

## The role of chloramines in enhancing soluble manganese removal by manganese contactors by W.R. Knocke, A.M. Weber, P.H. Hargette and E. Odom

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### ABSTRACT

Manganese (Mn) contactors have previously been shown to be quite effective in removing dissolved Mn from drinking water. To date, the contactor media have been regenerated by the application of free chlorine, either continuously in the contactor-applied water or via offline regeneration. This research study was the first to evaluate the potential role of chloramines for the online regeneration of  $\text{MnO}_{x(s)}$ -coated contactor media. Testing initially at the bench scale and then subsequently over 6 months at the pilot scale demonstrated that chloramines were quite effective at promoting significant media regeneration. Pilot-scale data showed that the presence of chloramines addressed approximately 80% of the media regeneration requirements, allowing for the addition of free chlorine following media backwashing to address the remaining oxidant needs for media regeneration. Hydraulic loading rates of up to 39 m/hr (16 gpm/ft<sup>2</sup>) could be employed and still produce highly effective Mn removal. The means by which these research results can be applied to other water treatment situations are also discussed.

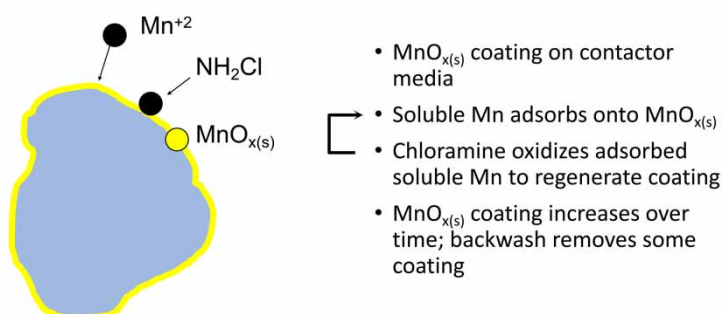
**Key words:** chloramines, manganese contactors, manganese control

### HIGHLIGHTS

- The novel use of chloramines allows for effective media regeneration in manganese (Mn) contactor treatment systems.
- Online chloramine application coupled with occasional offline free chlorine application keeps contactor media fully regenerated and effective for soluble Mn removal.
- Contactor-applied water should have a pH greater than or equal to 7.5 to insure effective soluble Mn uptake as well as media regeneration by chloramines.

### GRAPHICAL ABSTRACT

#### Chloramine - Manganese Interactions on $\text{MnO}_{x(s)}$ -Coated Media



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## INTRODUCTION

Elevated manganese (Mn) concentrations in drinking water can lead to consumer complaints regarding water discoloration. Currently, Mn is not regulated by the U.S. Environmental Protection Agency (EPA) as a primary drinking water standard; however, Mn is addressed as a secondary maximum contaminant level of 0.05 mg/L. However, water utilities are recommended to set effluent Mn concentrations of up to 0.015 mg/L to minimize water discoloration issues (Brandhuber *et al.* 2013). Mn removal during drinking water treatment typically involves the oxidation of reduced, soluble Mn(II) into insoluble  $\text{MnO}_{x(s)}$ , which is subsequently removed by a variety of solid-liquid separation processes. The reader is referred to Brandhuber *et al.* (2013) and Tobiasson *et al.* (2016) for a thorough review of the chemical and biological methods available for accomplishing Mn removal in drinking water treatment scenarios.

One proven method for removing soluble Mn from drinking water sources is the use of  $\text{MnO}_{x(s)}$ -coated filter media. Numerous authors (Knocke *et al.* 1988, 1991; Islam *et al.* 2010; Barlokova *et al.* 2017; Habib *et al.* 2020; Yang *et al.* 2021) have reported on the beneficial use of coated filter media for Mn removal, with the following being common findings:

- Soluble Mn removal can occur over a pH range of 6–6.2 and higher values.
- Typical filter hydraulic loading rates yield highly effective Mn removal.
- The maintenance of a chlorine residual across the filter media is essential for insuring continuous regeneration of the  $\text{MnO}_{x(s)}$  coating on the media surface.

