

57 (2016) 14355–14363 July



Comparing potassium permanganate, chlorine dioxide, and chlorine oxidation for manganese control of a volcanic island surface water treated with a conventional coagulation, sedimentation, and filtration process

Christine Hall, Erica R. LaBerge, Steven J. Duranceau*

Department of Civil, Environmental and Construction Engineering, University of Central Florida, Orlando, FL 32816-2450, USA, Tel. +1 407 823 1440; Fax: +1 407 823 3315; email: steven.duranceau@ucf.edu (S.J. Duranceau)

Received 30 December 2015; Accepted 7 February 2016

ABSTRACT

A comparison of the effectiveness of potassium permanganate (KMnO₄), chlorine dioxide (ClO₂), and chlorine (Cl₂) oxidation pretreatment for manganese (Mn) control from a surface water reservoir on the volcanic island of Guam has been completed. Source water dissolved Mn content was determined to be 7.34 μ g/L at a reservoir intake depth of 10 ft, 9.85 μ g/L at a depth of 20 ft, 41.6 μ g/L at a depth of 30 ft, and 775 μ g/L at a 40 foot depth. For the intake depth of 10 ft, it was found that a ClO₂ dose of 1.1 mg/L reduced Mn by an average of 98.7%, as compared to an average of 95.9% using a KMnO₄ dosage of 1.75 mg/L. Cl₂ was found not to reduce dissolved Mn to any extent at dosages of 1.25 mg/L. It was determined that pink water formation occurred with less than 0.5 mg/L of a permanganate overdose. Additionally, a 1.1 mg/L ClO₂ dose produced an average chlorite and chlorate by-product concentration of 780–1,080 μ g/L, respectively. Results demonstrated that ClO₂ would be the preferred oxidant for Mn control as compared to KMnO₄ or Cl₂ for the volcanic water supply evaluated in this study. The research also verified that a 0.10-micron filter produced more accurate dissolved Mn results than the standard method use of 0.45-micron filter in laboratory procedures.

Keywords: Oxidation; Manganese; Chlorine; Chlorine dioxide; Potassium permanganate; Surface water

1. Introduction

1.1. Chemical considerations

Manganese (Mn) is regulated in drinking water at a 50 μ g/L (0.05 mg/L) secondary maximum contaminant level, a standard established to address issues of aesthetics (discoloration) and not for health concerns at the levels normally encountered in drinking water.

Potassium permanganate (KMnO₄), chlorine dioxide (ClO₂), chlorine (Cl₂), ozone (O₃), and oxygen (O₂), have been used with varying degrees of success, to control Mn in water treatment plants. Unlike Cl₂, KMnO₄, and ClO₂ treatment minimizes the formation of total trihalomethanes (TTHMs) and haloacetic acids (HAAs) by oxidizing precursors and reducing the demand for other disinfectants [1,2]. Although KMnO₄ and O₂ have many potential uses as oxidants, they are not effective as disinfectants, whereas ClO₂, Cl₂, and O₃ are effective disinfectants [3].

^{*}Corresponding author.

^{1944-3994/1944-3986 © 2016} Balaban Desalination Publications. All rights reserved.

Oxidant	Reaction	Stoichiometry
Oxygen (O ₂)	$Mn^{2+} + \frac{1}{2}O_{2(aa)} + H_2O \rightarrow MnO_{2(s)} + 2H^+$	0.29 mg O ₂ /mg Mn
Ozone (O ₃)	$Mn^{2+} + O_{3(aq)} + 2H_2O \rightarrow MnO_{2(s)} + O_2 + 2H^+$	$0.88 \text{ mg O}_3/\text{mg Mn}$
Chlorine (Cl ₂)	$Mn^{2+} + Cl_{2(ag)} + H_2O \rightarrow MnO_{2(s)} + 2Cl^- + 4H^+$	$1.30 \text{ mg Cl}_2/\text{mg Mn}$
Chlorine dioxide (ClO ₂)	$Mn^{2+} + 2ClO_{2(aq)} + 2H_2O \rightarrow MnO_{2(s)} + 2ClO_2^- + 4H^+$	$2.45 \text{ mg ClO}_2/\text{mg Mn}$
Potassium permanganate (KMnO ₄)	$3Mn^{2+} + 2MnO_{4(aq)}^{-} + 2H_2O \rightarrow 5MnO_{2(s)} + 4\tilde{H}^+$	1.92 mg KMnO ₄ /mg Mn

