into the water treatment processes to remove these compounds. With respect to oxidation rate, the following general trend is typically observed: O_3> H_2O_2> HOCl > ClO_2> $KMnO_4$> Cl_2. However, discrepancies have been observed depending on the type of compound that is oxidized. Previous studies have demonstrated the efficiency of different oxidants potassium permanganate (Rodriguez et al., 2007a) and ozone (Onstad et al.,

2007), as well as Advanced Oxidation Processes (Cornish et al., 2000; Qiao et al., 2005) to oxidize extracellular MC.

Among the treatment options listed, PAC is most commonly utilized for control of taste and odor compounds as it has a lower cost and can be used in existing water treatment plant without any major adaptations and additional capital costs. Depending upon the season, the use of PAC can be applied intermittently and at varying doses for the control of microcystins. For an initial MIB concentration of 250 ng/l and PAC dosage of 40 mg/l, the MIB removal efficiency was 70% whereas the MIB removal efficiency lowered for experiments that included both processes of coagulation i.e. ferric sulphate and adsorption (Seckler et al. 2013). Micro pollutant removal efficiency increased by using recycled waste PAC and the optimum PAC used for the removal ranged between 15 and 20 mg/l (Boehler et al. 2012). Most of the studies pertaining to PAC adsorption of cyanotoxins have been conducted on the microcystins, in particular, MCLR (Falconer et al., 1989; Donati et al., 1994; Pendleton et al., 2001; Cook and Newcombe, 2002, 2008; Campinas and Rosa, 2010a,b). Experiments carried out by Cook and Newcombe (2002) for PAC adsorption on four variants of microcystin showed the differences in the adsorption of each variant with the ease of removal following the order: MCRR > MCYR > MCLR > MCLA. It was concluded by Margarida Campinas et al. (2010) that for low concentrations of microcystins (5 µg/L), 10mg/L of PAC effectively controlled the microcystins in a model water with M. aeruginosa culture whereas a PAC dose of 15 mg/L was necessary when the NOM surrogate concentration doubled. For high concentrations of microcystins (20 µg/L),15 mg/L of PAC were unable to achieve the WHO guideline-value.

Advanced oxidation processes (AOPs) involve the use of ozone and a hydroxyl radical. AOPs are strong oxidizing processes that have been used for organic matter oxidation. Ozone

has been used to control taste and odor, remove color, and control biological growth in treatments plants. AOPs have great potential for oxidation of double bonds and amines found in toxins, and that makes them useful in microcystin degradation (Brooke et.al 2006, Onstad et. al 2007). The ozonation process is favored for the treatment of drinking water because of its high oxidation efficiency by a direct pathway (O3 direct reaction) and an indirect pathway (OH radical reaction). The initial concentrations of MIB and GSM were varied between 43 and 220 ng/l, then removal efficiency of MIB rapidly increased in proportion to O_3 dosage and removal up to 84.8% for 2-MIB occurred at 3.8 mg/l for 6.4 minutes contact time (Jung et al. 2004). Collivignarelli and Sorlini, (2004) reported that a complete removal geosmin and MIB can be obtained only with the combination of ozone (conc. of 1.5–3 mg/l and contact time of 2–3 mins) with UV radiation (dose of 5,000–6,000 J/m^2). Yuan et al. (2013) identified that ozonation can lead to 99.9% of GSM removal rate within 30 min at the ozone dosage of 4.19 mg/l. The ozonation process led to the algae removal of 91.2% within 60 mins under the ozone dosage of 5 mg/l and the algae could not survive the dosage of 3 mg/l (Miao et al. 2004). Suffet et al. (1986) found that ozone is generally the most effective oxidant for use in taste and odor treatment, ozone doses of 2.5 to 2.7 mg/L and 10 minutes of contact time (residual 0.2 mg/L) significantly reduce levels of taste and odors.

Cheng et al. (2011) reported that better removal of MIB and GSM were observed with just chlorine dioxide (ClO_2) at an optimum dosage of 5 mg/l, in comparison to a mixture of ClO_2 and coagulant (poly. Aluminum chloride). Lalezary et al. (1986) used chlorine, chlorine dioxide, ozone, and permanganate to treat earthy-musty smelling compounds. In that study, chlorine dioxide was found most effective, although none of the oxidants were able to remove geosmin and MIB by more than 40 to 60 percent. Han et al. (2008) and Wu et al. (2012) found that with a

contact time of 30 minutes using ClO_2, removal of Coliform, Benzopyrene, COD, NH3-N and colour was possible at a dosage of 7.12 mg/l and 5 mg/l respectively. Chlorine-based weaker oxidants (and disinfectants) such as chlorine dioxide (ClO2) and chloramines have been used as alternative to chlorine but found ineffective due to their low reaction kinetic constant, k (Eva Rodriquez et. al 2005, 2007, Kull et al. 2006). Oxidants such as chloramines and chlorine dioxide are not plausible options for the removal of MC from natural waters, due to their low reactivity with these oxidants (Acero et al., 2005; Kull et al., 2004). ClO2 as an oxidant in drinking water treatment will have only a small or negligible impact on dissolved microcystins if these toxins are present in the raw water (Kull et. al 2006).

Permanganate ($KMnO_4$) is a strong oxidizing agent that has been used to control taste and odor, remove color, control biological growth in treatment plants and remove iron and manganese. Typical dosages of $KMnO_4$ vary from 0.25 to 20 mg/l for sulfide oxidation o grassy odors, however, it does a poor job of removing GSM and 2-MIB (MWH's Water Treatment: Principles and Design, John C. Crittenden). $KMnO_4$ ($\leq$3 mg/l) may be used for pre-oxidation in the presence of cyanobacteria without impacting cell membranes which is a benefit over other oxidants (Fan et al. 2013). Studies indicate that the application of permanganate was found to be effective for the removal of dissolved MC-LR, although with live intact cells toxin removal was much poorer, suggesting that permanganate was unable to effectively penetrate or lyse the cells (Rositano, 1996). Hall et al. (2000) reported that permanganate is a possible treatment for dissolved MC-LR in waters with low oxidant demand and must be applied before sedimentation/filtration of treatment train in order to control final manganese concentrations. However, the dose of permanganate must be controlled since the high doses might cause cell lysis and toxin release in raw water containing algal cells (Knappe et al., 2004; Pietsch et al.,

2002). Around 1–1.25 mg/L of permanganate was enough to reduce the concentration of MCs below the WHO guideline value of 1 µg/L in the experiments performed with surface water. Therefore, permanganate is a feasible option for the oxidation of MCs in natural waters prior to coagulation-sedimentation steps (Eva Rodriquez et. al 2007).

Chorine is a very effective method for taste and odor control, but use as a control chemical must be evaluated carefully due to the formation of THMs and chlorophenol when organics are present. Reactivity of chlorine with toxins is influenced by pH of the water and by the presence of NOM. Contact time (CT) values required for destruction of microcystins with free chlorine may be many times higher than required for the surface water treatment rule depending on specific water quality conditions (Ohio EPA, AWWA,2011). One study showed that even a 5 mg/L was ineffective for destroying the algal toxin extracts (Hoffman, 1976). A second study demonstrated that combined treatment processes which included chlorination at 0.5 mg/L were also ineffective (Keijola et al., 1988; Himberg et al., 1989). A third study showed chlorination achieved negligible reduction in microcystin levels of 0.3-0.5 µg/L in treated water (Lambert et al., 1996). However, chlorination was very effective at destroying microcystin-LR and nodularin with free chlorine residual of 0.5 mg/L after 30 minutes' contact time with pH < 8 (Nicholson et al., 1994). Dissolved microcystin-LR and anatoxin-a in the range 5-10 µg/L, using a chlorine residual of 0.7 mg/L showed at pH 5, removal was more than 93 % within 30 minutes but at pH 7 removal reached only 88 per cent after 22 hours (Carlile, 1994, Croll and Hart, 1996, Hart et al., 1997). Courchene and Chapman (1975) have stated that a free chlorine residual of 0.2-1.0 mg/L was very effective against most of the taste and odor or filter-clogging algae.

The mixed-oxidants (MIOX) disinfection system appears to provide a reasonable alternative for small distribution systems as a safe, reliable, and cost effective technology that is

easy to operate and is readily compatible with other treatment systems. A 5 mg/l dose of mixed oxidants reduced the mouse infectivity of C. parvum oocysts by >99.9 to >99.99% after 4 hours. Under the same conditions, the infectivity of C. perfringens spores was reduced by >99.5% (Venczel et al. 1997).

3.3 MATERIALS AND METHODS

3.3.1 Reagents and Supplies.

The high purity chemical microcystin-LR (CAS 101043-37-2) was purchased from Sigma Aldrich (Pittsburg, PA). Geosmin, 2-Methyl Isoborneol and 2,4,6-Trichloroanisole (CAS 16423-19-1) was purchased from Supelco (Belafonte, PA). Optima grade methanol (CAS 67-56-1) was obtained from; Fisher Scientific (Fair lawn, NJ). Standard solution of microcystin-LR were prepared in methanol at 10 mg/L, 50, 25, 10, 5 and 1 ug/L. Standard solutions of geosmin were prepared in methanol at 4 and 0.04 mg/L, 50, 25, 10, 5, and 1 ng/L. Standard solutions of 2-Methyl Isoborneol were prepared in methanol at 4 and 0.04 mg/L, 50, 25, 10, 5, and 1 ng/L. Standard solutions of 2,4,6-Trichloroanisole were prepared in methanol at 4 and 0.04 mg/L.

The lignite coal based Hydrodarco-B (PAC) was supplied by Norit America Inc. (Marshall, TX). The PAC solution was prepared using reverse osmosis (RO) water and PAC, bringing the concentration to 10g/L. The PAC dosages tested were 5, 10, 20, 40 and 60 mg/L.

Chlorine-di-oxide (ClO_2) (CAS 10049-04-4) was supplied by CDG Environmental (Bethlehem, PA). The concentration was measured using amperometrictitrator, bringing the concentration to 3035 mg/L. The ClO_2 dosages tested were 0.5, 0.9 and 1.3 mg/L.

Chlorine (Cl_2) was supplied by Hach (Loveland, CO). The stock solution was prepared RO water and ampules with 25-30mg/L as Cl_2. The Cl_2 dosages tested were 0.5, 1.0 and 2.0 mg/L.

Potassium permanganate ($KMnO_4$) was supplied by Fischer Chemical (Fair lawn, NJ). The stock solution was prepared using nano pure water and bringing the concentration to 1g/L. The $KMnO_4$ dosages tested were 0.5, 1.0 and 2.0 mg/L.

Mixed oxidants (MIOX) was prepared on-site using the MIOX generator (Rio Zuni 2.0, MIOX corporation inc.) the concentration was measured to be 2350 mg/L. The MIOX dosages tested were 0.5, 1.0 and 2.0 mg/L.

Ozone (O_3) was prepared on-site using the Ozone generator (APG Del Ozone generator) the concentration was measured for every run. The O_3 dosages tested were 0.3, 0.7 and 1/1.5 mg/L.

Sodium Thio-sulfate was supplied by Fischer Chemical (Fair lawn, NJ). The stock solutions were prepared using nano pure water and bring the concentration to 1g/L. Thio solution was mainly used for quenching the oxidants.

1-L Pyrex beakers, Whatman glass fiber filters, 40 ml amber glass (VOA) vials and 20ml glass vials were purchased from Fisher Scientific Inc. Solid-phase microextraction (SPME) fibers (65μm PDMS/DVB cross-linked) and holders were purchased from (Supelco, (Bellefonte, PA) were used in the geosmin/MIB analysis.

3.3.2 Water Samples

Raw water samples used in the experiments were provided by the Moffat WTP in blue plastic storage drums beginning in early April 2014 and stored at 4 ^{o}C for use. The basic water quality parameters such as dissolved organic carbon (DOC), pH, dissolved oxygen (DO), turbidity and conductivity were measured at CSU using Hach® sensIon 156 multi-parameter meter Hach turbidimeter. The water samples (500ml) were placed in 1 L glass beakers with Teflon coated stir bars. The beakers were spiked with odorants and treatment chemicals at selected concentrations. The samples were stirred to allow for complete mixing without creating a vortex for the selected contact time. Each run was duplicated to verify the validity of the experimental results. A sample solution of 100 mL was collected from the beaker at the selected contact time, and was either filtered through Whatman glass fiber 1.2 um filters to remove the PAC or was quenched using sodium thio sulphate to remove the oxidant present in the samples. The samples were placed into two 40 mL amber glass vials with open top screw caps lined with PTFE rubber septum to be stored at 4 ^{o}C for analysis.

3.3.3 Coagulation and Jar Tests

1-liter glass beakers were filled with (500ml) the source water and spiked with geosmin or 2-methylisoborneol or microcystin-LR to achieve levels that correspond to common bloom events. Total microcystin-LR concentrations tested were 10, 25 and 50 ug/L, total geosmin and concentrations tested were 10, 25 and 50 ng/L and total 2-Methylisoborneol concentrations tested were 10, 25 and 50 ng/L for the jar tests. The respected amount of PAC solution or the oxidant was then added to achieve desired concentrations. The experimental plan and levels of metabolites and adsorbent/oxidants are given in table 3-1.

Table 3-3-1: Experimental matrix for metabolite removal

Odorant (ng/L)	**PAC (mg/L)**	**ClO_2 (mg/L)**	**$KMnO_4$ (mg/L)**	**O_3 (mg/L)**	**MIOX (mg/L)**	**Cl_2 (mg/L)**
10	5, 10, 20	0.5, 0.9, 1.3	0.5, 1.0, 2.0	0.7, 1.5	0.3, 0.7, 1.0	0.5, 1.0, 2.0
25	10, 20, 40	0.5, 0.9, 1.3	0.5, 1.0, 2.0	0.7, 1.5	0.3, 0.7, 1.0	0.5, 1.0, 2.0
50	10, 20, 40	0.5, 0.9, 1.3	0.5, 1.0, 2.0	0.7, 1.5	0.3, 0.7, 1.0	0.5, 1.0, 2.0

MC-LR (ug/L)	**PAC (mg/L)**	**ClO_2 (mg/L)**	**$KMnO_4$ (mg/L)**	**O_3 (mg/L)**	**MIOX (mg/L)**	**Cl_2 (mg/L)**
10	5, 10, 20	0.5, 0.9, 1.3	0.5, 1.0, 2.0	0.3, 0.7, 1.0	0.3, 0.7, 1.0	0.5, 1.0, 2.0
25	10, 20, 40	0.5, 0.9, 1.3	0.5, 1.0, 2.0	0.3, 0.7, 1.0	0.3, 0.7, 1.0	0.5, 1.0, 2.0
50	10, 20, 60	0.5, 0.9, 1.3	0.5, 1.0, 2.0	0.3, 0.7, 1.0	0.3, 0.7, 1.0	0.5, 1.0, 2.0

Figure 3-3 Experimental Setup for Toxin and T&O Sample Analysis

A batch of four jars tests were simultaneously ran on a Fischer scientific magnetic stirrer using Teflon coated stir bars. The solutions in the beakers were spiked with geosmin/2-MIB and microcystin-LR, and the beakers were mixed for specific contact time to ensure proper mixing of the algal metabolites. Samples were drawn from each jar at approximately 1.5 inches below the water surface and were filtered by a 0.45 um glass filter or immediately quenched using thio solution (depending on the oxidant) and collected into in 40 mL amber glass vials for storage at 4 ^{o}C until analysis.

3.3.4 Solid Phase Microextraction coupled with GC/MS for T&O Analysis

The headspace solid phase micro-extraction (SPME) coupled with GC/MS method was adopted from procedures laid out by Omur-Ozbek and Dietrich, (2005) and Saito, (2008) for analysis. To improve odorant recovery by the SPME fiber and to increase the headspace concentrations, the 20 mL samples were placed in 40 mL amber vials, received 3 g of sodium chloride (NaCl) and was heated up to 65 ^{o}C ($\pm$ 2 ^{o}C). After 10 minutes of equilibration, the SPME fiber was inserted and exposed to the headspace of the vial for an adsorption time of 20

minutes. Calibration curve samples were prepared in 40 mL glass amber vials with 20 mL Geosmin/2-MIB standard solutions at 1, 5, 10, 20 and 50 ng/L.

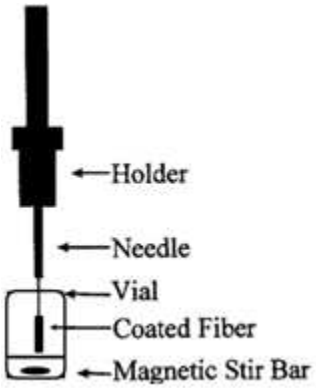


Figure 3-4: Sample Extraction with SPME

Figure 3-5 GC/MS Equipment Setup

The same extraction and analysis procedure was applied to the standard curve samples to quantify the GC/MS results. Trichloroanisole (TCA) was used as an internal standard, and all the samples were spiked with 20uL of 0.04 mg/L of TCA. Odorants extracted by the SPME fiber were analyzed by GC/MS. For the experiments, Agilent 5890 GC connected to an Agilent 5973 MS was employed. The SPME fiber was placed into the injection port of the GC set to 250 °C

and the odorants were desorbed in splitless mode for 3 minutes. The GC column selected was a DB-5 MS, (30 m, 0.25 mm ID., 0.25 µm) supplied by Agilent Technologies. The GC was programmed to start at an initial temperature of 100°C, and then the temperature was ramped up to 210 °C at a rate of 20 °C/min. The carrier gas was helium operated at a rate of 1 mL/min at a pressure of 145 kPa. The MS was set for selected ion monitoring (m/z 112, 125 and 182 for geosmin; and m/z 95, 107 and 168 for 2-MIB) to increase sensitivity of detection. The detection limit of odorants was at 0.5 ng/L. For the taste and odor analysis carried out with different oxidants/adsorbent, all samples were run as triplicates to validate the research.

3.3.5 LC/MS/MS Analysis for Microcystin-LR

Microcystin-LR was detected and quantified by liquid chromatography-mass spectrometry-mass spectrometry (LC/MS/MS) following the method by Triantis et al. (2010). Two different LC/MS/MS equipment were used depending on the availability. The parameters used for both are described below.