Mn post-filtration contactors use  $\text{MnO}_{x(s)}$ -coated media to take advantage of this effective Mn removal process. Contactor treatment systems use media sizes that are significantly larger than conventional filter media (e.g., the effective size (ES) of 1–2.5 mm for contactors as opposed to 0.4–0.8 mm for filtration systems). The use of larger media sizes allows for much higher hydraulic loading rates to be employed in a contactor design, resulting in the ability to treat substantial quantities of water with relatively small contactor footprints being required. Contactors can serve as a primary Mn removal method or as part of a multi-barrier approach to Mn control (Knocke *et al.* 2010; Brandhuber *et al.* 2013; Bierlein *et al.* 2015; Tobiasson *et al.* 2016). Previous studies have shown that a pH range of 7.0–8.0 produces the most effective Mn removal across the contactor depth since the more alkaline pH conditions increase the amount of available Mn adsorption sites on the media (Knocke *et al.* 2010).

One challenge that can occur with the use of free chlorine as an oxidant during water treatment is an increase in disinfection byproducts (DBPs) such as trihalomethanes and haloacetic acids, which are regulated as maximum contaminant levels (MCLs) by the EPA based upon human health concerns. As such the continuous addition of free chlorine to promote contactor media regeneration can have impacts on DBP formation that must be considered with relevant MCL requirements. It is important to note that the  $\text{MnO}_{x(s)}$ -coated media does not promote DBP production (Bazilio *et al.* 2022); rather, it is simply the presence of free chlorine in water in general that results in such DBP formation.

This study was initiated in response to a specific water treatment situation in Orangeburg, South Carolina. The community's water treatment plant is challenged by a river source water that contains relatively low levels of dissolved Mn (0.01–0.05 mg/L, occasionally exceeding 0.05 mg/L due to heavy rain events) coupled with low pH (pH typically between 5.2 and 5.8) and elevated dissolved organic carbon (DOC) concentrations (average DOC of 8–9 mg/L, but levels of 16–18 mg/L DOC are occasionally seen). Currently, the utility does not experience major water discoloration complaints; however, the utility would like to remove the soluble Mn in their source water to significantly lower concentrations. Previously, the utility explored the use of strong oxidants (e.g., potassium permanganate and chlorine dioxide) to oxidize soluble Mn; however, the relatively low levels of soluble Mn present coupled with the very elevated DOC concentrations in the river proved very challenging in terms of finding a workable oxidant to effectively oxidize the influent Mn. Also, given the very high DOC levels of the water, this water facility uses chloramines ( $\text{NH}_2\text{Cl}$ ) as a primary disinfectant throughout the treatment facility. As a result, the water always contains  $\text{NH}_2\text{Cl}$ . Breakpoint chlorination would be necessary upstream of any Mn contactor if free chlorine was desired for media regeneration. This would undoubtedly lead to significant DBP formation and as such precludes this option.

The water in this treatment facility could be considered a prime candidate for Mn removal by a contactor system. The relatively low Mn levels present are quite suitable for contactor deployment. However, a key challenge for implementing this treatment approach would be a means of regenerating the  $\text{MnO}_{x(s)}$  coating on the contactor media. If  $\text{NH}_2\text{Cl}$  was not able to regenerate the media during online operations, then the contactor would function as an adsorption process for soluble Mn removal and then be regenerated in an offline mode with free chlorine.

This research study was designed to assess whether  $\text{NH}_2\text{Cl}$  would function as a viable oxidant for regenerating  $\text{MnO}_{x(s)}$ -coated media during contactor operations. The research initially focused on a 3-month, bench-scale proof-of-concept evaluation. Once promising results were obtained, the decision was made to conduct a 6-month, pilot-scale evaluation of an Mn contactor system in Orangeburg to assess the longer-term performance of  $\text{NH}_2\text{Cl}$  for media regeneration during online water operations.