Table 1 Reactions of Mn(II) with alternative oxidants and theoretical reaction stoichiometry

When an oxidant is added to water containing Mn, soluble Mn will oxidize to particulate Mn dioxide. In conventional treatment plants, the oxidant is typically added to the raw water at the intake, prior to the coagulation process. In some instances $KMnO_4$ is added at clarifiers, upstream of filters. This is due to the fact that the Mn dioxide that is formed from oxidation is small enough to pass through conventional filters. Therefore, it is often recommended to add the $KMnO_4$, ClO_2 or O_3 upstream of the coagulant addition point. This is because of the coagulants' ability to destabilize the particles and allow for the coagulation process to effectively enhance filtration of the insoluble particulate Mn dioxide [4].

The theoretical reactions and associated stoichiometry for oxygen, Cl_2 , ClO_2 and $KMnO_4$ reacting with Mn are shown in Table 1. Based on the stoichiometry, the O_2 , Cl_2 , ClO_2 , and $KMnO_4$ dose required for oxidation is 0.29, 1.30, 2.45, and 1.92 mg/mg of Mn, respectively [5]. When $KMnO_4$ is added to oxidize Mn, the oxidation duration ranges from 5 to 10 min, provided the pH is greater than seven pH units [6].

1.2. Oxidant selection considerations

Though Cl₂ can be used to control Mn, it reacts so slowly that dissolved Mn may pass through conventional treatment and enter the water distribution system after 24 h, unless the pH is greater than nine pH units [7]. Despite this fact, Cl_2 is often used because it can provide residual disinfection and offer oxidative properties. O2 oxidation, like Cl2 oxidation, is extremely slow and requires significant contact time and is no longer discussed herein. O3, ClO2 and permanganate reacts rapidly with Mn, oxidizing it to Mn dioxide. Above pH 7, reaction kinetics are more favorable for oxidation to occur. However, it is noted that if excess KMnO₄ is added, or if O₃ is not properly dosed, the finished water can turn pink in color [6–8]. It is also noted that although O₃ is effective if demand substances are not present, this oxidant requires a greater amount of energy and more sophisticated dosing equipment than other chemical feed methods; for this reason O_3 is not typically used solely for Mn control, especially where electrical costs are elevated. Because dissolved Mn does not complex with humic and fulvic acids, the presence of DBP precursors does not significantly slow the rate of Mn(II) oxidation by KMnO₄ or ClO₂ [9,10]. Therefore, pretreatment with KMnO₄ or ClO₂ would offer an alternative since these chemicals have not been shown to produce TTHMs and HAAs [11]. Under this approach, not only are iron and Mn oxidized, but the concentration of DBP precursors may also be reduced.

1.3. Motivation for the study

For the reasons aforementioned, ClO₂ and permanganate were selected for use as a pretreatment method for Mn prior to conventional surface water treatment. The research was conducted to evaluate options for surface water that supplies the US Navy's Public Water System (PWS) located on the island of Guam in the Marianas Islands. The PWS draws its source water from the US Navy's Reservoir referred to as Fena Lake, as well as the Bona and Almagosa springs. The Fena Lake reservoir is a protected watershed as it is completely contained within the Naval Magazine, a controlled military compound, and serves as the primary source water for the PWS. Raw water is drawn from a constructed screen house complex located at Fena Lake that allows supply water to be extracted at depths that range from approximately 10-50 foot (ft); water is typically drawn at a 12 ft depth.

Raw water from the reservoir is pumped to the US Navy's conventional surface water treatment plant (WTP) where the surface supply is blended with the Almagosa Spring and Bona Spring supplies. The blended supply is then treated with alum coagulant aided by lime and polymer addition, and flocculated prior to undergoing sedimentation, filtration, and disinfection with free Cl₂. The treated water is then fluoridated and stored prior to being distributed to consumers. Under normal conditions, the raw water is routed to the conventional WTP; however, when turbidity levels are elevated, the raw water may be

routed to an integrated ballasted flocculation system designed to manage extreme turbidity events that occur in tropical environments.