The LC/MS/MS was running on an Agilent eclipse plus C18 coupled with an Agilent 5973 mass spectrometer equipped with an ESI source in the positive mode (Agilent, Santa Clara, CA).

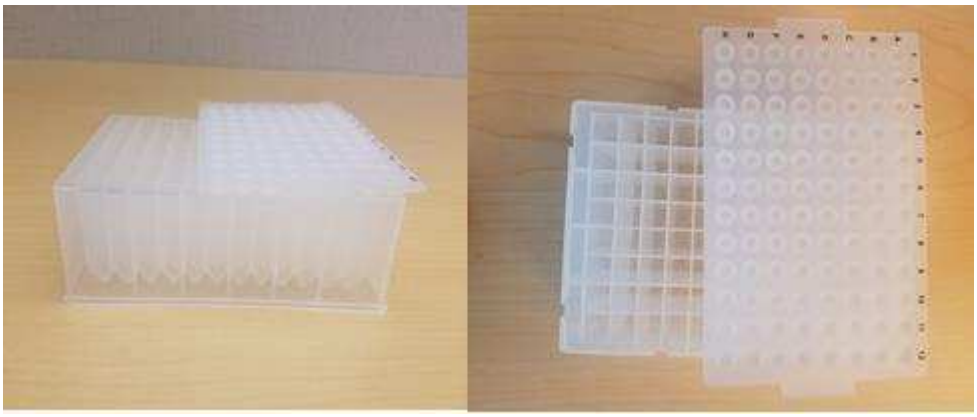


Figure 3-6 Analysis tray for toxin samples

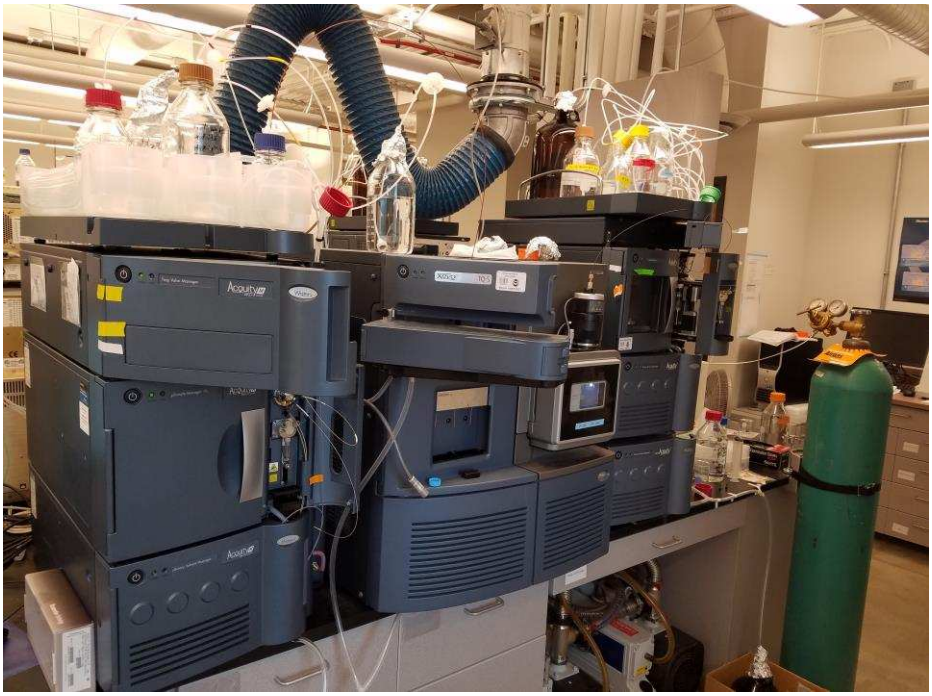


Figure 3-7 LC/MS Equipment Setup

The compound Microcystin-LR was separated on an Agilent Eclipse Plus C18 column (2.1 x 50mm, 1.8 um particle size) at 30 ºC. A sample volume of 20 µL was injected and a binary mixture of ammonium formate in 0.1% (v/v) formic acid (A) and CAN 0.1% (v/v) formic acid in LC grade water (Sigma, Pittsburg PA) (B) at a flow rate of 0.4 mL/min was passed through the column. The solvent gradient used was 15% B at start, increased to 100% at 3.5 min. The

ionization source conditions used were as follows: nebulizer gas flow of 8 L/min at 20 psi. Sheath gas temperature was set at 400 ^{o}C and sheath gas flow of was set to 10 L/min. The optimized fragmentor was set at 200 V with a cell accelerator voltage of 7 V. The precursor ion was set at 995.6 m/z and product ions of 70.1 and 135.0 m/z per produced with a collision energy of 90 V. The collection and processing of chromatograms was performed by using the Agilent Mass Hunter software (v B.04.01). The detection limit of microcystin-LR was at 0.5 ug/L. For the toxin analysis carried out with different oxidants/adsorbent, all samples were run as triplicates to validate the research.

When the other LC/MS/MS was utilized, it was performed on a Waters Acquity M-Class UPLC coupled to a Waters Xevo TQ-S triple quadrupole mass spectrometer. Chromatographic separations were carried out on a Waters BEH C18 stationary phase iKey separation device (150 µm x 50 mm, 1.7 µM). Mobile phases were 99.9% acetonitrile, 0.1% formic acid (B) and water with 0.1% formic acid (A). The analytical gradient was as follows: time = 0 min, 0.5 % B; time = 2.0 min, 3.0 % B; time = 6 min, 97 % B; time = 7.5 min, 97 % B; time 8.0 min, 0.5 % B; time 11 min, 0.5 % B. Flow rate was 5.0 µL/min and injection volume was 5.0 µL. Samples were held at 4^{o} C in the autosampler, and the iKey device was operated at 70^{o} C. The MS was operated in selected reaction monitoring (SRM) mode, where a parent ion is selected by the first quadrupole, fragmented in the collision cell, then a fragment ion selected for by the third quadrupole. Product ions, collision energies, and cone voltages were optimized for each analyte by direct injection of individual synthetic standards. Inter-channel delay was set to 3 ms. The MS was operated in positive ionization modes with the capillary voltage set to 3.6 kV. Source temperature was 120^{o} C and desolvation temperature 500^{o} C. Cone gas flow was 150 L/hr, and collision gas flow was 0.15 mL/min. Nebulizer pressure (nitrogen) was set to 7 Bar. Argon was used as the collision

gas. The precursor ion was set at 498.6 & 995.6 m/z and product ions of 135 and 125, 135.0 m/z per produced with a collision energy of 13,90 &75 V respectively. All Raw data files were imported into the Skyline open source software package[1]. Each target analyte was visually inspected for retention time and peak area integration. Peak areas were extracted for target compounds detected in biological samples and normalized to the peak area of the appropriate internal standard. Normalized peak areas were exported to Excel and absolute quantitation was obtained by using the linear regression equation generated for each compound from the calibration curve. Limits of detection (LOD) and limits of quantification (LOQ) were calculated as 3 times or 10 times the standard deviation of the blank divided by the slope of the calibration curve respectively[2, 3].

3.3.6 Data Analysis

Collected data was analyzed with the Stat-Ease® Design Expert® (Version 10.0.2) to determine the optimum PAC/oxidant dosing for various odorant/toxin concentrations, experimental design, data analysis, quadratic model buildings, and graph (three-dimensional response surface and contour) plotting.

3.4 RESULTS AND DISCUSSIONS

3.4.1 TASTE AND ODOR REMOVAL

Results for metabolite removal are shown in tables 3-2 through 3-13 as percent removal as a function of PAC or oxidant dosage. Percent removal was calculated relative to the average residual GSM and MIB concentration at the 0 mg/L dose of PAC or oxidant. Raw data is also summarized in Table 5-1.

A.Powdered Activated Carbon (PAC) as Adsorbent

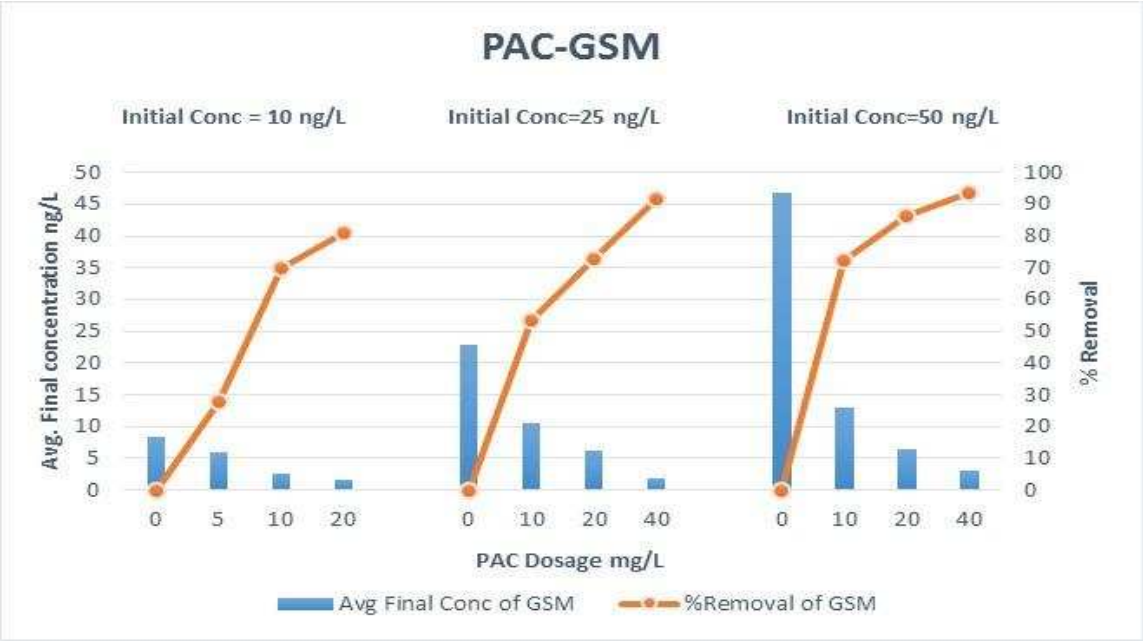


Figure 3-8: Interaction of GSM at different PAC dosages at different initial concentrations

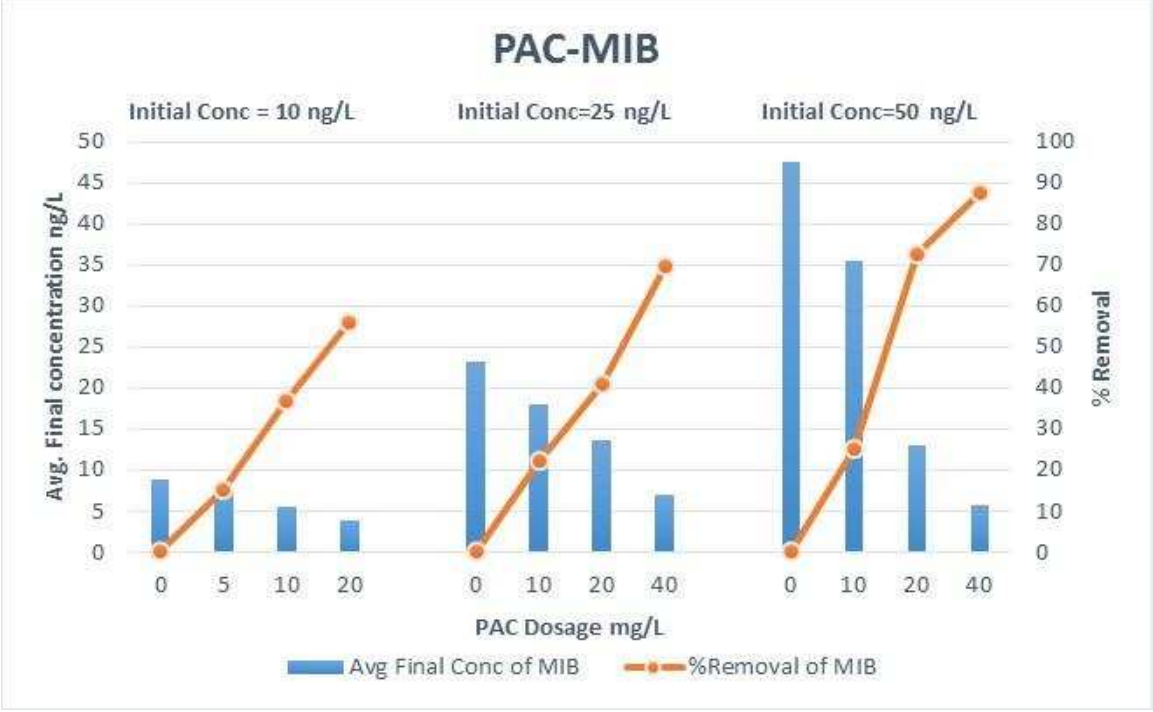


Figure 3-9: Interaction of MIB at different PAC dosages at different initial concentrations

Table 3-2 Average percent removal of GSM & MIB as a function of PAC dosage

Initial Conc. of Geosmin	Initial Conc. of 2-MIB	PAC Dosage	Contact Time	Removal of Geosmin	Std. Deviation	Removal of 2-MIB	Std. Deviation
(ng/l)	(ng/l)	(mg/l)	(mins)	%		%	
10	10	20	30	80.80	7.41	56.08	7.57
25	25	40		91.76	2.50	69.73	5.28
50	50	40		92.13	2.41	87.74	2.06

The results from the bench scale study were higher compared to the results from other researchers or studies. For the study with an initial 2-MIB concentration of 250 ng/l and PAC dosage of 40 mg/l, the MIB removal efficiency was 70% whereas the 2-MIB removal efficiency was lower for experiments that included both processes of coagulation i.e. ferric sulphate and adsorption (Seckler et al. 2013). The study by Omur-ozbek and Kirk (2011) suggest that 96% removal of Geosmin is possible with PAC at a dose of 20 mg/L with an initial conc. of 20ng/L, although, it should be noted that PAC/Geosmin concentrations combination matrix and TOC levels do affect the removal rates. Higher levels of TOC have a negative impact on removal of GSM and 2-MIB since the pores of PAC gets hindered by presence of NOM thereby reducing the efficiency of removal. The research carried out by Matthew (2004) towards his dissertation on two different source waters show that 87% and 62% removal of MIB was achieved with PAC, owing the difference in the removal rates to difference in fractionation of the NOM present.

B. Chlorine Dioxide (ClO_2) as Oxidant

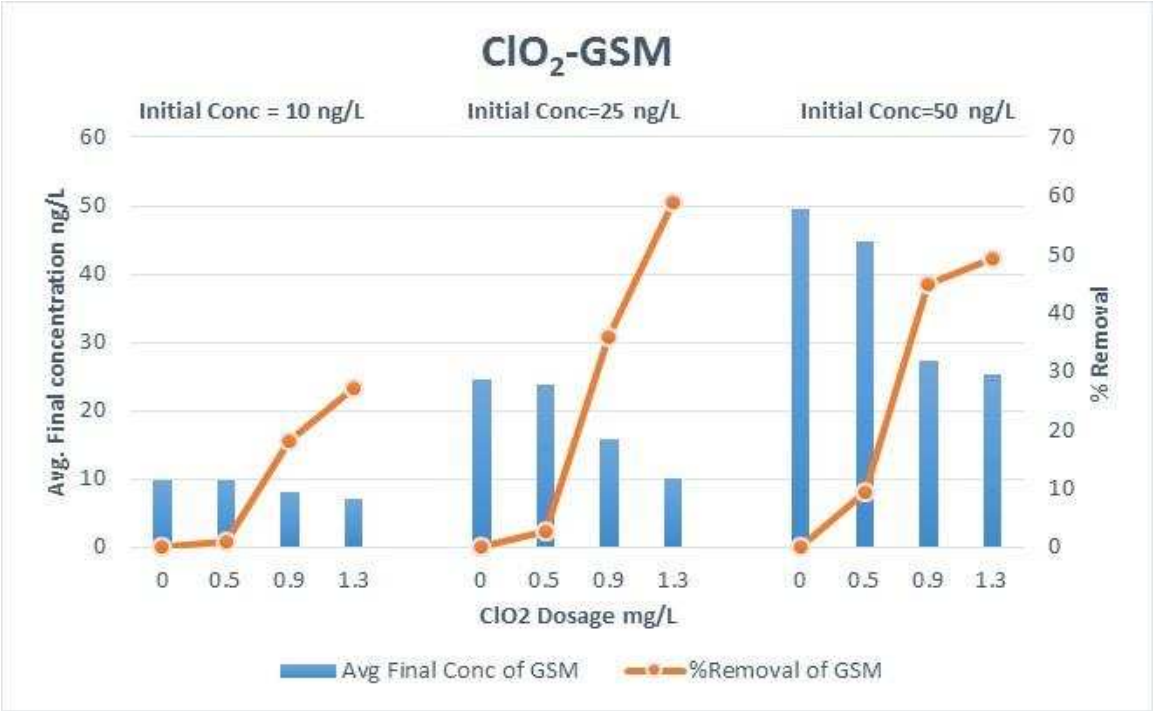


Figure 3-10: Interaction of GSM at different ClO_2 dosages at different initial concentrations

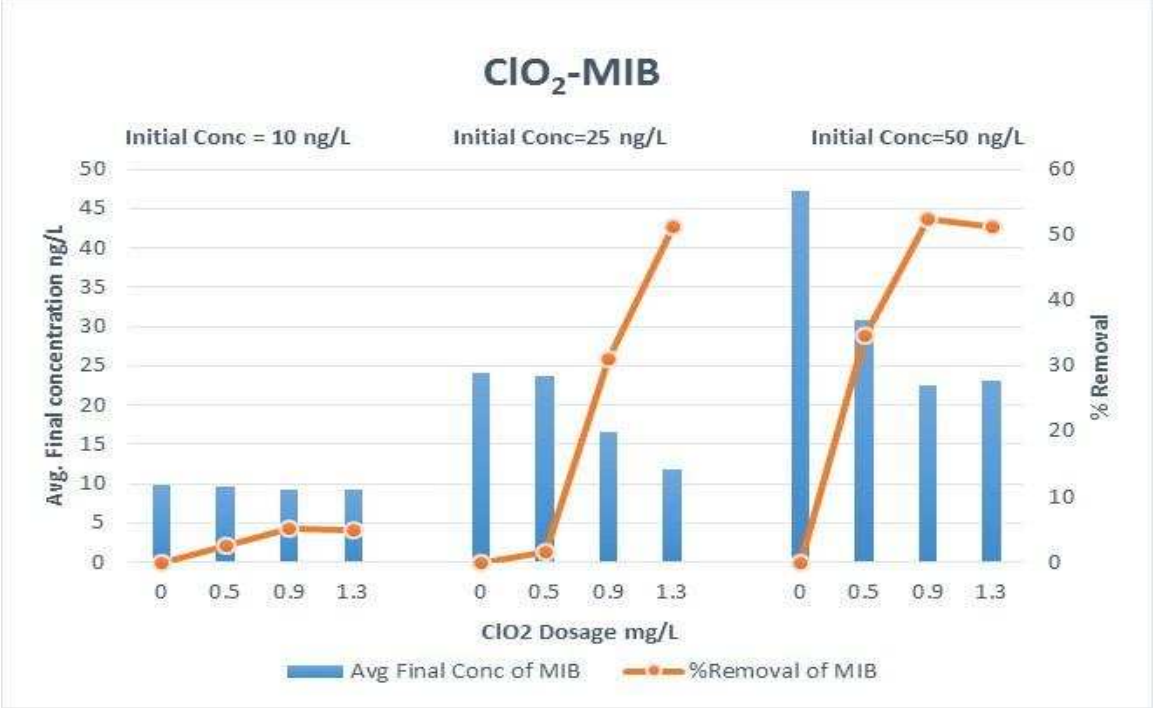


Figure 3-11: Interaction of MIB at different ClO_2 dosages at different initial concentrations

Table 3-3:Average percent removal of GSM&MIB as a function of ClO_2 dosage

Initial Conc. of Geosmin	Initial Conc. of 2-MIB	ClO_2 Dosage	Contact Time	Removal of Geosmin	Std. Deviation	Removal of 2-MIB	Std. Deviation
(ng/l)	(ng/l)	(mg/l)	(mins)	%		%	
10	10	1.3	30	27.24	21.83	4.86	0.78
25	25			58.97	5.33	51.19	12.75
50	50			49.16	1.71	51.24	18.46

Lalezary et al. (1986) found that chlorine dioxide was not able to remove geosmin and 2-MIB by more than 40 to 60 %. Chlorine-based weaker oxidants (and disinfectants) such as chlorine dioxide (ClO_2) have been used as alternative to chlorine but found ineffective due to their low reaction kinetic constant, k (Rodriquez et. al 2005, 2007, Kull et al. 2006). The results from this analysis also indicate the same results as found by other studies.