## EXPERIMENT METHODS AND MATERIALS

The following sections describe the experimental and analytical methods employed during this research study.

### Bench-scale contactor experiments

Bench-scale Mn contactor experiments employed the use of a ceramic media (Ceralite-A; Wateropolis, Newbury, OH) with  $\text{MnO}_{x(s)}$  coating applied by the manufacturer (coating was between 6.5 and 7.5 mg Mn/g Ceralite-A media). The media had an effective size of approximately 0.65 mm and a uniformity coefficient of  $<1.5$ . The media was initially batch treated (12-h contact time) in a strong bleach solution (30–35 mg/L free chlorine) to help ensure that the  $\text{MnO}_{x(s)}$  coating was fully regenerated at the start of any contactor experiments. The media was also rinsed thoroughly to remove any fines prior to experimental use.

Bench-scale testing employed glass columns of 1.6 cm internal diameter. A media depth of 0.3 m (12") was used for initial contactor tests that were conducted at a hydraulic loading rate (HLR) of 4.9 m/hr (2 gpm/ft<sup>2</sup>), whereas a media depth of 0.45 m (18") was used for subsequent contactor tests that employed an HLR of either 19.6 or 39.2 m/hr (8 or 16 gpm/ft<sup>2</sup>, respectively). An intermediate sampling port allowed for Mn testing to occur at multiple media depths. The duration of contactor loading varied from 16 to 40 days, with the shortest duration being associated with the highest HLR evaluated and the longest duration associated with the 4.9 m/hr (2 gpm/ft<sup>2</sup>) experiment.

The water fed to the columns was deionized water to which sodium bicarbonate was added to produce an alkalinity of 100 mg/L as  $\text{CaCO}_3$  and calcium chloride was added to yield a hardness of 50 mg/L as  $\text{CaCO}_3$ . The pH of the water applied to the contactors was typically between 8.0 and 8.3, a range chosen as often typical of finished water pH conditions at a water treatment facility (for corrosion control) and very comparable to that used at the full-scale treatment facility in Orangeburg. The soluble Mn concentration of the contactor feed water was adjusted by feeding a known amount of manganous sulfate into each batch of water prepared. The target influent soluble Mn concentration for the studies using an HLR of 4.9 m/hr (2 gpm/ft<sup>2</sup>) was 0.20 mg/L, whereas a target Mn concentration of 0.05–0.06 mg/L was employed for the testing at HLR values of 19.6 and 39.2 m/hr (8 and 16 gpm/ft<sup>2</sup>, respectively). Fresh feed water was prepared every 12–24 h throughout the bench-scale contactor studies depending upon the HLR being employed.

A monochloramine ( $\text{NH}_2\text{Cl}$ ) stock solution was prepared by reacting a high-strength ammonia solution (1,400 mg/L as  $\text{NH}_3\text{-N}$ ) with a high-strength sodium hypochlorite solution (5,000 mg/L as  $\text{Cl}_2$ ) using a well-ventilated fume hood. A known amount of chloramine stock solution was added to the feed water batch to achieve the desired feed concentration (typically 4 mg/L; some initial testing involved no chloramine addition to allow for the side-by-side evaluation of the soluble Mn removal that would occur due to simple adsorptive uptake on the  $\text{MnO}_{x(s)}$ -coated media). Preliminary testing demonstrated that chloramines were unable to oxidize soluble Mn to any significant degree in bulk solution over a multi-day period of contact. Likewise, periodic testing of the stock solution showed no evidence of Mn oxidation taking place. Finally, the 4 mg/L  $\text{NH}_2\text{Cl}$  concentration was chosen to reflect typical operating conditions at the Orangeburg treatment facility; likewise, it represents the maximum concentration in drinking water allowed by the U.S. EPA regulation.