Cl₂ had historically been the preferred chemical added at the Fena Lake pump station for iron and Mn oxidation prior to transport to the WTP blend chamber and rapid mix location. This practice at the time had been used as it was simple and effective. It was reasoned at the time that because the pH of Fena Lake averaged approximately 7.0 pH units when treated with Cl₂, and given the slow Mn oxidation reaction kinetics and other competing Cl₂ demands, the actual time required for Cl₂ contact could be exerted in the transmission line between Fena Lake and the WTP. Although the PWS saw complete control of iron that originated from Fena Lake or the springs, dissolved Mn would be intermittently detected in the distribution system. A complicating factor to the use of Cl₂ was the promulgation of the Stage two Disinfectant/ Disinfection By-Products Rules (DBPR) by the US Environmental Protection Agency, as the DBPR was found to cause conflict with the traditional chlorination practices conducted at Fena Lake. Because the PWS recognized that the Cl₂ dose required to promote soluble Mn oxidation was higher than the theoretical stoichiometry due to demand, and because variations in source supply pH and temperature impacted chlorination demands (that in turn impacted the formation of newly regulated DBPs), the PWS eliminated pre-chlorination at Fena Lake and this study was initiated [12].

1.4. Focus of the study

Although much effort has been expended on the study of Mn removal from surface and groundwater [10,11,13–19], less research has been published where comparisons between Cl₂, ClO₂, and KMnO₄ for treatment of volcanic surface water supplies has been published. Research by Roccaro and coworkers [15] reported on the use of KMnO4 for iron removal for Volcano Etna groundwater supplies in Sicily, Italy. It was determined that Volcano Etna groundwater, containing Mn as high as $1,810 \mu g/L$, could be reduced to less than 50 μ g/L by treatment with 0.5 stoichiometric dose of KMnO₄ followed by the addition of polyelectrolytes at pH 8.5 prior to flocculation, settling, and filtration. However, information regarding the use of alternative oxidants for Mn control in volcanic island surface water supplies is not generally available and has not been widely reported in the literature. As a result, the research reported herein provides information regarding an evaluation of three chemical oxidants (Cl₂, ClO₂, and KMnO₄) for Mn control at Fena Lake, located on the volcanic island of Guam.

2. Methods and materials

Analytical evaluations were performed at two primary locations: (1) at the PWS laboratory facilities operated and managed by the US Navy's contracted laboratory (referred to as DZSP21), located at the WTP

Summary of analytical testing methods used for characterization of water samples

Test	Method reference number (standard method) and/or instrument	Method reporting level (MRL) or reporting range
Manganese (total and dissolved)	SM 3120 B-inductively coupled plasma	2 μg/L
Turbidity	EPA 180.1	0.05 NTU
Total organic carbon	SM 5310C or EPA 415.1	0.25 mg/L
Dissolved organic carbon	SM 5310C	0.5 mg/L
UV-254	SM 5910B	0.03 cm^{-1}
Chlorine, total, and free	SM 4500-Cl G DPD; Pocket Colorimeter II	0.10 mg/L
рН	SM: 4500-H+ B. electrometric method/HQ40d portable ph, conductivity and temperature meter	2–14 pH range
Chlorine, free and total	Hach pocket colorimeter II	0.02–2.0 mg/L Cl_2 for free chlorine;
		0.1–8.0 mg/L Cl ₂ total chlorine
Conductivity	SM: 2510 B. laboratory/HQ40d portable pH, conductivity and temperature meter	0.1 µS/cm-200.0 mS/cm
Dissolved oxygen	SM 4500-O G; Hach LDO101 DO Probe	0–20 mg/L O ₂ Range

Notes: SM = Standard Methods for the Examination of Water and Wastewater [20], EPA = United States Environmental Protection Agency, Washington, DC.

site, and (2) the University of Central Florida's (UCF's) drinking water research facilities located in Florida (Environmental Systems Engineering Institute, UCF, Orlando, FL). The analytical testing methods that were used in the laboratory and field in support of the research are provided in Table 2. Protocols were developed for ClO_2 and permanganate testing; however, Cl_2 testing was based on existing operational conditions.