C. Potassium Permanganate ($KMnO_4$) as Oxidant

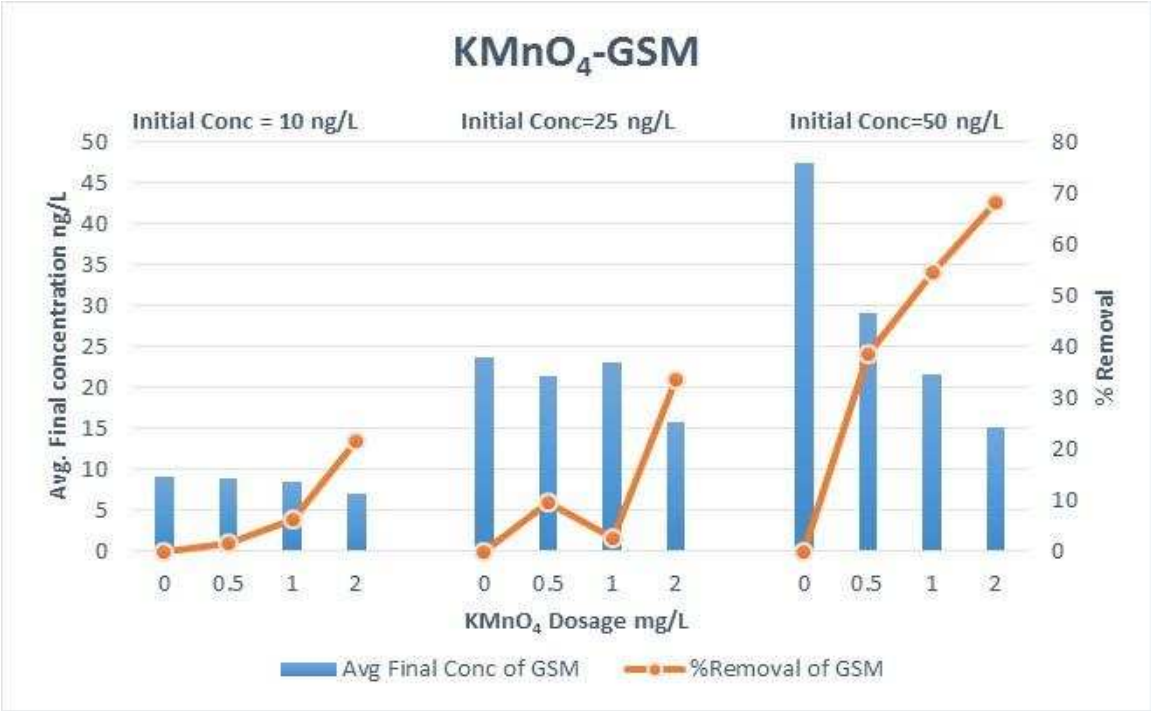


Figure 3-12: Interaction of GSM at different $KMnO_4$ dosages at different initial concentrations

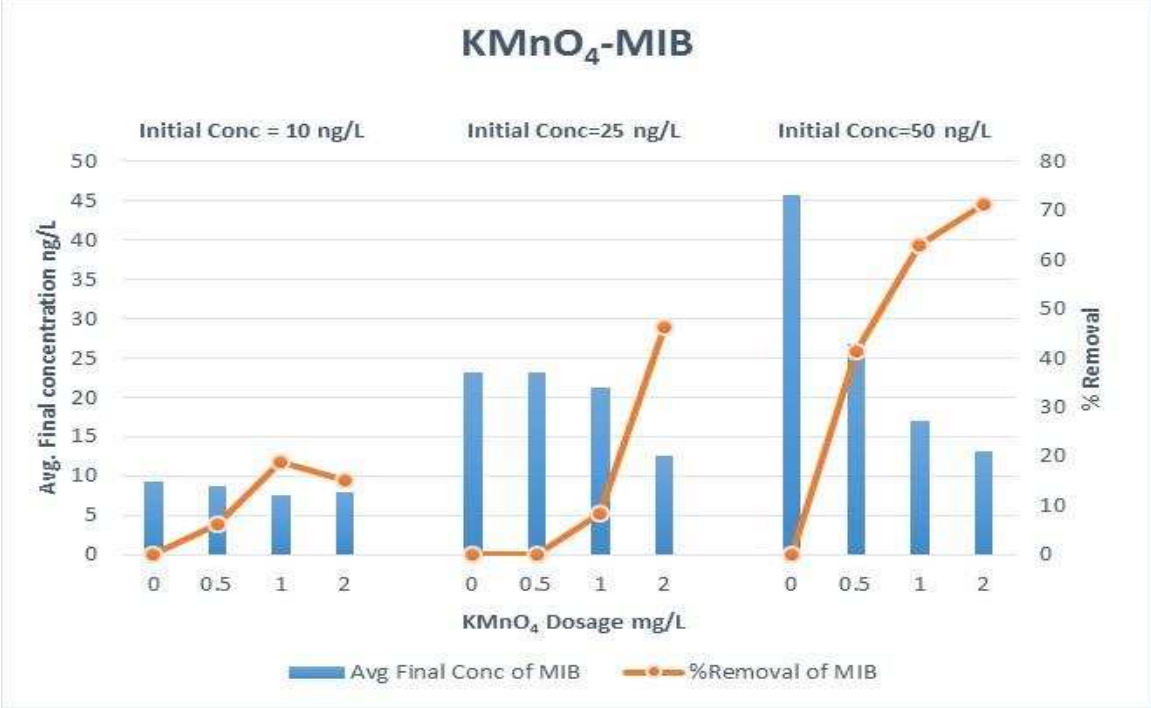


Figure 3-13: Interaction of MIB at different $KMnO_4$ dosages at different initial concentrations

Table 3-4: Average percent removal of GSM & MIB as a function of $KMnO_4$ dosage

Initial Conc. of Geosmin	Initial Conc. of 2-MIB	$KMnO_4$ Dosage	Contact Time	Removal of Geosmin	Std. Deviation	Removal of 2-MIB	Std. Deviation
(ng/l)	(ng/l)	(mg/l)	(mins)	%		%	
10	10	2	30	21.7	2.86	15.12	19.47
25	25			33.63	10.68	46.26	9.86
50	50			68.3	3.16	71.18	2.26

The studies from other researchers show that typical dosages of $KMnO_4$ vary from 0.25 to 20 mg/l for sulfide oxidation of grassy odors, however, it does a poor job of removing GSM and 2-MIB (Crittenden, 2012). $KMnO_4$ ($\leq$3 mg/l) may be used for pre-oxidation in the presence of cyanobacteria without impacting cell membranes which is a benefit over other oxidants (Fan et al. 2013). This study showed a removal of 65-70% of GSM and 2-MIB which can be utilized as a pre-oxidant in many plants due to it easy maintenance and cost of use.

D. Mixed Oxidant (MIOX) as Oxidant

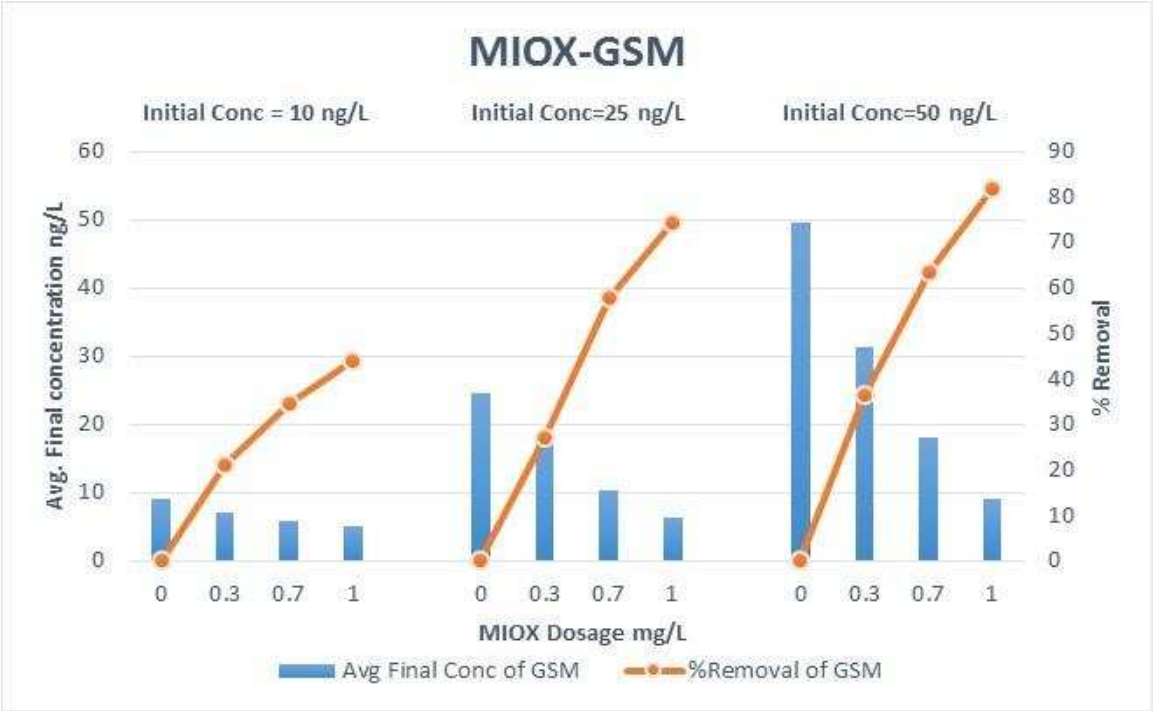


Figure 3-14: Interaction of GSM at different MIOX dosages at different initial concentrations

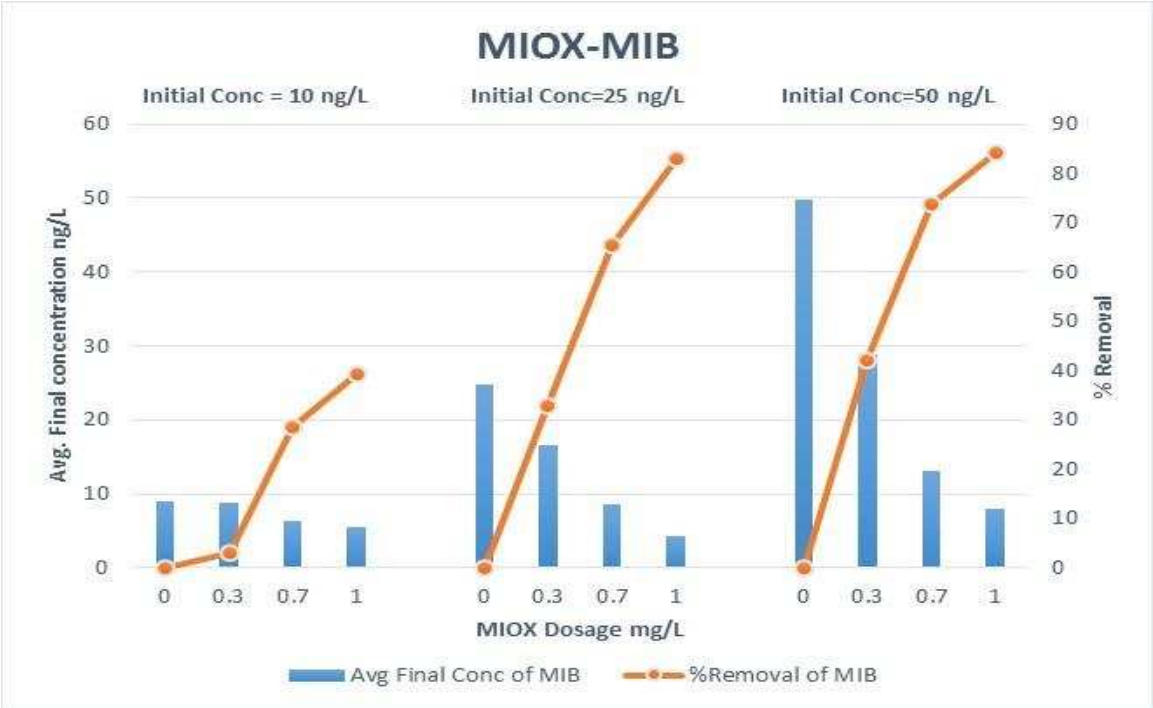


Figure 3-15: Interaction of MIB at different MIOX dosages at different initial concentrations

Table 3-5: Average percent removal of GSM & MIB as a function of MIOX dosage

Initial Conc. of Geosmin	Initial Conc. of 2-MIB	MIOX Dosage	Contact Time	Removal of Geosmin	Std. Deviation	Removal of 2-MIB	Std. Deviation
(ng/l)	(ng/l)	(mg/l)	(mins)	%		%	
10	10	2	30	43.88	10.95	39.39	12.78
25	25			74.15	1.76	83.06	4.17
50	50			81.89	0.48	84.09	0.72

MIOX performed really well for the removal of GSM and 2-MIB, but the further studies need to be carried out like its effect on pH, TOC etc. to make it a reliable oxidant for use in plants. From the above table, MIOX clearly indicates that though it can't be used as a primary oxidant as it does not bring the odor levels below the threshold but definitely can be considered as a pre-oxidant in the water treatment process.

E. Ozone (O_3) as Oxidant

Figure 3-16:Interaction of GSM at different O_3 dosages at different initial concentrations

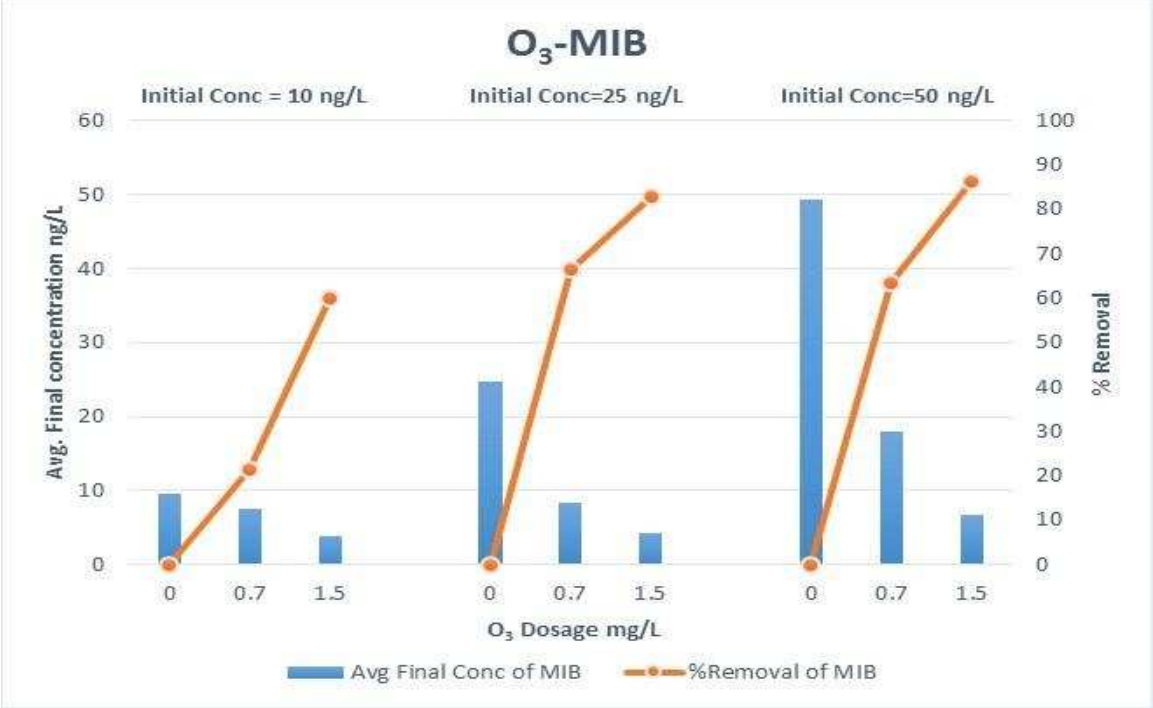


Figure 3-17:Interaction of MIB at different O_3 dosages at different initial concentrations

Table 3-6: Average percent removal of GSM as a function of O_3 dosage

Initial Conc. of Geosmin	Initial Conc. of 2-MIB	O_3 Dosage	Contact Time	Removal of Geosmin	Std. Deviation	Removal of 2-MIB	Std. Deviation
(ng/l)	(ng/l)	(mg/l)	(mins)	%		%	
10	10	1	10 to 15	97.90	4.91	60.04	8.41
25	25			96.68	6.55	83.04	1.1
50	50			94.03	1.11	86.32	1.07

Collivignarelli and Sorlini, (2004) reported that a complete removal geosmin and 2-MIB can be obtained only with the combination of ozone (conc. of 1.5–3 mg/l and contact time of 2–3 mins) with UV radiation (dose of 5,000–6,000 J/m^2). Yuan et al. (2013) identified that ozonation can lead to 99.9% of GSM removal rate within 30 min at the ozone dosage of 4.19 mg/l. The results also show that ozone is very good oxidant for removal of GSM. Removal of 2-MIB is also considerably high but with higher dosage or contact time, rate of removal will be equal to GSM.