Initial bench-scale testing involved side-by-side contactor columns loaded at a HLR of 4.9 m/hr (2 gpm/ft<sup>2</sup>) and an influent Mn concentration of approximately 0.2 mg/L. One column had no  $\text{NH}_2\text{Cl}$  in the feed water, whereas the other column received feed water containing 4 mg/L  $\text{NH}_2\text{Cl}$ . Following the completion of this initial comparative performance study, subsequent contactor testing employed a HLR of either 19.6 or 39.2 m/hr (8 or 16 gpm/ft<sup>2</sup>, respectively). Feed solutions for these latter studies had  $\text{NH}_2\text{Cl}$  present.

Samples of both the influent (feed) and contactor effluent were collected on at least a daily basis. The Mn concentration of samples was analyzed by a Thermo Electron iCAP-RQ (Thermo Electron North American LLCL, West Palm Beach, FL) inductively coupled plasma mass spectrometer (ICP-MS) per Standard Method 3125-B (APHA, AWWA, and WEF 1998). Samples and calibration standards were prepared in a matrix of 2% nitric acid by volume. A HACH spectrophotometer (DR 2800) was used to measure  $\text{NH}_2\text{Cl}$  concentrations using method 10171. Solution pH and temperature were measured by a Fisher Scientific Accumet AE150 benchtop pH meter.

### Pilot-scale Mn contactor studies

Pilot testing was conducted at the John F. Pearson Water Treatment Plant in Orangeburg. Two pilot-scale Plexiglas columns (0.1 m ID (4" ID)) were installed in the filter pipe gallery at the plant. Pilot testing had a goal of achieving Mn levels in the treated water at or below 0.02 mg/L. Each contactor was filled with graded support gravel (0.3 m (12") depth) and 0.7 m (28") of  $\text{MnO}_{x(s)}$ -coated media:

- *Column 1:* 1.6 mm effective size ceramic media (Ceralite-A, coated with  $\text{MnO}_{x(s)}$  from Wateropolis; same type of media as used in bench-scale testing) and
- *Column 2:* 2.0 mm effective size anthracite media (coated with  $\text{MnO}_{x(s)}$  from WesTech).

The use of two different media sizes allowed for an evaluation of media size on both observed Mn removal efficiency and head loss accumulation across the contactors.

Influent water for the pilot contactors was collected post-filtration in the water plant and then pumped to a constant head tank located in the filter gallery. The filtered water received lime addition in the full-scale plant to raise the pH to a target range of 8.0–8.5, as well as supplemental  $\text{NH}_2\text{Cl}$  to a target of approximately 4.0 mg/L. For much of the pilot study, the ambient Mn in the filtered water was supplemented to achieve a 0.05–0.06 mg/L Mn influent concentration to the contactors. This was achieved by metering in a concentrated manganous chloride solution. There were limited periods of time when no supplemental Mn was added to evaluate the contactor performance at day-to-day levels of Mn experienced at the plant. Near the end of the pilot study, there was one test that involved spiking to a target contactor influent Mn level into the range of 0.08–0.10 mg/L.

Pilot-scale testing involved the HLR being set at either 29.4 or 37.8 m/hr (12 or 15 gpm/ft<sup>2</sup>). High HLRs were employed based upon a practical consideration of the full-scale treatment facility. Limited space was available to possibly retrofit Mn contactors into the plant layout; as such, using higher HLRs in design would decrease the footprint of a full-scale Mn contactor installation.

Water samples were collected daily at the contactor influent at a media depth of 0.25 m (10") (i.e., intermediate port) and at the contactor effluent port. Samples were analyzed onsite for Mn concentrations using a HACH test kit and corresponding methodology. Thirty of these samples during the study were also analyzed using ICP-MS (detection limit of 0.0004 mg/L). The comparative results confirmed that the onsite HACH method provided reliable Mn analyses down to concentrations near 0.007 mg/L. The contactor feed water samples were also analyzed for pH, chloramine concentration, and temperature.