2.1. Potassium permanganate stock solution

Since the KMnO₄ used was in a crystal form, a solution had to be prepared for dosing. The KMnO₄ stock solution was prepared by first making a stock solution that may then be diluted to provide a more accurate dose when iron and Mn concentrations were less than $1,000 \ \mu g/L$. Since the stock solution of KMnO₄ is dark purple, it can be difficult to see whether or not the crystals are completely dissolved. Therefore, the volumetric flask was shaken vigorously prior to use. Once the stock solution was prepared, the test stock solution was prepared.

2.2. Chlorine dioxide generation

In order to produce ClO₂ chemical for use in experimentation, an Evoqua (formerly Siemens) AC-10 ClO₂ generator was installed at UCF's laboratories for use in studying Fena Lake's ClO2 demand at the bench-scale. The generator works on the basis of the acid-chlorite process and generates ClO₂ as an aqueous solution. Dilute hydrochloric acid (9%) and dilute sodium chlorite (7.5%) are used as starting components for the generation of ClO₂. In the ClO₂ bench-scale unit, reagents are fed from carboys to the reaction tank with a peristaltic pump where a solution with approximately 20 g ClO_2 is generated in a batch mode. This solution is flushed with water into the preparation tank after a defined reaction time. This generated a defined ClO2 solution with less than 2.5 g/L of ClO₂. The ClO₂ solution was pumped from the generator into 125 mL amber bottles, capped, and stored in a refrigerator. The initial concentration of the ClO₂ solution was measured immediately after collection.

In the event of any deviation, the control unit automatically activates an alarm. If there is insufficient operating water available for dilution, the system switches to a stop mode. Vapors produced during the solution flow within the tanks are safely absorbed in the absorption unit that is installed in the generator equipment and connected to a fume hood. The system is controlled by programmable logic controller in combination with an operating and observation panel with a sealed keypad.

2.3. Sample filtration procedure

In preliminary experiments conducted by the authors, it was observed that the use of a 0.45-micron filtration procedure would not completely remove particulate (oxidized) Mn. Although the water industry's standard method for Mn sample preparation (Standard Method 3120B, Inductively Coupled Plasma) recommended filtering through 0.45-micron filters for dissolved Mn analysis [20], the analytical procedure used in the current study was modified where a 0.1micron rated filter was used in lieu of the recommended 0.45-micron filter method. A verification evaluation was hence conducted to determine if naturally oxidized Mn had the potential to pass through the 0.45-micron filter, and to confirm the validity of a modification of the sample preparation procedure used in this research. An evaluation was hence performed that compared filtration using a 0.45-micron filter to a 0.1-micron filter, and included an enhanced test where coagulant addition preceded the use of a 0.45-micron filter. Samples that were pretreated with coagulant addition underwent rapid mix, flocculation, and sedimentation processes as described previously. Once settled, the coagulated samples were then again taken and filtered through a 0.45-micron filter.

2.4. Fena lake reservoir sampling procedures

A review of data collected indicated that the iron and Mn quality varied in lake depth. Water was collected from Fena Lake reservoir in plastic one-liter amber bottles. The depths varied for each jar test performed, as explained in Section 2.4. Bulk water was collected at depths of approximately 10, 20, 30, and 40 ft. The most common depths drawn were 40 ft as this depth was chosen because at that depth, higher iron and Mn concentrations were detected. Over time the water quality in the lake varies, especially after a significant storm event. When any specific depth did not have an adequate amount of iron and Mn suitable for jar testing, iron and Mn was added to the samples prior to dosing with KMnO₄. However, samples taken from the depth that the water was typically drawn and pumped to the WTP (typically around 12 ft depth) varied, and at times was relatively near Mn method detection limits, hence, did not require analytical pretreatment. Water was collected in bulk from the lake using a crane and a container that locked in the water at the desired depth. The bulk water was then transferred to a plastic amber bottle and then prepared for shipping. Water that was shipped was placed in a cooler with ice packs to maintain a cooler temperature. Upon arrival to UCF, the bottles were transferred to a refrigerator kept at 4° C.