F. Chlorine (Cl_2) as Oxidant

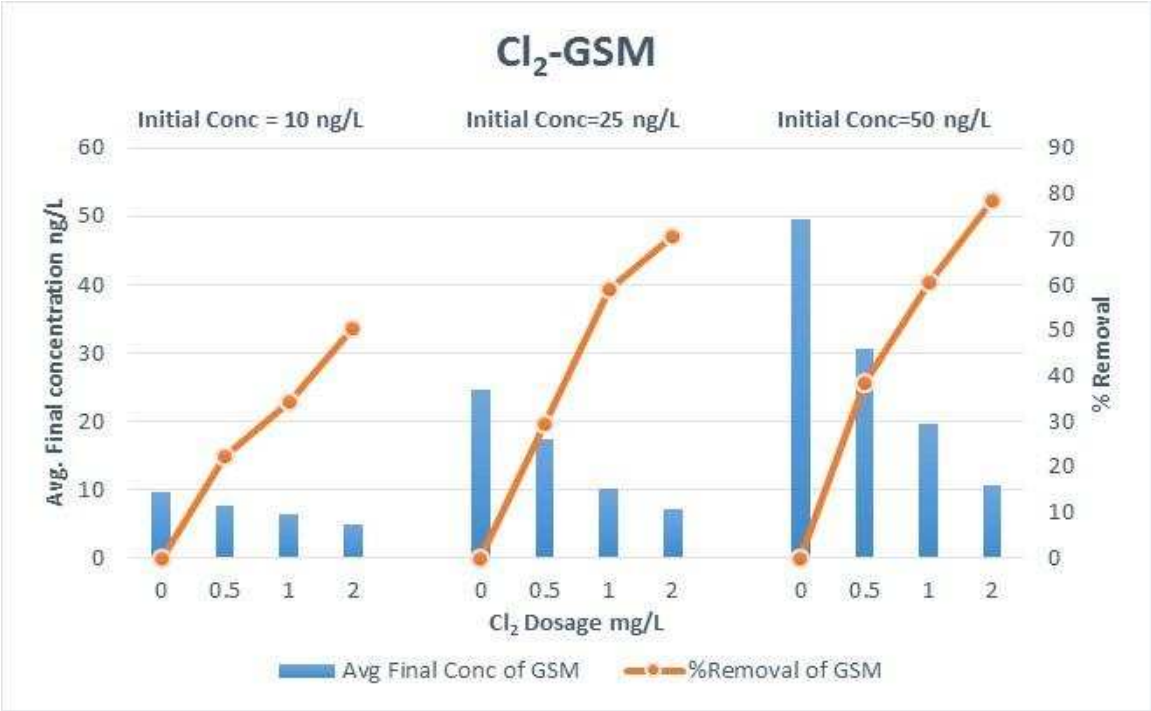


Figure 3-18:Interaction of GSM at different Cl_2 dosages at different initial concentrations

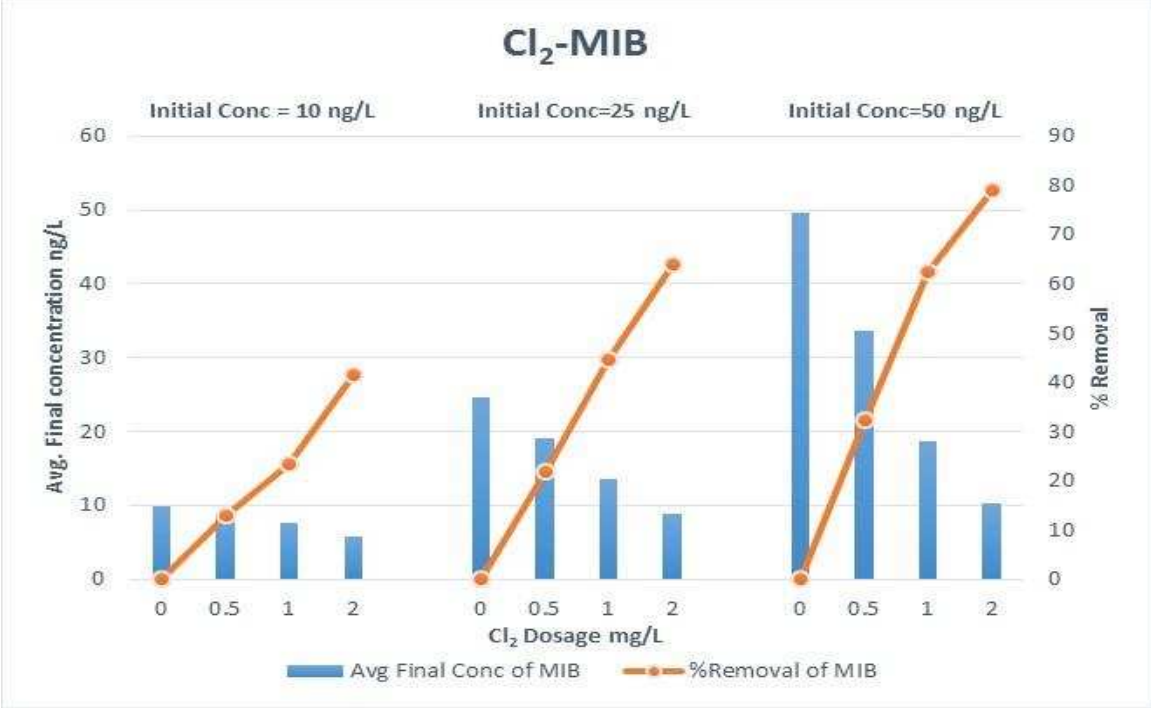


Figure 3-19:Interaction of MIB at different Cl_2 dosages at different initial concentrations

Table 3-7: Average percent removal of GSM & MIB as a function of Cl_2 dosage

Initial Conc. of Geosmin	Initial Conc. of 2-MIB	Cl_2 Dosage	Contact Time	Removal of Geosmin	Std. Deviation	Removal of 2-MIB	Std. Deviation
(ng/l)	(ng/l)	(mg/l)	(mins)	%		%	
10	10	2	30	50.26	5.82	41.65	10.06
25	25			70.70	1.96	63.93	9.37
50	50			78.51	3.72	79.16	4.58

Chorine is a very effective method for taste and odor control, but use as a control chemical must be evaluated carefully due to the formation of THMs and chlorophenol when organics are present. Courchene and Chapman (1975) have stated that a free chlorine residual of 0.2-1.0 mg/L was very effective against most of the taste and odor. A second study demonstrated that even combined treatment processes which included chlorination at 0.5 mg/L were also ineffective (Keijola et al., 1988; Himberg et al., 1989). Chlorine is available easily in all water treatment plants so it can be quite effective when used as pre-oxidant but its dose needs to be monitored as seen in literature due to its harmful byproducts.

3.4.2 TOXIN REMOVAL

Toxins were analyzed using liquid chromatography mass spectrometry (LC-MS) for PAC and oxidant tests. Analysis of water samples was carried out using duplicates or quadruplicates after the reaction with oxidants or an adsorbent for a given contact time. Results are shown in below figures as percent removal as a function of PAC or oxidant dosage.

A. Powdered Activated Carbon (PAC) as Adsorbent

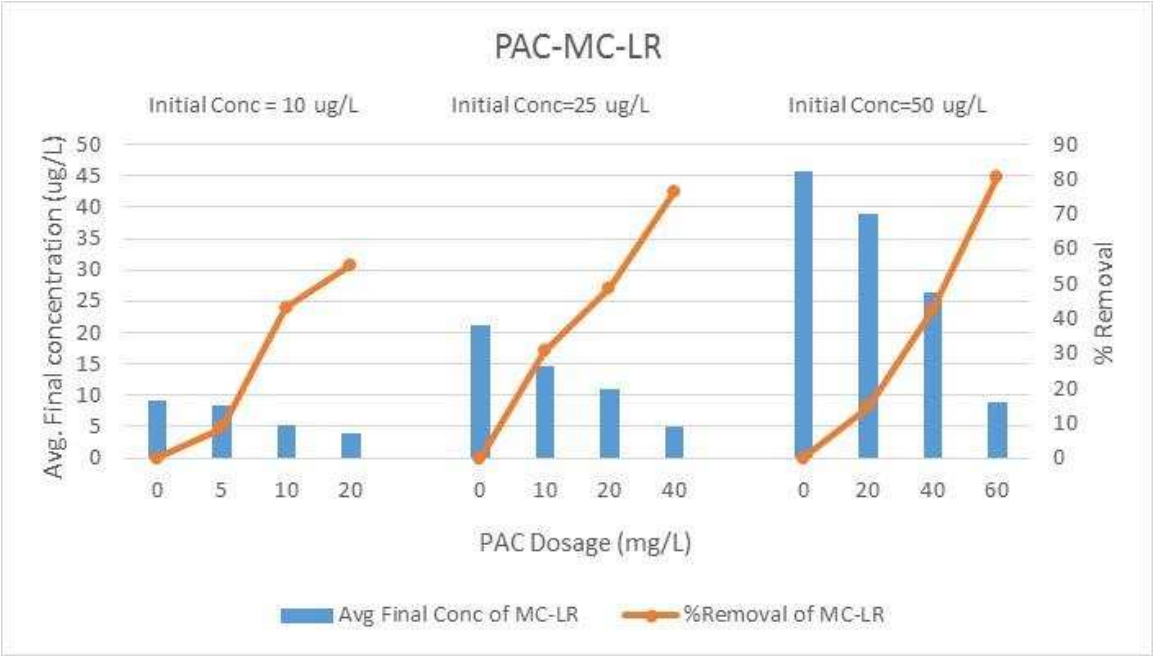


Figure 3-20:Interaction of MC-LR at different PAC dosages at different initial concentrations

Table 3-8: Average percent removal & Conc. of MC-LR as a function of PAC dosage

Initial Conc. of MC-LR	**PAC Dosage**	**Contact Time**	**Removal**	**Std. Deviation**
(ug/l)	**(mg/l)**	**(mins)**	**%**	
10	20	30	55.27	21.01
25	40		76.25	9.6
50	60		80.65	10.35

In comparison to the above results, Campinas et al. (2010) showed that for low concentrations of microcystins (5 µg/L), 10 mg/L of PAC effectively controlled the microcystins in a model water with M. aeruginosa culture whereas a PAC dose of 15 mg/L was necessary when the NOM surrogate concentration doubled. Also, GAC filtration and PAC with conventional treatment in full scale application were both generally observed to reduce raw water microcystins by more than 80 % except when raw water levels dropped below 0.5 µg/L (Lambert et. al 1996).

B. Chlorine Dioxide (ClO_2) as Oxidant

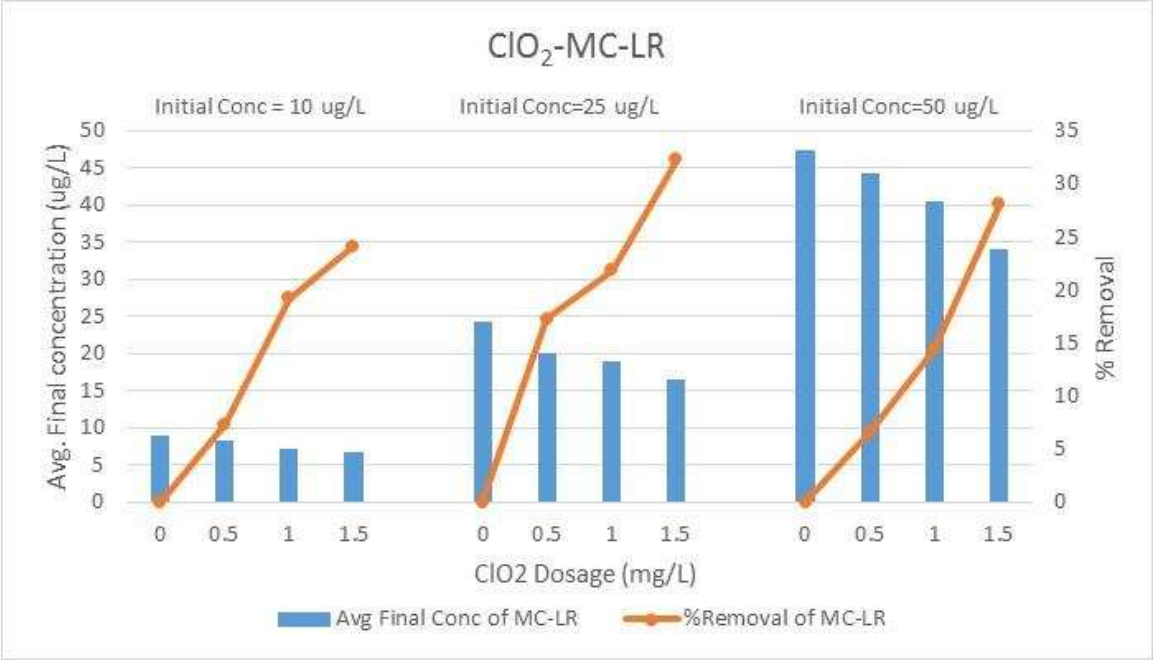


Figure 3-21: Interaction of MC-LR at different ClO_2 dosages at different initial concentrations

Table 3-9: Average percent removal & Conc. of MC-LR as a function of ClO2 dosage

Initial Conc. of MC-LR	ClO_2 Dosage	Contact Time	Removal	Std. Deviation
(ug/l)	(mg/l)	(mins)	%	
10	1.5	30	24.11	10.44
25			32.24	6.03
50			28.05	5.03

The results clearly show that ClO_2 is not a good oxidant for the removal of microcystins which is substantiated with the literature. Oxidants such as chloramines and chlorine dioxide are not plausible options for the removal of MC from natural waters, due to their low reactivity with these oxidants (Acero et al., 2005; Kull et al., 2004). ClO_2 as an oxidant in drinking water treatment will have only a small or negligible impact on dissolved microcystins if these toxins are present in the raw water (Kull et. al 2006).

C. Potassium Permanganate ($KMnO_4$) as Oxidant

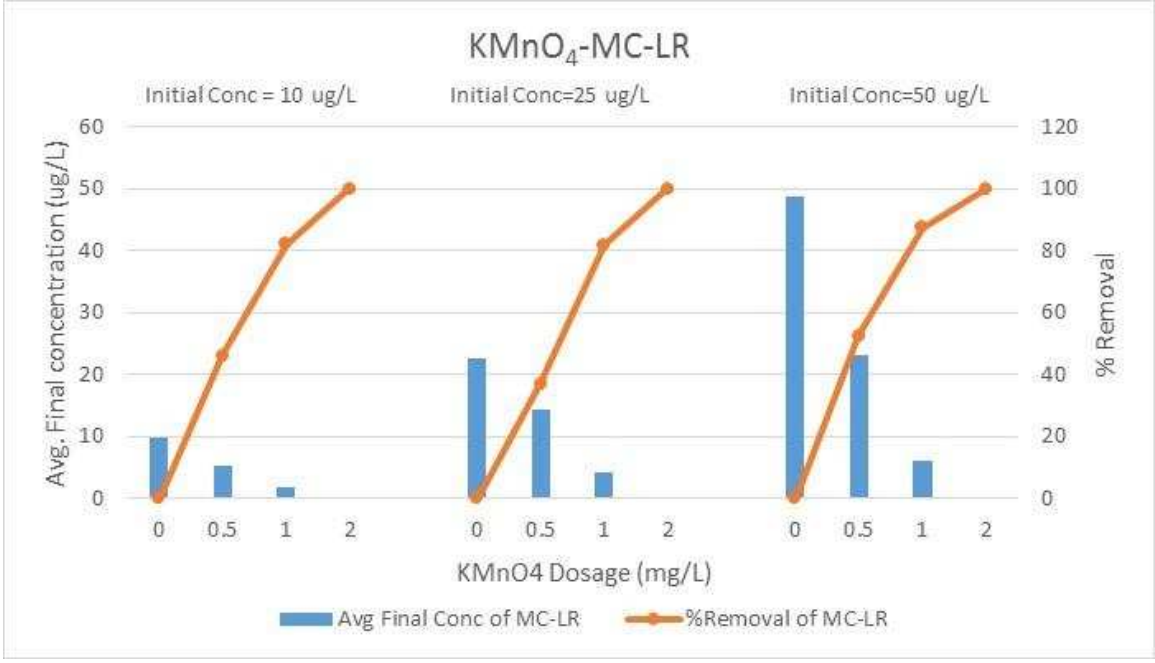


Figure 3-22: Interaction of MC-LR at different $KMnO_4$ dosages at different initial concentrations

Table 3-10: Average percent removal & Conc. of MC-LR as a function of $KMnO_4$ dosage

Initial Conc. of MC-LR	**$KMnO_4$ Dosage**	**Contact Time**	**Removal**	**Std. Deviation**
(ug/l)	**(mg/l)**	**(mins)**	**%**	
10	2	30	100.00	0.01
25			100.00	0.03
50			100.00	0.01

Rodriquez et. al (2007) state in his research that around 1–1.25 mg/L of permanganate was enough to reduce the concentration of MCs below the WHO guideline value of 1 µg/L in the experiments performed with surface water. Hall et al. (2000) reported that permanganate is a possible treatment for dissolved MC-LR in waters with low oxidant demand and must be applied before sedimentation/filtration of treatment train in order to control final manganese concentrations. However, the dose of permanganate must be controlled since the high doses might cause cell lysis and toxin release in raw water containing algal cells (Knappe et al., 2004; Pietsch et al., 2002).