The maximum operational head loss accumulation across the pilot-scale contactors was approximately 0.7–0.9 m (30–35") due to the hydraulic configuration at the treatment plant. Contactor columns were taken offline to backwash when head loss accumulation exceeded the system capacity. Backwashing used finished water from the treatment facility. Prior research (Subramaniam 2010) had shown that Mn contactors do generate some amount of head loss over several weeks of operation, most likely due to a buildup of additional  $\text{MnO}_{x(s)}$  coating on the contactor media. Backwashing was shown to be a very effective way of addressing any head loss accumulation.

In addition, an offline, free chlorine regeneration step was employed after most backwashes to restore the media  $\text{MnO}_{x(s)}$  coating to a fully oxidized state. The regeneration step was undertaken to ultimately assess the degree to which chloramines were able to regenerate the  $\text{MnO}_{x(s)}$  media coating during online operations. In two instances, only backwashing was employed without free chlorine regeneration to assess whether offline regeneration was necessary after each backwashing cycle.

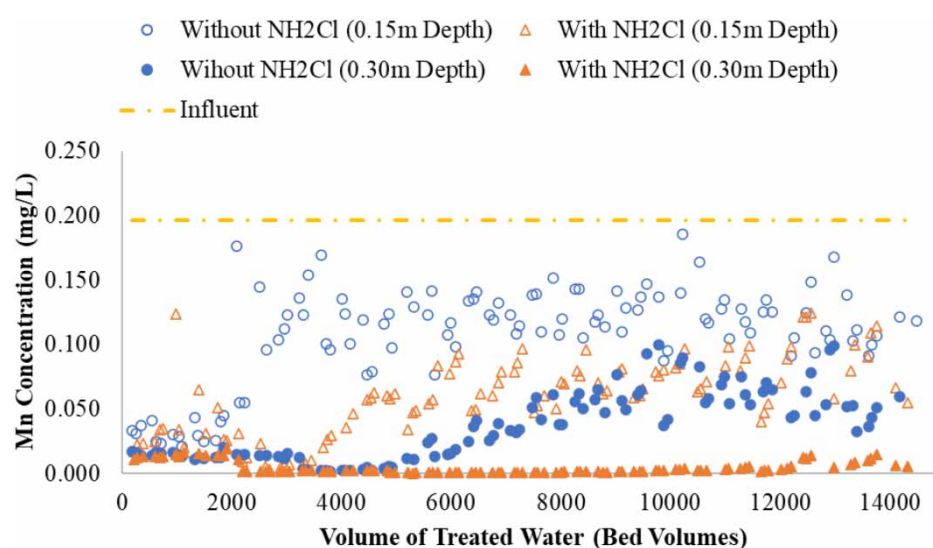
Regeneration of the  $\text{MnO}_{x(s)}$  coating involved soaking the media in a strong free chlorine solution, which would oxidize any portion of the  $\text{MnO}_{x(s)}$  media coating that was not oxidized by the presence of chloramines during conventional contactor operations. Media regeneration consisted of two soak periods with a free chlorine solution concentration of approximately 200–220 mg/L as  $\text{Cl}_2$ . In each instance, the chlorine was allowed to be in contact with the media for approximately 2 h. Water samples were collected from the two depths (0.25 and 0.7 m) into the media and tested for residual free chlorine concentration between each soaking period. When the residual free chlorine concentration was higher than approximately 10 mg/L at the end of a soak period, the media in the column was deemed to be appropriately regenerated. At that point, the media was backwashed again to remove any residual free chlorine, and the next contactor testing period was initiated.