2.5. Laboratory jar testing activities

Cl₂ was added to Fena Lake samples to simulate historical use of the oxidant for iron and Mn oxidation, based on historical records. To simulate chemical feed of the alternative oxidants, a Phipps and Bird jar tester was used for treatment simulations, and consisted of six two-liter square jars. The paddles could be operated at various rotational speeds as measured in revolutions per minute (rpm). The volume of water in each jar was fixed at one-liter each. The bulk water that was acquired from the lake, after being mixed thoroughly, was allowed to warm to room temperature, measured in a graduated cylinder at 1,000 mL, and then transferred to the jar. The initial conductivity, pH, temperature, and turbidity were recorded from each of the jars. The dissolved Mn concentration was determined using inductively-coupled plasma spectrophotometry.

Each of the jars was dosed with alternative oxidants with various concentrations to represent different treatment levels. When KMnO4 was added to the water, the samples often turned varying shades of vellow to orange-brown, indicating the presence of oxidized iron and Mn. The samples that retained an orange-brown or yellow color indicated that the oxidation process is incomplete and required the addition of additional KMnO₄. When the water had reached its oxidation endpoint, the water exhibited a pink color. This pink color remained for at least 10 min. Over time, the pink color dissipated. The jars that were dosed higher than the recommended concentrations resulted in pink water, which was undesirable. The jars were subsequently mixed, covered, and stirred at 120 rpm for 2 h to simulate pipe flow. According to the plant operators, the water takes 2 h to reach the WTP after being pumped from the lake intake structure.

As stated previously, when a strong oxidant is added, the particulate by product Mn oxide ($MnO_{x(s)}$) is formed. The Mn oxide that is formed is small enough to pass through 0.45-micron filters. Studies have shown that, when possible, the KMnO₄ should be added upstream prior to the coagulation and flocculation process [6]. Mn oxide is colloidal in nature and has a particle size below one micron. Adding the coagulant after the oxidant destabilizes the particles and the particles appropriately aggregate for subsequent solid—liquid separation. Therefore, once the jars were mixed for 2 h, aluminum sulfate was then added to each of the jars.

During the coagulation-flocculation phase, paddle speeds were chosen based on typical jar tests performed with a coagulant. The different coagulationflocculation phases consisted of a rapid mix at a speed of 150 rpm for 3 min and a slow agitation phase at the speed of 25 rpm for 15 min [14]. The water was then allowed to settle for 1 h for sedimentation. The addition of the aluminum sulfate took place during the rapid mix. The dose was determined to be 35-40 mg/ L based on daily plant operations data acquired from the WTP. This was based on a day of operation when the water was the most turbid when entering the coagulation-flocculation chamber. Once settled, the final conductivity, pH, temperature, and turbidity were taken from each of the jars. Samples were also taken for metals analysis. Once the jars were coagulated and settled, samples were then collected for analysis in 250 mL Erlenmeyer flasks. A vacuum filter apparatus was used to filter the collected samples through a 0.1-micron filter. In between each filtered sample, the vacuum apparatus was cleaned and a new filter was used for each new sample. The samples were then acidified with nitric acid to a pH less than two pH units. Once acidified, the samples were left in a refrigerator for 24 h or longer at 4°C.

3. Results and discussion

3.1. Laboratory filter method modification

It was found that filtration through a 0.1-micron was equivalent to using coagulation prior to a 0.45-micron filter procedure for dissolved Mn sample preparation. In addition, filtration using a 0.45-micron filter alone consistently yielded on an average a Mn measurement that was 10% greater than the corresponding 0.1-micron filter method. Additionally, the coagulation modified 0.45-micron filter method yielded a Mn concentration equivalent to a corresponding 0.1-micron filter method. Consequently, experiments performed in this research were modified. Water samples collected for iron and Mn evaluations were filtered through 0.1-micron filters as opposed to the 0.45-micron filters identified in Standard Methods [20].

3.2. Fena lake water quality

Water quality was collected from several different available sources of varying dates between 1999 and

Representative average Fena lake and combined spring water quality data^a

Parameter	Reservoir water	Spring water
pH	7.5	7.7
Alkalinity (mg/L as $CaCO_3$)	93	173
Turbidity (NTU)	14	0.41
UV-254 (cm ⁻¹)	0.059	0.025
Color (CPU)	20	5.0
Dissolved organic carbon (mg/L)	2.94	0.59
Aluminum ($\mu g/L$)	136	22.3
Total iron $(\mu g/L)$	119	59.0
Total manganese (μ g/L)	17.5	11.6
Calcium (mg/L)	18.3	60
Magnesium (mg/L)	4.5	1.7
Sodium (mg/L)	9.0	8.2
Bromide (mg/L)	<0.1	<0.1
Chloride (mg/L)	11.7	12.6
Sulfate (mg/L)	4.6	4.4

^aData for the reservoir is based on no specific depth as operations varies depth depending on need.