D. Mixed Oxidant (MIOX) as Oxidant

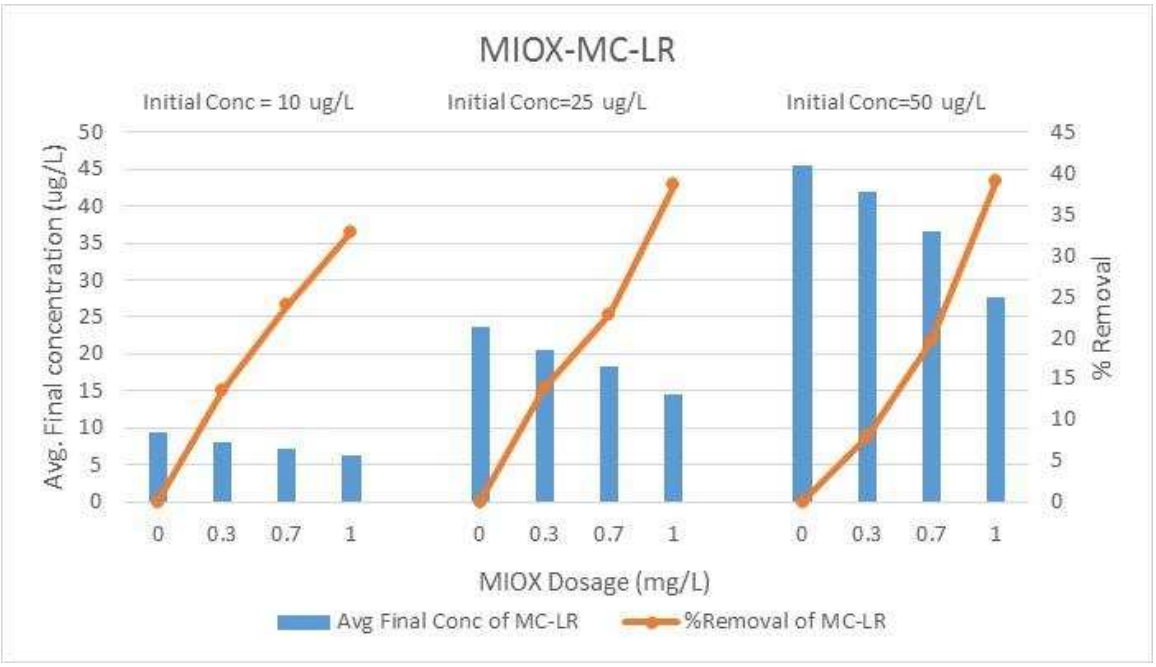


Figure 3-23: Interaction of MC-LR at different MIOX dosages at different initial concentrations

Table 3-11: Average percent removal & Conc. of MC-LR as a function of MIOX dosage

Initial Conc. of MC-LR	**MIOX Dosage**	**Contact Time**	**Removal**	**Std. Deviation**
(ug/l)	**(mg/l)**	**(mins)**	**%**	
10	2	30	32.81	7.45
25			38.56	7.5
50			39.09	3.21

MIOX can be used as pre-oxidant for removal of microcystin-LR as it is little effective for its removal. Further research needs to be carried out to see the reliability and other factors influencing the removal using MIOX as oxidant.

E. Ozone (O_3) as Oxidant

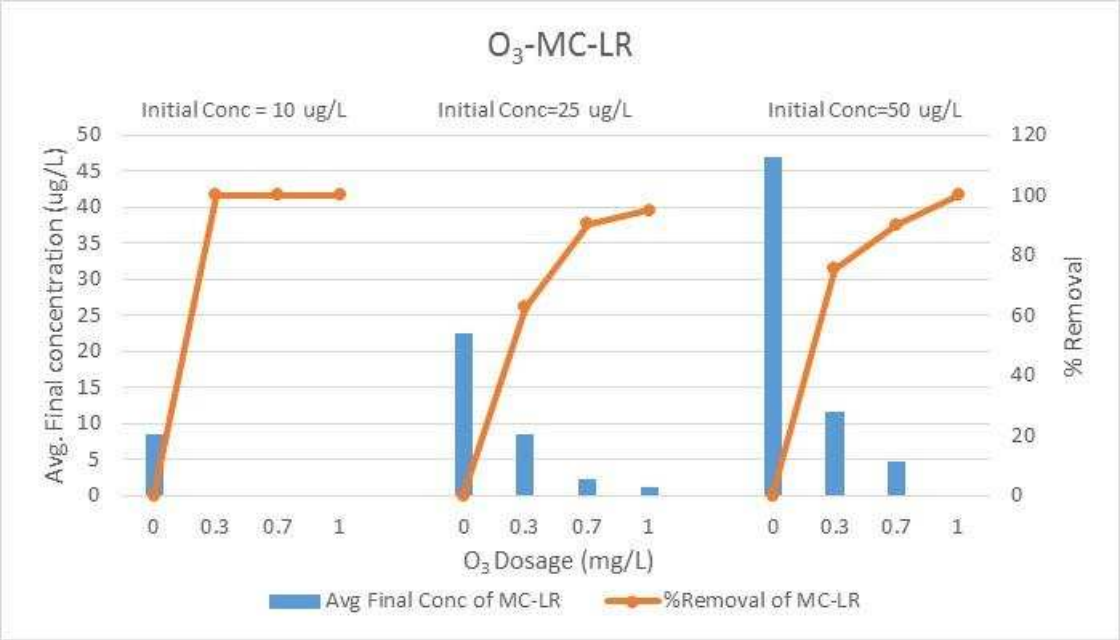


Figure 3-24: Interaction of MC-LR at different O_3 dosages at different initial concentrations

Table 3-12: Average percent removal & Conc. of MC-LR as a function of O_3 dosage

Initial Conc. of MC-LR	O_3 Dosage	Contact Time	Removal	Std. Deviation
(ug/l)	(mg/l)	(mins)	%	
10	1	10	100.00	0.13
25			94.98	2.88
50			100.00	0.01

Momani et. al (2008) and Rodriguez et. al (2007) stated that ozone was very efficient for any type of toxin degradation. Total toxin degradation was obtained by an ozone dosage of less

than 2 mg/L and a reaction time of 144s (Momani et. al 2010). The ozonation process led to the algae removal of 91.2% within 60 mins under the ozone dosage of 5 mg/l and the algae could not survive the dosage of 3 mg/l (Miao et al. 2004). Ozone has been very effective for taste and odor compounds and toxin removal as shown in many studies carried out by Momani et. Al (2010) and Rodriguez et al. (2007).

F. Chlorine (Cl_2) as Oxidant

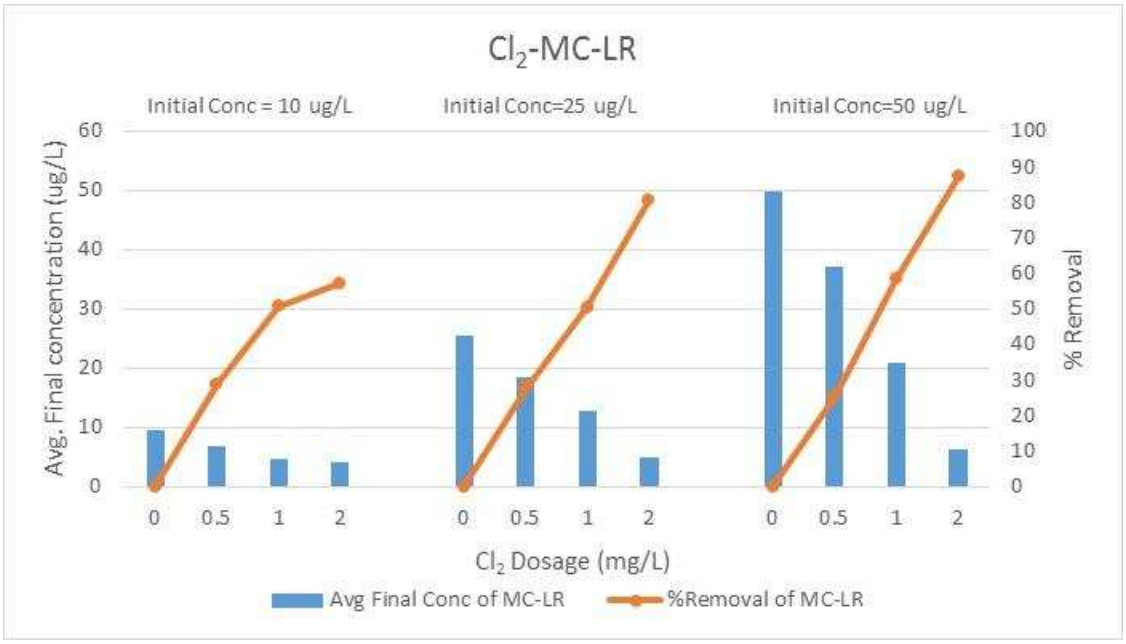


Figure 3-25: Interaction of MC-LR at different Cl_2 dosages at different initial concentrations

Table 3-13: Average percent removal & Conc. of MC-LR as a function of Cl_2 dosage

Initial Conc. of MC-LR	Cl_2 Dosage	Contact Time	Removal	Std. Deviation
(ug/l)	(mg/l)	(mins)	%	
10	0.5	30	57.26	23.73
25	1		80.58	10.45
50	2		87.28	0.69

Studies by Nicholson et al., (1994) indicate that chlorination was very effective at destroying microcystin-LR with free chlorine residual of 0.5 mg/L after 30 minutes contact time. Dissolved microcystin-LR in the range 5-10 μg/L, using a chlorine residual of 0.7 mg/L showed at pH 5, removal was more than 93 % within 30 minutes but at pH 7 removal reached only 88 per cent after 22 hours (Carlile, 1994), (Croll and Hart, 1996) (Hart et al., 1997). The results indicate that chlorine is quite effective though the removal rate of MC-LR doesn't fall below the WHO guidelines, it can be used as pre-oxidant but its dose needs to be monitored as seen in literature due to its harmful byproducts.

3.5 RESPONSE SURFACE METHODOLOGY (RSM) ANALYSIS USING DESIGN EXPERT®

Stat Ease® Design Expert® (version 10.0.2) was employed to create a model for the GSM, 2-MIB, and MC-LR removal and oxidant combinations for this study. For this study, a multifactor Response Surface Model (RSM) was utilized to determine the model or equation for obtaining the remaining conc. of the metabolite and thereby, optimize the dosage of oxidant. Unrealistic combinations suggested by the software were eliminated from the identified matrix. Two important parameters, initial concentration and oxidant dose, were considered for the model. The 54 data points obtained from the laboratory measurements for the twelve different combinations of the matrix at three doses of oxidant were entered into the software.

The data obtained from the experimental runs were used to create a model in Stat-Ease® Design Expert® (version 10.0.2) software to predict remaining GSM, 2-MIB, and MC-LR concentrations. The model predicted all the tested values within the measured GSM, 2-MIB, and MC-LR concentrations, mostly predicting a higher value for the GSM, 2-MIB, and MC-LR remaining. The results showed that Design Expert® underestimates the amount of toxin or T&O

compounds removed. This will give confidence to the water utilities in predicting their toxin removal and will account for any error in oxidant dosing, initial concentration, or contact time. Though, contact time has been kept constant for this bench scale study it will be considered depending on the site conditions and requirements. Linear, 2FI (2-factor interaction), and quadratic models were analyzed for all the analysis to predict the remaining MC-LR concentrations.

For RSM analysis carried out by Design Expert, the results of both T&O and toxin removal have been established only for those oxidants which could effectively remove the compounds. For the oxidants whose effective removal is low or moderate from the experimental analysis, only the equation from the model is generated so that the water treatment operators can use them if the oxidant is planned for use as a pre-oxidant for a cost effective and efficient removal method.

3.5.1 T&O ANALYSIS

From the experimental results, it is very much clear that PAC and Ozone were very effective in the removal of geosmin and 2-MIB and lowering their concentration below the odor thresholds i.e. 4 ng/L and 7 ng/L respectively.

Among the various models analyzed by the Design Expert, the Quadratic model had the best fit for the actual versus predicted data for both PAC and Ozone as it contained additional interaction terms in the equation obtained for prediction. A regression analysis by the Design Expert® (R^2=0.89 and R^2=0.96 respectively) showed that there was no significant difference between the measured and the predicted values.

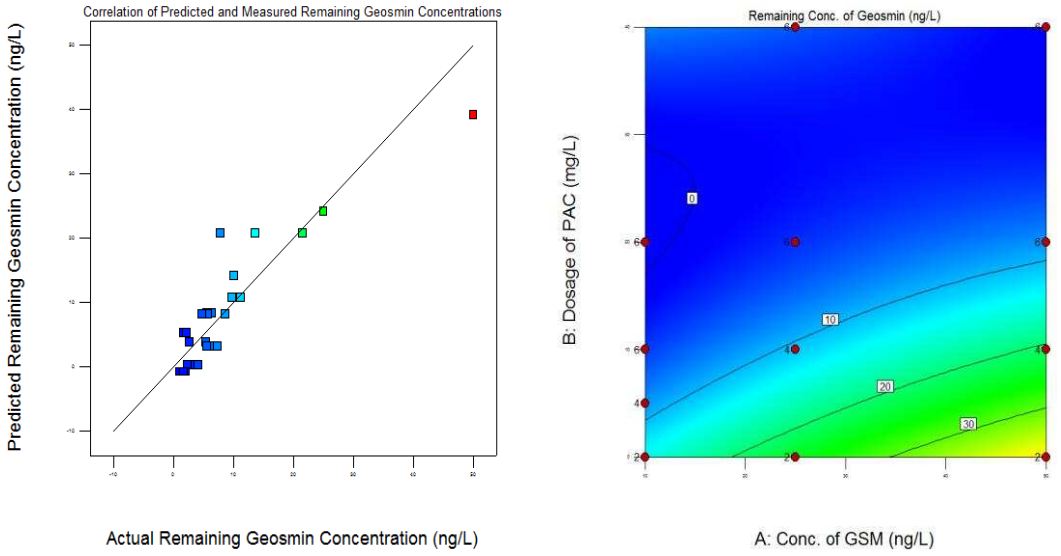


Figure 3-26: Graph of predicted and measured remaining conc. of GSM and the contour plots for PAC

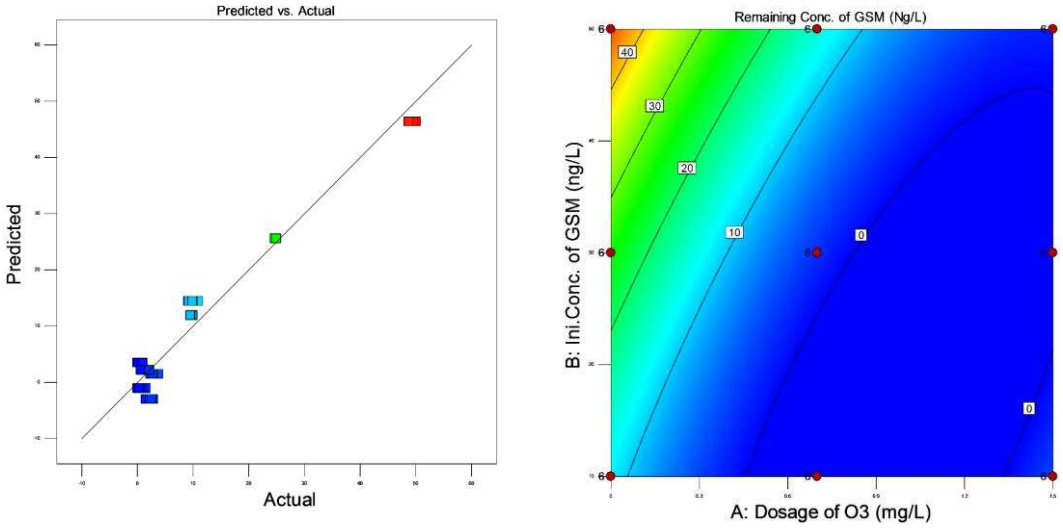


Figure 3-27: Graph of predicted and measured remaining conc. Of GSM and the contour plots for Ozone

A simple equation was obtained from the Design Expert® model for remaining geosmin concentration predictions using the initial geosmin concentration, PAC/Ozone dosage and keeping a constant contact time. The equation created by the quadratic model (that includes the interactions between the parameters) may guide the water utilities in quickly determining

PAC/Ozone dosages and contact times to best treat geosmin their source waters and is given below:

Remaining Concentration of Geosmin = + 7.21760
+ 0.71620 * Initial Conc. of GSM
-1.12298 * Dosage of PAC
- 0.019926 * Dosage of PAC* Initial Conc. of GSM
- 1.54757E-003 * (Initial Conc. of GSM)^2
+ 0.028710 * (Dosage of PAC)^2

Remaining Concentration of Geosmin = + 7.74338
+ 0.32762 * Initial Conc. of GSM
- 28.93243 * Dosage of O_3
- 0.60683 * Dosage of O_3* Initial Conc. of GSM
+ 8.881525E-003 * (Initial Conc. of GSM)^2
+ 19.58036* (Dosage of O_3)^2

As can be observed from the equation, dosage of PAC/Ozone and Initial conc. of geosmin are important parameters in predicting the remaining geosmin concentration. The above figures demonstrate how well the predicted and measured data correlate, as well as the contour plots to be used for prediction. The red data points indicate the measured values for the remaining geosmin concentrations