## RESULTS AND DISCUSSION

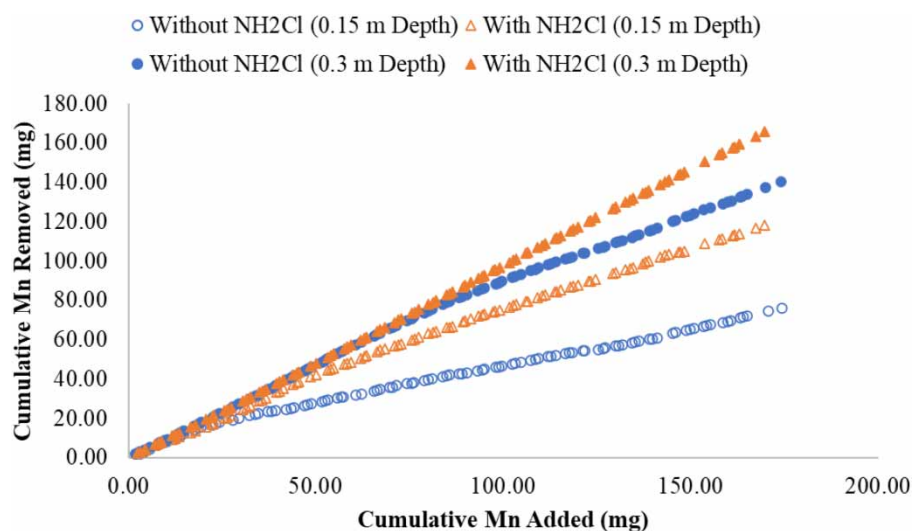
### Bench-scale column experiments

The initial bench-scale experiment involved a side-by-side comparison of two contactors, with one unit having 4 mg/L  $\text{NH}_2\text{Cl}$  in the feed water and the other having no  $\text{NH}_2\text{Cl}$  present. This experiment was conducted at a low HLR of 4.9 m/hr (2 gpm/ft<sup>2</sup>); results are presented in Figure 1.

As shown in Figure 1, the presence of  $\text{NH}_2\text{Cl}$  did improve overall Mn removal, as evidenced by significantly lower effluent Mn concentrations after the initial period of operation. These results are presented in Figure 2 based on the total mass of Mn accumulated on the media in the presence and absence of  $\text{NH}_2\text{Cl}$ , considering the removal observed at media depths of 0.15 m (6") and 0.3 m (12"). The data clearly indicate significantly more Mn removal occurred due to the presence of  $\text{NH}_2\text{Cl}$ . Therefore, the addition of  $\text{NH}_2\text{Cl}$  to the water applied to the  $\text{MnO}_{x(s)}$ -coated media did result in at least partial



**Figure 1** | Effect of the presence of  $\text{NH}_2\text{Cl}$  on Mn removal across  $\text{MnO}_{x(s)}$ -coated contactor media (HLR = 4.9 m/hr (2 gpm/ft<sup>2</sup>)).



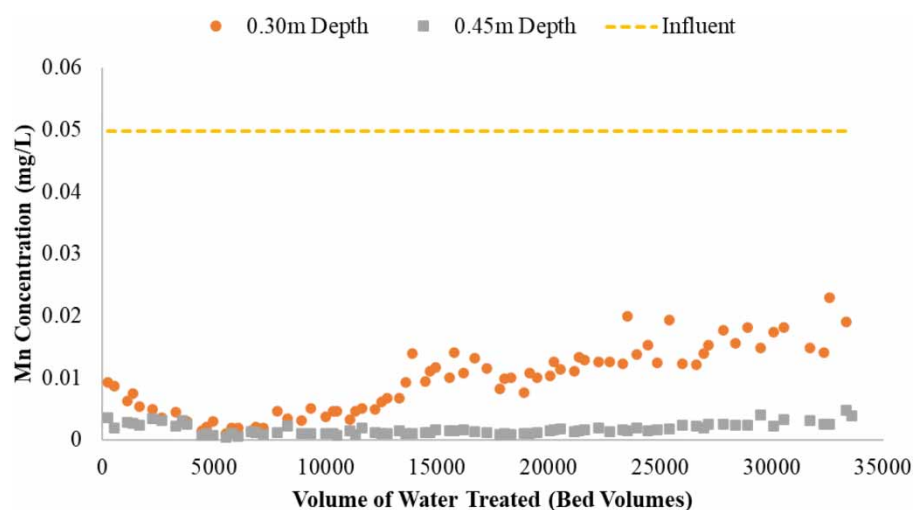
**Figure 2** | Impacts of the presence or absence of chloramines on observed mass removal of Mn across contactor media (HLR = 4.9 m/hr (2 gpm/ft<sup>2</sup>)).