2003, in addition to testing results collected in 2013–2014 as part of the study [21–26]. The data provide a general overview of water quality understanding that the lake water quality can be variable due to seasonal impacts, especially during significant storm events. Table 3 presents average Fena Lake and combined spring water quality data. In general, the reservoir water has a relatively higher metal content (Al, Fe and Mn) than local spring water. However, the spring water has a higher alkalinity and hardness than the reservoir water. Chloride, sodium, and sulfate are similar in both source waters; bromide is non-detectable.

3.3. Fena lake profile

Results of the average Mn content of water samples collected at reservoir depths of 10, 20, 30, and



Fig. 1. Average total Mn concentration at Various depths in fena lake.

40 ft are provided in Fig. 1. Results obtained determined that the lake was stratified and Mn concentrations increased with depth unless weather events disrupted Fena Lake. These results agreed with observations made by Chen and colleagues [26] that showed a decline in dissolved O_2 from 12 to 2.0 mg/L in the bottom of a reservoir resulted in an increase in Mn from 100 to $400 \,\mu\text{g/L}$. The importance of storm impacts on Fena Lake Mn quality was experienced in September 2013 whereupon a tropical storm upset the reservoir, and surrounding runoff disturbed the entire lake. After the storm had passed, Mn was not detected at any significant level for several months. Once the lake re-stratified, dissolved Mn levels increased because the lower depths of Fena Lake had returned to an anaerobic condition. It was also determined that iron that was present in the source water was removed by the WTP coagulation process; hence the research reported herein focused on Mn.

3.4. Alternative oxidant jar testing results

Once settled, samples were then taken and filtered through 0.45-micron filters for iron and Mn analysis. Water quality analyzed included pH, conductivity, temperature, turbidity, dissolved iron, and dissolved Mn. The oxidant dose varied for each water shipment received and tested. Once the dose exceeded the recommended stoichiometric dose, the water exhibited an undesired pink water color in the permanganate samples. Fig. 2 indicates that the percent removal of iron was the same for the recommended doses of KMnO₄



Fig. 2. Average percent removal of iron and mn at recommended doses of potassium permanganate and ClO_2 .

and ClO₂. However, a ClO₂ dose of 1.1 mg/L ClO₂ was slightly more effective in reducing Mn at an average of 98.7% removal, as compared to a 95.9% removal with a KMnO₄ dose of 1.75 mg/L KMnO₄. It was also determined that Cl₂ did not fully oxidize dissolved Mn at the near neutral pH conditions of Fena Lake. Control of Mn in the Fena water system was found to be primarily controlled by coagulation, sedimentation, filtration, and disinfection (Cl₂) and not Cl₂ pretreatment at Fena Lake.

Since the use of ClO_2 results in the formation of the regulated DBP chlorite, additional analysis was performed. The Safe Drinking Water Act's Stage one DBPR established the maximum contaminant level (MCL) for chlorite in water at 1.0 mg/L (1,000 µg/L). Fig. 3 presents the average chlorite concentrations for the various ClO_2 doses that were tested. A ClO_2 dose of 1.1 mg/L ClO_2 produced an average chlorite concentration of 780 µg/L, and therefore did not exceed the federal MCL. The data collected in the overall evaluation indicated that Mn was below the secondary MCL of 50 µg/L when Fena Lake depths above 20 ft are withdrawn for treatment. Because the secondary MCL was typically exceeded at depths of greater than



Fig. 3. Average chlorite concentrations for various ClO_2 doses.

30 ft, these depths were not often used for source water extraction.