A simple equation was obtained from the Design Expert® model for remaining 2-MIB concentration predictions using the initial 2-MIB concentration, PAC dosage and keeping a constant contact time (for the values within: PAC concentrations of 5 to 40 mg/L, initial 2-MIB concentrations of 10 to 50 ng/L, and contact time of 30 minutes). The equation created by the quadratic model (that includes the interactions between the parameters) may guide the water

utilities in quickly determining PAC dosages and contact times to best treat MIB their source waters and is given below:

Remaining Concentration of MIB = -0.20732
+1.29035 * Initial Conc. of MIB
-0.59219 * Dosage of PAC
- 0.023795 * Dosage of PAC* Initial Conc. of MIB
- 7.41648E-003 * (Initial Conc. of MIB)^2
+ 0.018209 * (Dosage of PAC)^2

Remaining Conc. of MIB =
+5.02920
-14.30200 * Dosage of O3
+0.68272 * Ini.Conc. of MIB
-0.59947 * Dosage of O3 * Ini.Conc. of MIB
+10.54709 * Dosage of $O3^2$
+3.37037E-003 * Ini.Conc. of MIB^2

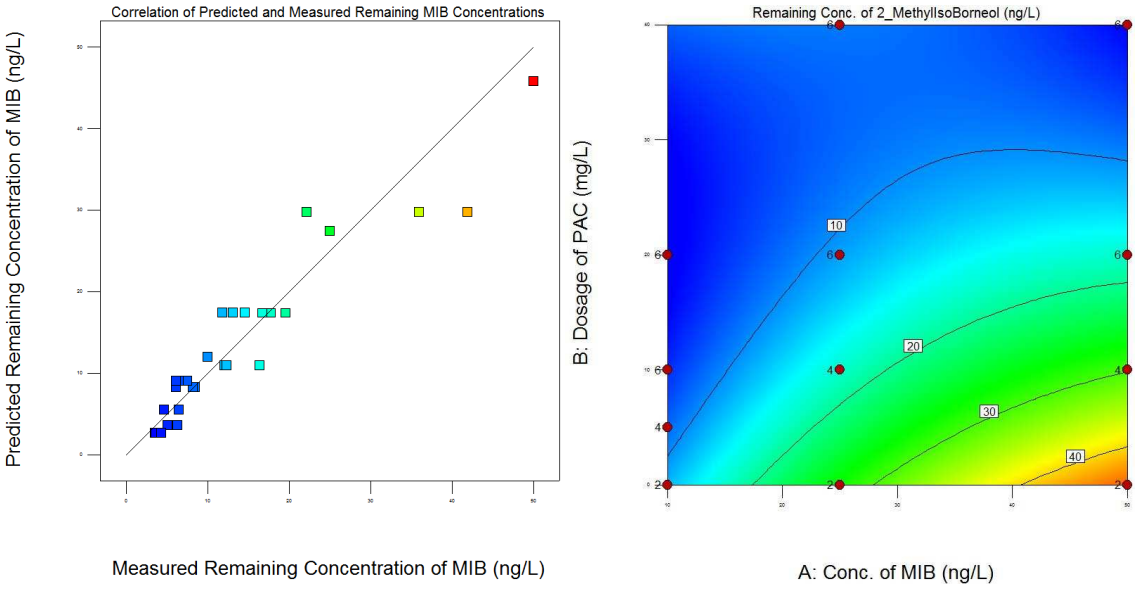


Figure 3-28: Graph of predicted and measured remaining conc. Of MIB and the contour plots for PAC

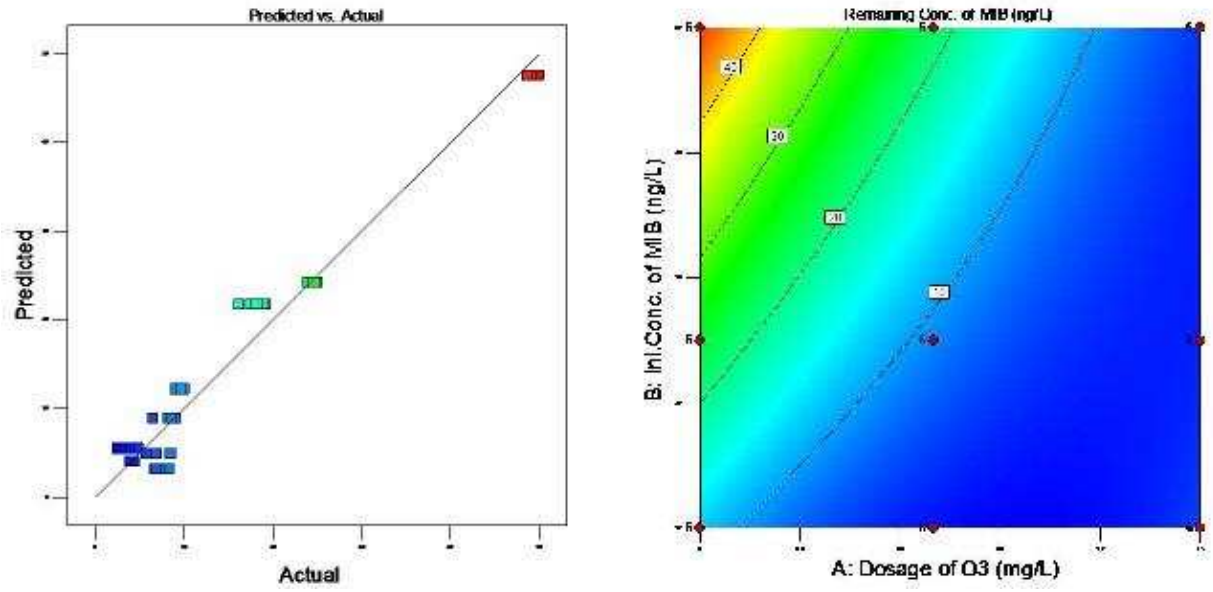


Figure 3-29: Graph of predicted and measured remaining conc. Of MIB and the contour plots for Ozone

As can be observed from the equation, dosage of PAC and Initial conc. of MIB are important parameters in predicting the remaining MIB concentration. The above figures demonstrate how well the predicted and measured data correlate, as well as the contour plots and 3-D plots to be used for prediction. The red data points indicate the measured values for the remaining MIB concentrations.

3.5.2 TOXIN ANALYSIS

From the experimental results, it is very much clear that PAC and Ozone were very effective in the removal of microcystin-LR and lowering its concentration below the WHO guidelines i.e. 1 ug/L. Among the various models analyzed by the Design Expert, the Quadratic model had the best fit for the actual versus predicted data for both $KMnO_4$ and ozone as it contained additional interaction terms in the equation obtained for prediction. The Quadratic model had the best fit for the actual versus predicted data as it contained additional interaction

terms in the equation obtained for prediction. A regression analysis by the Design Expert® (R^2=0.94 and R^2=0.92 respectively) showed that there was no significant difference between the measured and the predicted values. The equation created by the quadratic model (that includes the interactions between the parameters) may guide the water utilities in quickly determining PAC dosages and a contact time to best treat MC-LR from their source waters and is given below:

Remaining Concentration of MC-LR = + 8.25526
- 24.81417 * Dosage of $KMnO_4$
+ 0.77418 * Initial Conc. of MC-LR
- 0.40893* Dosage of $KMnO_4$* Initial Conc. of MC-LR
+10.83208 * (Dosage of $KMnO_4$)^2
-7.73519E-004 * (Initial Conc. of MC-LR)^2

Remaining Concentration of MC-LR = + 4.96721
- 44.42235 * Dosage of O_3
+ 0.79976 * Initial Conc. of MC-LR
- 0.76835* Dosage of O_3* Initial Conc. of MC-LR
+41.24184 * (Dosage of O_3)^2
-1.61537E-003 * (Initial Conc. of MC-LR)^2

As can be observed from the equation, dosage of $KMnO_4$/ Ozone and Initial conc. of MC-LR are important parameters in predicting the remaining MC-LR concentration. The below figures demonstrate how well the predicted and measured data correlate, as well as the contour to be used for prediction. The red data points indicate the measured values for the remaining MC-LR concentrations.

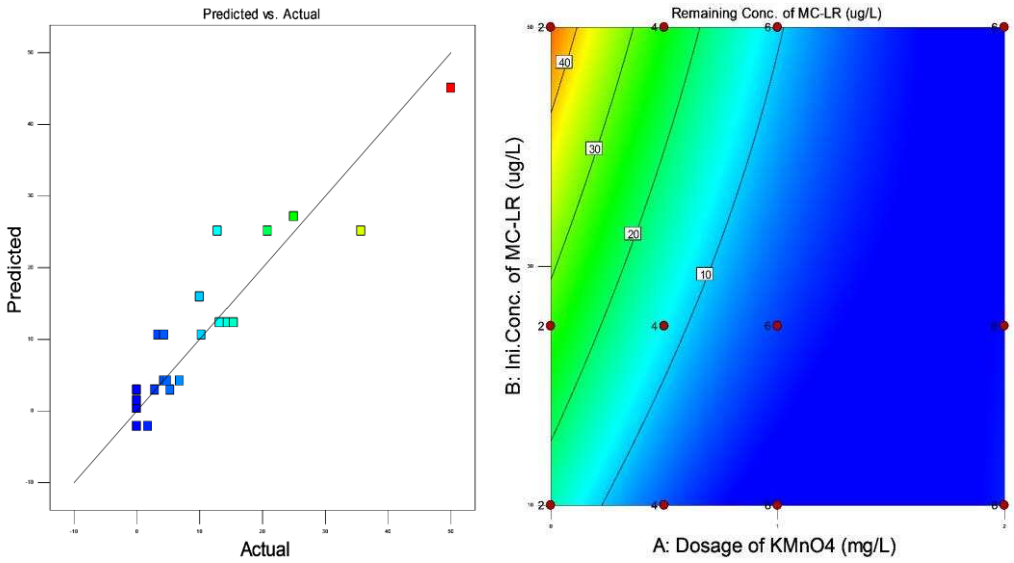


Figure 3-30: Graph of predicted and measured remaining conc. Of MC-LR and the contour plots for $KMnO_4$

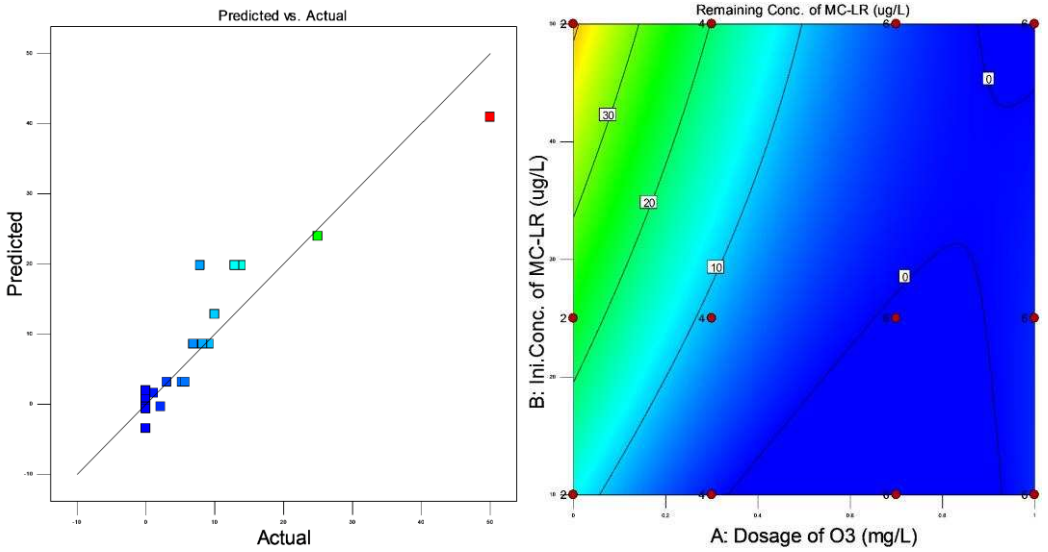


Figure 3-31: Graph of predicted and measured remaining conc. Of MC-LR and the contour plots for Ozone

For ClO_2, 2FI model had the best fit for the actual versus predicted data as it contained additional interaction terms in the equation obtained for prediction. A regression analysis by the

Design Expert® (R^2=0.97) showed that there was no significant difference between the measured and the predicted values.

Remaining Conc. of MC-LR =

-1.14301

+1.01502 * Conc. of MC-LR

+0.094372 * Dosage of ClO_2

-0.20606 * Conc. of MC-LR * Dosage of ClO_2

For MIOX, 2FI model had the best fit for the actual versus predicted data as it contained additional interaction terms in the equation obtained for prediction. A regression analysis by the Design Expert® (R^2=0.97) showed that there was no significant difference between the measured and the predicted values.

Remaining Conc. of MC-LR =

-0.73878

+1.00244 * Conc. of MC-LR

+1.45291 * Dosage of MIOX

-0.44434 * Conc. of MC-LR * Dosage of MIOX

For PAC, the quadratic model had the best fit for the actual versus predicted data as it contained additional interaction terms in the equation obtained for prediction A regression analysis by the Design Expert® (R^2=0.96) showed that there was no significant difference between the measured and the predicted values.

Remaining Concentration of MC-LR =

+ 3.45774

- 0.11680 * Dosage of PAC

+ 0.40312 * Initial Conc. of MC-LR

- 9.74001E-003 * Dosage of PAC* Initial Conc. of MC-LR

- 1.36453E-003 * (Dosage of PAC)^2

+ 0.010972 * (Initial Conc. of MC-LR)^2

3.6 CONCLUSIONS AND RECOMMENDATIONS

A summary of trends for removal of GSM, 2-MIB and MC-LR using various oxidants and adsorbent is shown in Figures 3-14 and 3-16 below. The dose of reactants (oxidants/adsorbent) are delineated as low, medium, and high based on the range studied.

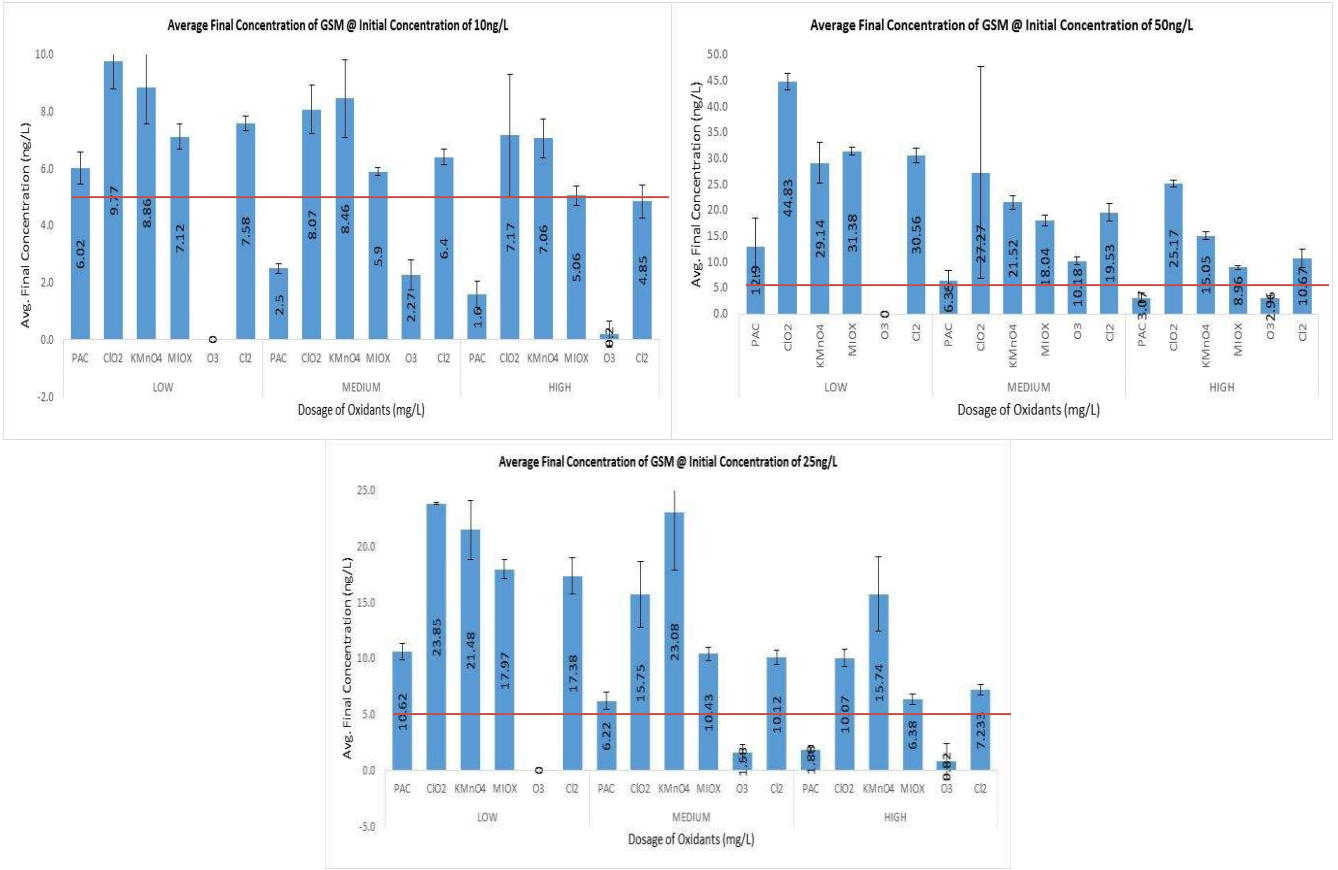


Figure 3-32: Average final concentration of GSM as a function of dosage of reactants