4. Conclusions

4.1. Filtering procedure

A verification of filter size used prior to Mn analysis was accomplished in this study. Samples were processed using 0.45-micron as well as 0.1-micron filters. A third sample was coagulated, settled and then filtered through 0.45-micron filters. The results showed that the 0.1-micron filter closely matched the coagulated, 0.45-micron filtered water. Based on the experiments conducted in this study, it is recommended that 0.1-micron filters be used instead of 0.45-micron as stated in Standard Methods for the Examination of Water and Wastewater [20]. It is hence recommended that when evaluating for dissolved Mn content in drinking water supplies that the samples be filtered through a 0.1-micron filter.

4.2. Chlorine oxidation

 Cl_2 did not oxidize dissolved Mn effectively at the near neutral pH conditions of Fena Lake. Control of Mn in the Fena water system was found to be primarily controlled by alum coagulation, sedimentation, filtration, and disinfection (Cl_2) and not Cl_2 pretreatment at Fena Lake.

4.3. Permanganate oxidation

The results showed that 95.9% of Mn was removed when a KMnO₄ dose of 1.75 mg/L KMnO₄ was added to Fena Lake water. However, a slight over-dosage of excess permanganate leads to the formation of pink water; consequently, caution must be taken so as to not overdose the water with the chemical. The data developed in this work indicates that pink water formation can occur with less than 500 μ g/L of a permanganate overdose. Therefore, Mn concentrations in the source water must be monitored closely so that an accurate permanganate dose may be determined and subsequently applied if this oxidizer is to be used. An overdose that results in pink water will contribute to customer complaints.

4.4. Chlorine dioxide oxidation

Results indicated that a 98.7% decrease in Mn content was achieved when 1.1 mg/L ClO_2 was added to Fena Lake water. At this dose, the federal chlorite MCL of 1.0 mg/L was not exceeded. While the regulatory secondary standard for Mn in drinking water is $50 \ \mu g/L$, it was recommended that the PWS should set a target Mn concentration in finished water of $15 \ \mu g/L$ because at this concentration issues of deposition in the distribution system are minimized.

Acknowledgments

The work was supported by Naval Facilities Engineering Command (NAVFAC) A-E Contract N62742-11-D-0101 (Pearl Harbor, HI) as administered by Brown and Caldwell (Honolulu, HI) through UCF Funding Agreement 16208121. The authors would also like to express their gratitude to the DZSP21 laboratory staff in Santa Rita, Guam. Without their help the project would have not been possible. The authors would also like to express gratitude to Brown and Caldwell, specifically Doug Lee, Bill Persich and Lynn Williams for their guidance throughout the course of this research. Also, the significant assistance of Maria Lewis of NAVFAC, Guam, Marianas Islands, in this research was greatly appreciated.

References

- USEPA, Alternative Disinfectants and Oxidants: Guidance Manual, US Environmental Protection Agency, Office of Water, Washington, DC, 1999.
- [2] E.A. Bryant, G.P. Fulton, G.C. Budd (Eds.), Disinfection Alternatives for Safe Drinking Water, Van Nostrand Reinhold, New York, NY, 1992.
- [3] K.J. Howe, D.W. Hand, J.C. Crittenden, R.R. Trussell, G. Tchobanoglous, Principles of Water Treatment, Wiley, New York, NY, 2012.
- [4] USEPA, Guidance Manual for Compliance with the Filtration and Disinfection Requirements for Public Water Systems Using Surface Water Sources, US Environmental Protection Agency, Office of Water, Washington, DC, 1991.
- [5] S. Kawamura, Integrated Design and Operation of Water Treatment Facilities, second ed., John Wiley & Sons, New York, NY, 2000.
- [6] P. Branhuber, S. Clark, W. Knocke, J. Tobiason, Guidance for the Treatment of Manganese, Water Research Foundation, Denver, CO, 2013.
- [7] W.R. Knocke, J.E. Van Benschoten, M. Kearney, A. Soborski, D. Reckhow, Alternate Oxidants for the Removal of Soluble Iron and Mn, Water Research Foundation, Denver, CO, 1990.
- [8] J.J. Cleasby, Iron and manganese removal: A case study, J. Am. Water Works Assoc. 67(2) (1975) 147–151.
- [9] W.R. Knocke, J.E. van Benschoten, M.J. Kearney, A.W. Saborsky, D.A. Reckhowe, Kinetics of manganese and iron oxidation by potassium permanganate and chlorine dioxide, J. Am. Water Works Assoc. 83(6) (1991) 80–87.

- [10] D. Gates, G. Ziglio, K. Ozekin, State of the Science of Chlorine Dioxide in Drinking Water, Water Research Foundation, Denver, CO, 2009.
- [11] K.J. Ficek, J.E. Boll, Potassium permanganate: An alternative to prechlorination, Aqua 7 (1980) 153–156.
- [12] Brown and Caldwell, Disinfection-By-Product (DBP) Reduction Study for Navy Water Sources, Production and Treatment, and Distribution Systems, US Navy A-E Contract No. N62742-11-D-0101, Guam, Marianas Islands, 2014.
- [13] S. Lalezary, M. Pirbazari, M.J. McGuire, Oxidation of five earthy-musty taste and odor compounds, J. Am. Water Works Assoc. 78(3) (1986) 62–69.
- [14] D. Zogo, L.M. Bawa, H.H. Soclo, D. Atchekpe, Influence of pre-oxidation with potassium permanganate on the efficiency of iron and manganese removal from surface water by coagulation-flocculation using aluminium sulphate: Case of the okpara dam in the Republic of Benin, J. Environ. Chem. Ecotoxicol. 3(1) (2011) 1–8.
- [15] P. Roccaro, C. Barone, G. Mancini, F.G.A. Vagliasindi, Removal of manganese from water supplies intended for human consumption: A case study, Desalination 210(1–3) (2007) 205–214.
- [16] P. Phatai, J. Wittayakun, W.H. Chen, C.M. Futalan, N. Grisdanurack, C.C. Kan, Removal of manganese (II) and iron (II) from synthetic groundwater using potassium permanganate, Desalin. Water Treat. 52(31–33) (2013) 5942–5951.
- [17] R.P. Liu, L.H. Sun, R. Ju, H.J. Liu, J.N. Gu, G.B. Li, Treatment of low-turbidity source water by permanganate preoxidation: In situ formed hydrous manganese dioxide as a filter aid, Sep. Purif. Technol. 117 (2014) 69–74.
- [18] J.E. Van Benschoten, L. Wei, W.R. Knocke, Kinetic modeling of manganese(II) oxidation by chorine dioxide and potassium permanganate, Environ. Sci. Technol. 26(7) (1992) 1327–1333.
- [19] K.H. Carlson, W.R. Knocke, Modeling manganese oxidation with KMnO₄ for drinking water treatment, J. Environ. Eng. ASCE 125(10) (1995) 892–896.
- [20] A.D. Eaton, M.A.H. Franson, Standard Methods for the Examination of Water & Wastewater, American Public Health Association, American Water Works Association, Water Environment Federation, Washington, DC, 2005.
- [21] Camacho & Assoc., US Navy Potable Water System, Guam Corrosion Control and Protection Plan Desk Top Evaluation, US Navy AE Contract N62766-96-D-0006, Guam, Marianas Islands, September 1999.
- [22] Duenas & Associates, Inc. and Boyle Engineering Corp., Comprehensive Performance Evaluation of the Fena Water Treatment Plant, US Navy AE Contract N62766-00-D-0012, Guam, Marianas Islands, February 2001.
- [23] Duenas & Associates, Inc. and Boyle Engineering Corp., Volume I: US Navy Potable Water System, Guam: Fena Water Treatment Plant Comprehensive Technical Assistance, US Navy AE Contract N62766-00-D-0012, US Navy Potable Water System, Guam, Marianas Islands, April 2003.

- [24] Duenas & Associates, Inc. and Boyle Engineering Coporation, US Navy Potable Water System, Guam Treatability Study for the Fena Water Treatment Plant, US Navy AE Contract N62766-00-D-0012, US Navy Potable Water System, Guam, Marianas Islands, March 2003.
- Water System, Guam, Marianas Islands, March 2003.
 [25] S.M.G. Rios, TOC Removal from Surface Water Supply on a Volcanic Island Using Enhanced

Coagulation and Granular Activated Carbon, M.S. Thesis, University of Central Florida, Orlando, FL, 2003.

[26] Y.J. Chen, F. Xiao, Y.K. Liu, D.S. Wang, M. Yang, H. Bai, J. Zhang, Occurance and control of manganese in a large scale water treatment plant, Front. Environ. Sci. Eng. 9(1) (2015) 66–72.