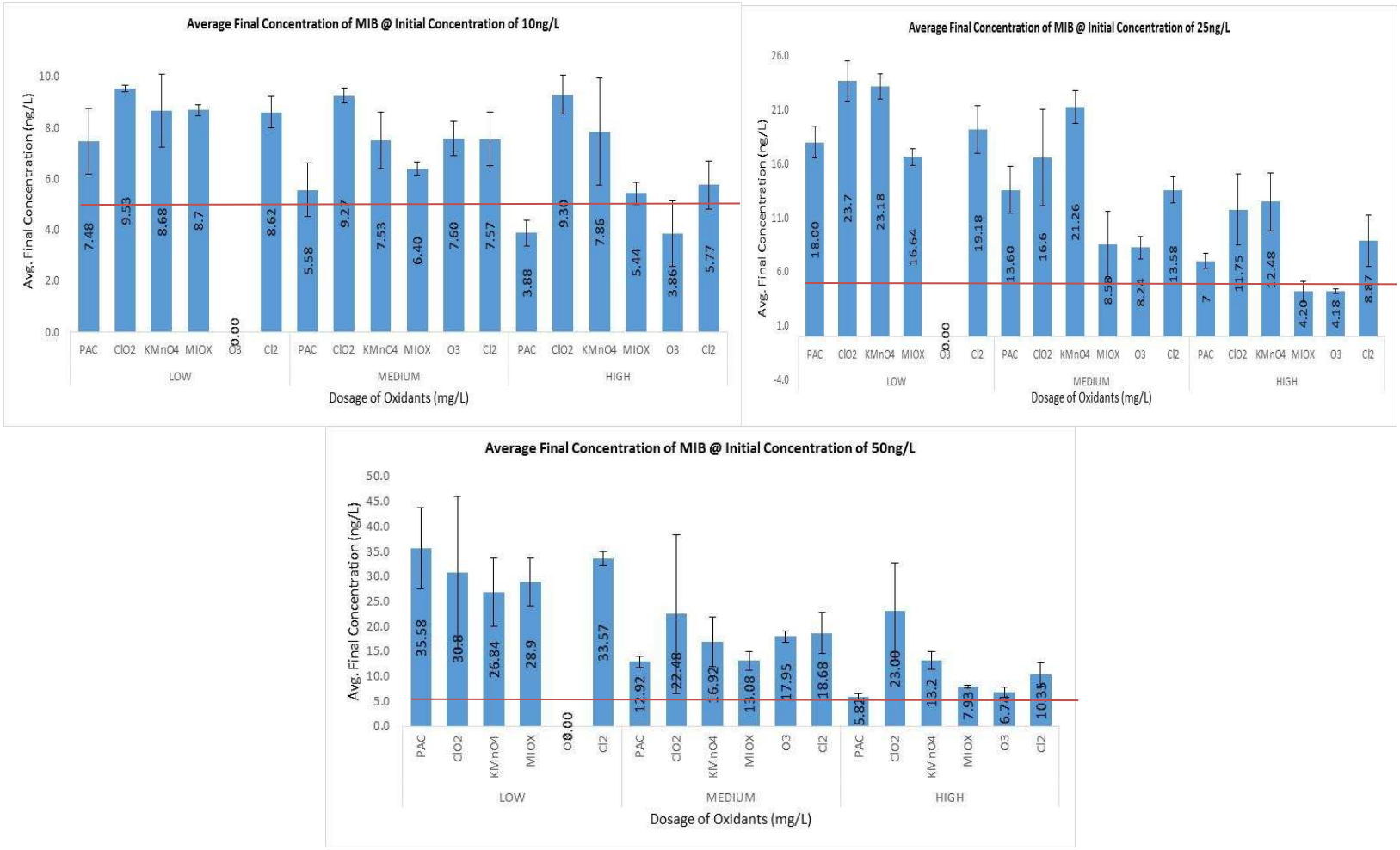


Figure 3-33: Average final concentration of MIB as a function of dosage of oxidants

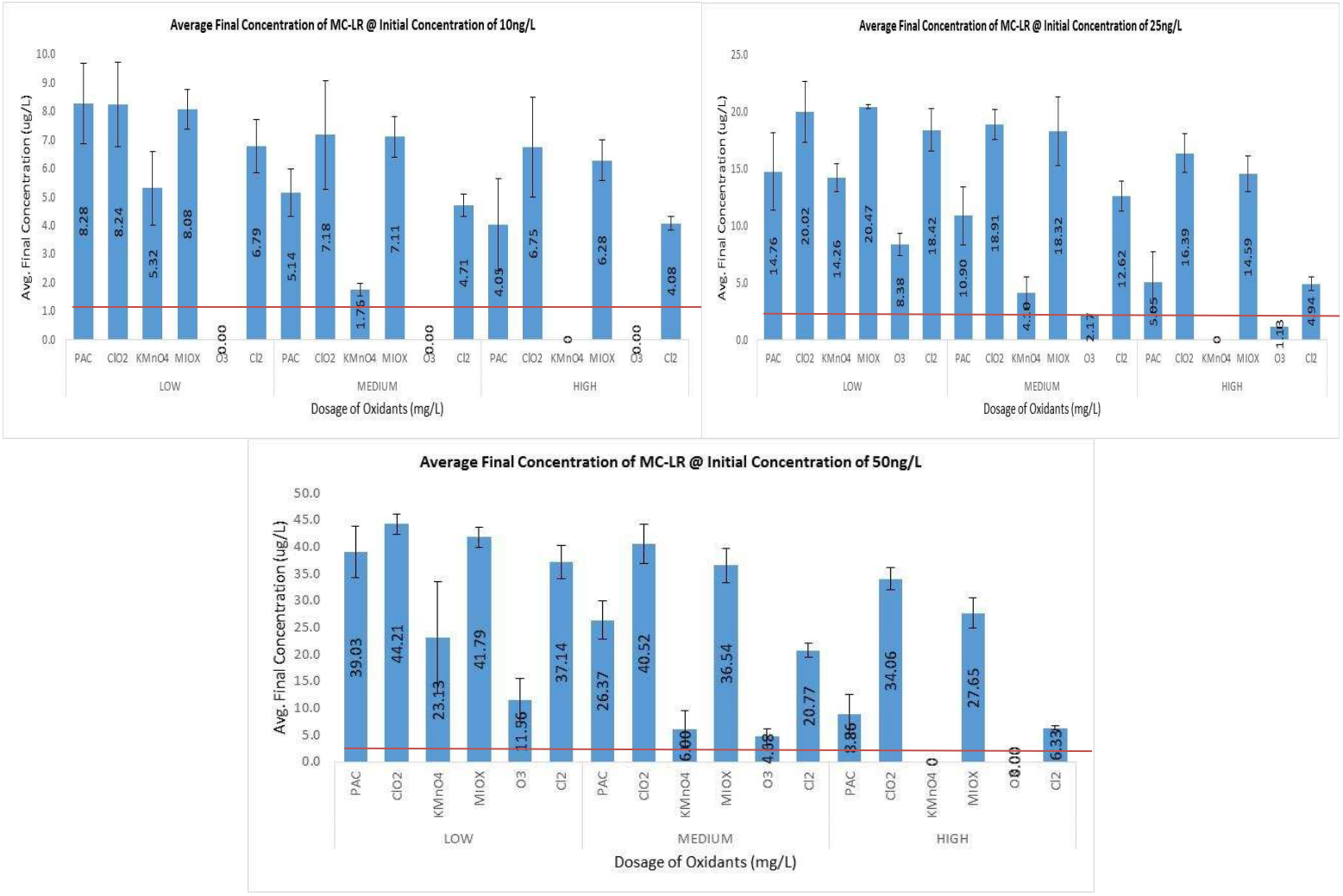


Figure 3-34: Average percent removal of MC-LR as a function of dosage of oxidants

The results from the bench scale study carried out show that ozone is the best oxidant for removal of taste, odor and toxin compounds in the event of occurrence for Denver Water. Powdered activated carbon (PAC) is also effective for removal at low and high concentrations of the T&O compounds and has the benefit of being able to be used for individual taste and odor events with minimal start-up time. Potassium Permanganate ($KMnO_4$) is also effective for removal of all concentrations of the toxin compounds and has the benefit of being able to be used for individual events with minimal start-up time.

Using ozone episodically may be difficult because bio-filtration is often desired after the oxidation to control by-products and this process requires a relatively long period of acclimation. The capital and operating costs associated with ozone are high so use of PAC for removal of G0SM and MIB is recommended, due to smaller footprint, cost effectiveness and the occurrence of taste and odor compounds being seasonal. The use of chlorine and $KMnO_4$ can be established based on the site conditions and requirements. They can be used a pre-oxidant, especially chlorine as it is available in most of the plants. MIOX can potentially become a good oxidant but lot of studies and research needs to be carried out. Training is essential for its effective use by operators.

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5 APPENDIX

5.1 Design Expert® INFORMATION

The various factors represented in a Central composite design model are explained as follows:

Replicates of factorial points: This is the number of times each factorial run will be performed. Replicating the factorial point improves the estimates of the model coefficients, but will increase the axial distance required to achieve the rotatable and orthogonal properties listed below.

Replicates of axial (star) points: This is the number of times each axial run will be performed. Replicating the axial points improves the estimates of the model coefficients, and will reduce the axial distance required to achieve the rotatable and orthogonal properties listed below.

Center points: This is the number of center points that will be in the design. The default is the minimum suggested number of center points. Reducing this number can severely impact the prediction precision of the interior of the experiment. Increasing the number of center points improves the prediction precision, while increasing the axial distance required toachieve the orthogonal quadratic property.

Alpha values: The distance from the center to place the axial runs in coded scale.

Rotatable (k<6): the default setting for up to 5 factors, this creates a design that has the standard error of predictions equal at points equidistant from the center of the design.

Orthogonal blocks: Only present when the CCD is built with blocks. The use of this axial setting causes any block effects to be estimated independently of model coefficients.

Spherical: This puts all factorial and axial points on the surface of a sphere of radius = square root of k (the number of factors)

Orthogonal Quadratic: The alpha distance where the quadratic terms are independently estimated from the other terms.

Practical (k>5): This is the default for designs that have 6 or more factors. The alpha value is the 4th root of the number of factors. This has been shown to produce axial values that can practically be run, and yet the design still has sound statistical properties.

Face Centered: Pull the axial points into the faces of the cube - at +/- 1 levels. This produces a design where each factor only has 3 levels. It is used when the area of interest is nearly as large as the area of operability.

Other: Specify any alpha value desired. We recommend you check Design Evaluation before completing the runs.

If the practical alpha is too large consider using "Other" with a value of no less than 1.5. This alpha distance will provide a more realistic range for the experiment than practical alpha while providing better estimating properties than a face centered alpha range.

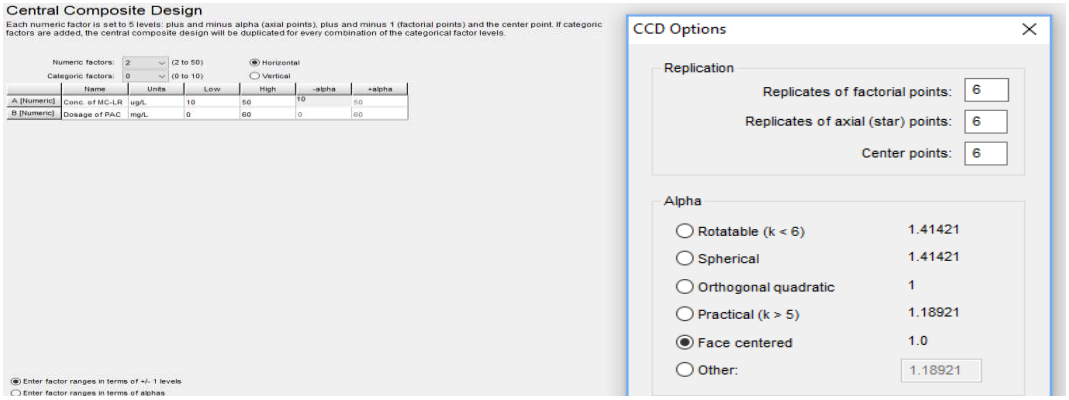

Figure 5-1: View if inputs in CCD model as seen in Design Expert

5.2 EXPERIMENTAL DATA

Table 5-1 Quality of Raw Water as received from Denver Water

Raw Water Data(n=3)				**Avg.**	**Std. Deviation**
pH	6.3	6.5	6.2	6.33	0.15
DOC (mg/L)	4.8	4.5	4.3	4.53	0.25
Conductivity (µs/cm)	146.4	144.5	147.6	146.17	1.56
Turbidity (NTU)	2.73	2.8	3.01	2.85	0.15
Dissolved Oxygen (mg/L)	5.6	5.1	5.5	5.40	0.26

5.2.1TASTE AND ODOR REMOVAL

A. Powdered Activated Carbon (PAC) as Adsorbent

Table 5-2: Results of PAC Analysis

Initial Conc. (ng/L)		**PAC Dosage (mg/L)**	**Contact Time (mins)**	**Trial-1 Final Conc. (ng/L)**		**Trial-2 Final Conc. (ng/L)**		**Trial-3 Final Conc. (ng/L)**		**Trial-4 Final Conc. (ng/L)**		**Avg. Final Conc. (ng/L)**		**%Removal**	
GSM	**MIB**			**GSM**	**MIB**	**GSM**	**MIB**	**GSM**	**MIB**	**GSM**	**MIB**	**GSM**	**MIB**	**GSM**	**MIB**
10	10	0	30	6.8	7.2	7.2	6.8	9.9	9.8	9.7	10.1	8.33	8.83	0	0
		5		5.2	6	6	6.2	6.1	8.3	6.7	8.7	6.02	7.48	27.80	15.32
		10		-	-	2.4	4.7	2.5	6.8	2.4	6.1	2.50	5.58	70.00	36.89
		20		1.7	3.8	1.8	3.5	1.2	4.7	0.9	3.9	1.60	3.88	80.80	56.08
25	25	0		19.2	21.2	20.5	22.5	24.9	24.7	-	-	22.77	23.13	0.00	0.00
		10		9.5	17.4	10.1	16	10.5	17.4	11.1	18.1	10.62	18.00	53.37	22.16
		20		6	11.9	6.5	12.3	5.4	12.4	5.8	12.2	6.22	13.60	72.68	41.19
		40		2.4	7.9	2	7.2	1.5	6.1	1.9	5.6.	1.88	7.00	91.76	69.73
50	50	0		42.3	43.8	43.3	44.5	49.8	50.2	49.2	49.9	46.80	47.48	0.00	0.00
		10		21.5	22.2	-	-	13.1	35.1	14.2	36.8	12.90	35.58	72.44	25.07
		20		9.2	13.4	8.2	12.9	5.4	12.1	5.9	11.6	6.35	12.92	86.43	72.79
		40		3.7	6.8	4.5	5.8	2.6	5.3	2.1	4.9	3.07	5.82	93.45	87.74

B.Chlorine Dioxide (ClO_2) as Oxidant

Table 5-3: Results of ClO_2 Analysis

Initial Conc. (ng/L)		ClO_2 Dose (mg/L)	Contact Time (mins)	Trial-1 Final Conc. (ng/L)		Trial-2 Final Conc. (ng/L)		Trial-3 Final Conc. (ng/L)		Avg. Final Conc. (ng/L)		% Removal	
GSM	MIB			GSM	MIB	GSM	MIB	GSM	MIB	GSM	MIB	GSM	MIB
10	10	0	30	9.9	10	9.6	9.7	10.1	9.8	9.85	9.78	0	0
		0.5		-	-	9.3	9.5	9.1	9.7	9.77	9.53	0.85	2.56
		0.9		7.1	9.6	8.7	9.2	-	-	8.07	9.27	18.10	5.20
		1.3		4.7	10.3	8.2	8.9	8.6	9.1	7.17	9.30	27.24	4.86
25	25	0		24.8	23.1	24.6	24.8	24.2	25.1	24.53	24.08	0.00	0.00
		0.5		23.8	19.8	-	-	23.9	22.4	23.85	23.70	2.79	1.56
		0.9		17.7	10.2	17.9	19.7	15.8	18.6	15.75	16.60	35.80	31.05
		1.3		9.3	5.9	-	-	10.9	-	10.07	11.75	58.97	51.19
50	50	0		48.9	43.6	49.5	49.9	50.1	48.9	49.50	47.17	0.00	0.00
		0.5		45.3	15.5	46.8	45.4	44.2	46.1	44.83	30.80	9.44	34.70
		0.9		43	7.8	34.6	37.1	-	-	27.27	22.48	44.92	52.35
		1.3		25.8	8	24.5	24.8	25.2	24.9	25.17	23.00	49.16	51.24

C.Potassium Permanganate ($KMnO_4$) as Oxidant

Table 5-4: Results of $KMnO_4$ Analysis

Initial Conc. (ng/L)		$KMnO_4$ Dosage (mg/L)	Contact Time (mins)	Trial-1 Final Conc. (ng/L)		Trial-2 Final Conc. (ng/L)		Trial-3 Final Conc. (ng/L)		Trial-4 Final Conc. (ng/L)		Trial-5 Final Conc. (ng/L)		Trial-6 Final Conc. (ng/L)		Avg. Final Conc. (ng/L)		%Removal	
GSM	MIB			GSM	MIB	GSM	MIB	GSM	MIB	GSM	MIB	GSM	MIB	GSM	MIB	GSM	MIB	GSM	MIB
10	10	0	30	9.9	9.8	9.7	10.2	8.1	8.5	7.1	7.6	9.5	10.2	-	-	9.02	9.26	0	0
		0.5		-	-	-	-	7.5	8.9	7.7	6.6	9.3	9.5	9.1	9.7	8.86	8.68	1.74	6.32
		1		10.2	7.2	9.9	8	8.4	5.6	6.7	6.4	7.9	8.1	7.6	8.4	8.46	7.53	6.17	18.74
		2		7.4	10	7.8	9.7	6	4.8	-	-	7.2	7.3	6.9	7.5	7.06	7.86	21.70	15.12
25	25	0		-	-	24.3	23.2	22.9	22.7	21.1	22.1	24.8	24.9	24.7	24.4	23.72	23.23	0.00	0.00
		0.5		-	-	-	-	19.9	22.5	18.6	-	23.5	22.9	23.9	22.4	21.48	23.18	9.45	0.22
		1		28.3	22.8	28.1	22.5	16	19	-	-	21.4	21.2	21.6	20.8	23.08	21.26	2.68	8.46
		2		17.4	10	17.9	9.4	-	-	9.9	13.1	16.4	15.2	17.1	14.7	15.74	12.48	33.63	46.26
50	50	0		49.9	42.9	49.6	42.5	45.4	44.2	43.5	45.3	49.4	50.1	49.5	49.8	47.48	45.80	0.00	0.00
		0.5		24.8	20.3	24.5	19.8	29.8	24.2	27.6	25.4	32.5	35.1	34.1	34.8	29.14	26.84	38.63	41.40
		1		23	11.7	22.8	11.8	19.7	13.7	20.5	14.4	21.2	22.4	21.9	22.3	21.52	16.92	54.68	63.06
		2		14.2	11.3	14.7	10.7	14.6	13.3	16.3	11.7	15.4	14.9	15.1	14.8	15.05	13.20	68.30	71.18

D.Mixed Oxidant (MIOX) as Oxidant

Table 5-5: Results of MIOX Analysis

Initial Conc. (ng/L)		MIOX Dosage (mg/L)	Contact Time (mins)	Trial-1 Final Conc. (ng/L)		Trial-2 Final Conc. (ng/L)		Trial-3 Final Conc. (ng/L)		Trial-4 Final Conc. (ng/L)		Trial-5 Final Conc. (ng/L)		Trial-6 Final Conc. (ng/L)		Avg. Final Conc. (ng/L)		Standard Deviation		%Removal	
GSM	MIB			GSM	MIB	GSM	MIB	GSM	MIB	GSM	MIB	GSM	MIB	GSM	MIB	GSM	MIB	GSM	MIB	GSM	MIB
10	10	0	30	7.9	8.1	7.3	7.8	9.5	10.2	9.8	-	9.9	9.8	9.7	10.1	9.02	8.98	1.12	1.16	0	0
		0.3		6.5	8.8	6.7	8.6	7.6	8.3	7.4	8.9	7.1	8.7	7.4	8.9	7.12	8.7	0.44	0.23	21.07	3.06
		0.7		-	-	5.9	6.5	6.1	6.8	-	6.2	5.8	6.7	6	6.3	5.9	6.4	0.13	0.25	34.57	28.69
		1		5.1	5.6	5.4	6.1	4.8	4.9	4.4	5	5.1	5.4	4.9	5.2	5.06	5.44	0.34	0.44	43.88	39.39
25	25	0		23.2	22.9	-	-	25	24.5	24.8	25.2	24.9	24.7	25.4	-	24.66	24.8	0.85	0.99	0	0
		0.3		18.1	15.4	18.7	16.3	17.1	17.4	16.7	17.2	18.4	-	18.8	16.9	17.97	16.64	0.87	0.81	27.14	32.9
		0.7		-	-	10.5	4.9	9.8	12.4	9.5	11.9	10.9	8.6	10.5	8.4	10.43	8.58	0.57	3.04	57.73	65.42
		1		6.3	4.4	6	3.8	6.9	5.9	7.1	5.4	6.1	3.9	5..8.	3.5	6.38	4.2	0.49	0.96	74.15	83.06
50	50	0		47.3	49	-	-	49.4	50.1	49.5	49.8	49.8	50.2	49.2	49.9	49.48	49.8	1	0.47	0	0
		0.3		-	-	30.5	23.6	32.5	35.1	32.1	34.6	31.5	28.7	31	28.2	31.38	28.9	0.81	4.82	36.58	41.97
		0.7		19.7	16.9	-	-	17.4	12.1	17.1	12.3	18.2	14.2	17.8	13.7	18.04	13.08	1.02	1.93	63.54	73.74
		1		-	-	9.5	8	9.1	8.4	8.9	8	8.8	7.6	8.5	7.7	8.96	7.93	0.37	0.31	81.89	84.09

E.Ozone (O_3) as Oxidant

Table 5-6: Results of O_3 Analysis

Initial Conc. (ng/L)		O_3 Dosage (mg/L)	Contact Time (mins)	Trial-1 Final Conc. (ng/L)		Trial-2 Final Conc. (ng/L)		Trial-3 Final Conc. (ng/L)		Trial-4 Final Conc. (ng/L)		Trial-5 Final Conc. (ng/L)		Trial-6 Final Conc. (ng/L)		Avg. Final Conc. (ng/L)		% Removal	
GSM	MIB			GSM	MIB	GSM	MIB	GSM	MIB	GSM	MIB	GSM	MIB	GSM	MIB	GSM	MIB	GSM	MIB
10	10	0	30	8.9	9.1	-	-	9.8	9.8	9.6	9.7	10.1	9.8	9.6	9.9	9.52	9.66	0	0
		0.7	15	1.5	8.3	2.4	8	1.8	6.9	2.4	6.7	2.9	8.1	2.6	7.6	2.27	7.60	76.18	21.33
		1.5	15	-	-	1	5.8	0	4.2	0	3.9	0	2.9	0	2.5	0.20	3.86	97.90	60.04
25	25	0	30	24.7	24.6	24.1	24	24.8	24.6	25	24.5	24.8	25.2	24.7	25	24.68	24.65	0.00	0.00
		0.7	15	0.7	6.5	-	-	2.1	8.6	2.2	8.2	1.8	9.1	2.1	8.8	1.58	8.24	93.59	66.57
		1.5	15	-	-	0.4	4.4	0	4.3	0	4	0	3.9	3.7	4.3	0.82	4.18	96.68	83.04
50	50	0	30	-	-	-	-	49.8	49.1	49.5	49.9	50.1	48.9	49.6	49.8	49.60	49.28	0.00	0.00
		0.7	15	9.1	17.5	9.9	16.2	10.1	18.2	9.2	17.7	10.8	19.2	11	18.9	10.18	17.95	79.48	63.58
		1.5	15	-	-	2.3	8.5	2.9	6.4	2.7	5.8	3.2	6.9	3.8	6.1	2.96	6.74	94.03	86.32

F.Chlorine (Cl_2) as Oxidant

Table 5-7: Results of Cl_2 Analysis

Initial Conc. (ng/L)		Cl_2 Dosage (mg/L)	Contact Time (mins)	Trial-1 Final Conc. (ng/L)		Trial-2 Final Conc. (ng/L)		Trial-3 Final Conc. (ng/L)		Trial-4 Final Conc. (ng/L)		Trial-5 Final Conc. (ng/L)		Trial-6 Final Conc. (ng/L)		Avg. Final Conc. (ng/L)		%Removal	
GSM	MIB			GSM	MIB	GSM	MIB	GSM	MIB	GSM	MIB	GSM	MIB	GSM	MIB	GSM	MIB	GSM	MIB
10	10	0	30	9.8	9.9	9.6	10.2	9.8	9.8	9.6	9.7	10.1	9.8	9.6	9.9	9.75	9.88	0	0
		0.5		7.4	8.2	7.5	8	7.9	8.1	7.3	8.8	-	9.1	7.8	9.5	7.58	8.62	22.26	12.82
		1		6.3	6.9	6.5	6.1	5.9	7.2	6.5	7.8	6.5	8.8	6.7	8.6	6.4	7.57	34.36	23.44
		2		4.5	4.9	3.9	4.5	5.4	6.1	4.8	5.6	5.1	6.6	5.4	6.9	4.85	5.77	50.26	41.65
25	25	0		24.6	24.8	24.2	24.1	24.7	24.3	24.8	24.6	25	24.5	24.8	25.2	24.68	24.58	0.00	0.00
		0.5		16.9	18.1	17.2	18	19.9	-	18.6	22.5	15.4	18.1	16.3	-	17.38	19.18	29.57	22.00
		1		9.7	-	9.2	13.1	10.5	14.7	11.1	15	10.3	12.2	9.9	12.9	10.12	13.58	59.01	44.76
		2		6.9	5.7	6.8	6.1	7.9	10	7.8	9.7	6.8	10.6	7.2	11.1	7.233	8.87	70.70	63.93
50	50	0		50.1	49.8	49.5	49.4	49.9	50	49.6	49.8	49.2	49.9	49.5	49.1	49.63	49.67	0.00	0.00
		0.5		31.7	34.9	32.3	34.6	30.2	33.8	29.7	34.2	-	32.5	28.9	31.4	30.56	33.57	38.43	32.42
		1		17.7	12.9	17.7	-	19.1	17.2	19.9	18	21.1	22.5	21.7	22.8	19.53	18.68	60.64	62.39
		2		8.8	8.1	8.2	7.8	11.1	9.4	11.2	11.1	12.9	13.1	11.8	12.6	10.67	10.35	78.51	79.16

5.2.2TOXIN REMOVAL

A.Powdered Activated Carbon (PAC) as Adsorbent

Table 5-8: Results of PAC Analysis

Initial Conc. of MC-LR	PAC Dosage	Contact Time	Remaining Concentration of MC-LR						Avg. Conc. Of MC-LR	Std. Dev	Removal
			Run 1.1	Run 1.2	Run 2.1	Run 2.2	Run 3.1	Run 3.2			
(ug/l)	(mg/l)	(mins)	(ug/l)	(ug/l)	(ug/l)	(ug/l)	(ug/l)	(ug/l)	(ug/l)		%
10	0	30	8.31	7.94	9.82	9.49	9.38	9.34	9.05	0.74	-
	5		6.56	6.42	8.94	9.44	9.3	9	8.28	1.40	8.5
	10		-	6.19	5.83	4.74	4.24	4.69	5.14	0.83	43.2
	20		5.83	5.52	5.17	2.64	2.59	2.53	4.05	1.61	55.27
25	0		14.52	16.64	23.33	23.7	25.4	24.04	21.27	4.51	-
	10		11.12	10.01	18.15	17.14	15.32	16.83	14.76	3.39	30.61
	20		8.4	7.04	12.62	12.4	12.96	11.96	10.9	2.52	48.77
	40		1.14	2.24	7.21	7.18	5.74	6.8	5.05	2.68	76.25
50	0		41.75	42.45	49.97	48.03	46.71	-	45.78	3.56	-
	20		41	30.18	40.55	40.38	44.07	37.98	39.03	4.75	14.75
	40		25.54	20.2	29.85	28.06	29.52	25.04	26.37	3.62	42.4
	60		15.74	10.27	6.63	7.57	6.44	6.5	8.86	3.67	80.65

B.Chlorine Dioxide (ClO_2) as Oxidant

Table 5-9: Results of ClO_2 Analysis

Initial Conc. of MC-LR	ClO_2 Dosage	Contact Time	Remaining Concentration of MC-LR						Avg. Conc. Of MC-LR	Std. Dev	Removal
			Run 1.1	Run 1.2	Run 2.1	Run 2.2	Run 3.1	Run 3.2			
(ug/l)	(mg/l)	(mins)	(ug/l)	(ug/l)	(ug/l)	(ug/l)	(ug/l)	(ug/l)	(ug/l)		%
10	0	30	7.77	6.75	10.12	9.82	9.38	9.5	8.89	1.33	-
	0.5		6.38	6.41	9.67	9.32	8.74	8.92	8.24	1.47	7.31
	1		4.6	4.96	7.68	8.96	8.42	8.47	7.18	1.91	19.22
	1.5		-	4.23	7.42	7.09	8.25	-	6.75	1.75	24.11
25	0		23.83	23.09	24.55	25.39	24.12	-	24.2	0.85	-
	0.5		16.88	16.87	23.03	22.12	21.71	19.53	20.02	2.70	17.24
	1		16.95	-	20.51	18.82	19.29	18.97	18.91	1.28	21.85
	1.5		14.2	15.42	18.62	17.74	17.18	15.2	16.39	1.71	32.24
50	0		46.95	-	48.55	46.44	-	47.39	47.33	0.90	-
	0.5		44.28	43.27	46.22	46.02	44.1	41.36	44.21	1.81	6.6
	1		37.05	39.96	45.14	44.85	38.35	37.76	40.52	3.60	14.4
	1.5		30.49	32.74	34.84	35.69	35.69	34.9	34.06	2.05	28.05

C.Potassium Permanganate ($KMnO_4$) as Oxidant

Table 5-10: Results of $KMnO_4$ Analysis

Initial Conc. of MC-LR	$KMnO_4$ Dosage	Contact Time	Remaining Concentration of MC-LR						Avg. Conc. Of MC-LR	Std. Dev	Removal
			Run 1.1	Run 1.2	Run 2.1	Run 2.2	Run 3.1	Run 3.2			
(ug/l)	(mg/l)	(mins)	(ug/l)	(ug/l)	(ug/l)	(ug/l)	(ug/l)	(ug/l)	(ug/l)		%
10	0	30	10.19	9.51	9.63	10.01	9.96	10.1	9.9	0.27	0
	0.5		4.4	4.22	4.66	4.96	6.09	7.57	5.32	1.29	46.29
	1		BQL	BQL	1.91	1.6	BQL	BQL	1.76	0.91	82.24
	2		BQL	BQL	BQL	BQL	BQL	BQL	0	0.00	100
25	0		23.96	25.11	19.63	18.32	24.94	24.29	22.71	2.95	0
	0.5		15.14	13.18	14.8	16.08	13.15	13.2	14.26	1.26	37.22
	1		BQL	BQL	2.97	2.8	5.46	5.17	4.1	2.38	81.96
	2		BQL	BQL	BQL	BQL	BQL	BQL	0	0.00	100
50	0		47.67	49.39	50.03	45.62	49.19	50.23	48.69	1.75	0
	0.5		20.49	21.17	35.46	35.95	12.81	12.92	23.13	10.37	52.49
	1		5.49	3.17	10.86	9.7	3.48	3.31	6	3.44	87.67
	2		BQL	BQL	BQL	BQL	BQL	BQL	0	0.00	100

D.Mixed Oxidant (MIOX) as Oxidant

Table 5-11: Results of MIOX Analysis

Initial Conc. of MC-LR	MIOX Dosage	Contact Time	Remaining Concentration of MC-LR						Avg. Conc. Of MC-LR	Std. Dev	Removal
			Run 1.1	Run 1.2	Run 2.1	Run 2.2	Run 3.1	Run 3.2			
(ug/l)	(mg/l)	(mins)	(ug/l)	(ug/l)	(ug/l)	(ug/l)	(ug/l)	(ug/l)	(ug/l)		%
10	0	30	9.04	9.09	9.82	9.49	9.38	9.3	9.35	0.29	0
	0.3		8.41	8.8	6.95	7.96	8.66	7.68	8.08	0.69	13.62
	0.7		6.53	6.25	7.05	6.94	8.06	7.82	7.11	0.71	23.99
	1		6.1	6.23	6.12	7.35	6.72	5.2	6.28	0.72	32.81
25	0		24.04	25.88	23.96	23.33	23.7	21.6	23.75	1.38	0
	0.3		20.57	-	20.64	20.31	20.56	20.29	20.47	0.16	13.8
	0.7		16.23	15.17	23.07	16.82	17.99	20.61	18.32	2.98	22.88
	1		12.87	13.58	15.26	14.87	17.19	13.78	14.59	1.54	38.56
50	0		43.54	45.1	49.97	48.03	42.18	43.53	45.39	3.01	0
	0.3		39.51	41.03	44.15	43.84	41.66	40.57	41.79	1.85	7.93
	0.7		35.41	34.56	42.46	38.06	34.7	34.02	36.54	3.23	19.51
	1		28.24	26.34	30.84	30.84	24.55	25.08	27.65	2.78	39.09

E.Ozone (O_3) as Oxidant

Table 5-12: Results of O_3 Analysis

Initial Conc. of MC-LR	O_3 Dosage	Contact Time	Remaining Concentration of MC-LR						Avg. Conc. Of MC-LR	Std. Dev	Removal
			Run 1.1	Run 1.2	Run 2.1	Run 2.2	Run 3.1	Run 3.2			
(ug/l)	(mg/l)	(mins)	(ug/l)	(ug/l)	(ug/l)	(ug/l)	(ug/l)	(ug/l)	(ug/l)		%
10	0	10	6.56	6.45	9.82	9.49	9.5	9.3	8.52	1.57	0
	0.3		BQL	BQL	BQL	BQL	BQL	BQL	0	0.00	100
	0.7		BQL	BQL	BQL	BQL	BQL	BQL	0	0.00	100
	1		BQL	BQL	BQL	BQL	BQL	BQL	0	0.00	100
25	0		18.85	20.15	24.04	23.96	23.09	24.36	22.41	2.33	0
	0.3		-	6.91	9.37	9.05	8.16	8.4	8.38	0.95	62.6
	0.7		2.21	2.13	BQL	BQL	BQL	BQL	2.17	1.12	90.32
	1		1.12	1.13	BQL	BQL	BQL	BQL	1.13	0.58	94.98
50	0		42.64	43	50.54	49.25	-	49.64	47.01	3.86	0
	0.3		3.51	12.3	13.27	14.46	12.14	13.7	11.56	4.04	75.41
	0.7		1.87	4.23	5.79	5.65	4.77	5.76	4.68	1.51	90.05
	1		BQL	BQL	BQL	BQL	BQL	BQL	0	0.00	100

F.Chlorine (Cl_2) as Oxidant

Table 5-13: Results of Cl_2 Analysis

Initial Conc. of MC-LR	Cl_2 Dosage	Contact Time	Remaining Concentration of MC-LR						Avg. Conc. Of MC-LR	Std. Dev	Removal
			Run 1.1	Run 1.2	Run 2.1	Run 2.2	Run 3.1	Run 3.2			
(ug/l)	(mg/l)	(mins)	(ug/l)	(ug/l)	(ug/l)	(ug/l)	(ug/l)	(ug/l)	(ug/l)		%
10	0	30	9.89	9.51	9.46	10.42	8.43	-	9.54	0.73	-
	0.5		6.82	7.11	7.67	7.79	5.87	5.49	6.79	0.94	28.82
	1		4.4	4.22	4.56	5	5.27	4.83	4.71	0.39	50.6
	2		0	0	4.02	4.43	3.9	3.96	4.08	2.11	57.26
25	0		24.6	25.51	25.42	26.14	-	25.45	25.42	0.55	-
	0.5		15.97	17.09	18.86	-	19.59	20.57	18.42	1.87	27.56
	1		13.75	13.56	13.05	13.44	10.69	11.24	12.62	1.32	50.36
	2		0	0	4.09	5.09	5.14	5.43	4.94	2.59	80.58
50	0		49.61	51.2	49.24	-	49.65	49.32	49.8	0.80	-
	0.5		37.82	39.87	36.11	31.86	40.64	36.55	37.14	3.14	25.42
	1		21.21	20.99	22.11	20.29	18.5	21.51	20.77	1.26	58.3
	2		5.8	6.1	6.54	7.02	6.47	6.08	6.33	0.43	87.28