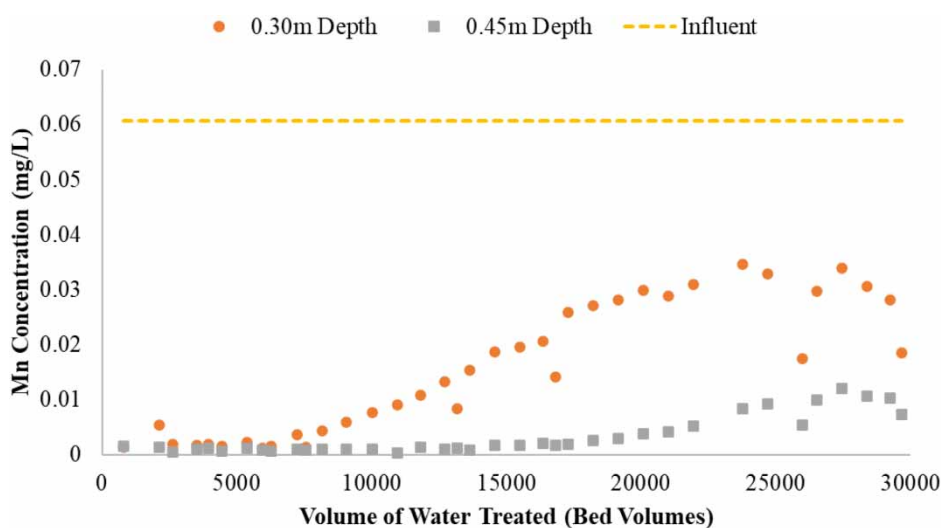
regeneration of media surface during the column operation, demonstrating some ability for  $\text{NH}_2\text{Cl}$  to oxidize previously adsorbed Mn.

Further bench-scale testing was undertaken to evaluate the effects of HLR on contactor performance. Parallel testing was conducted at HLRs of 19.6 and 39.2 m/hr (8 and 16 gpm/ft<sup>2</sup>, respectively) using a lower initial Mn concentration of 0.05–0.06 mg/L. In these tests, the overall  $\text{MnO}_{x(s)}$ -coated media depth was increased to 0.45 m (18"), with sampling capabilities also available at a 0.3 m (12") media depth. These results (shown in Figures 3 and 4 for the two HLR conditions, respectively) show that the effective Mn removal was obtained across the media depth, even for a relatively extended period of operation (up to and exceeding 30,000 bed volumes). As expected, operating at a higher HLR did decrease the total volume of water (expressed in bed volumes) that could be effectively treated before seeing Mn breakthrough into the contactor effluent.

The effluent  $\text{NH}_2\text{Cl}$  concentration was sampled periodically from each of the Mn contactor columns to assess the  $\text{NH}_2\text{Cl}$  demand being exerted in association with soluble Mn removal. The theoretical stoichiometry of oxidation–reduction interaction between  $\text{NH}_2\text{Cl}$  and reduced Mn should have produced  $\text{NH}_2\text{Cl}$  reductions of 0.1–0.3 mg/L across the contactor,



**Figure 3** | Effect of the presence of  $\text{NH}_2\text{Cl}$  on Mn removal across  $\text{MnO}_{x(s)}$ -coated contactor media (HLR = 19.6 m/hr (8 gpm/ft<sup>2</sup>)).



**Figure 4** | Effect of the presence of  $\text{NH}_2\text{Cl}$  on Mn removal across  $\text{MnO}_{x(s)}$ -coated contactor media (HLR = 39.2 m/hr (16 gpm/ft<sup>2</sup>)).

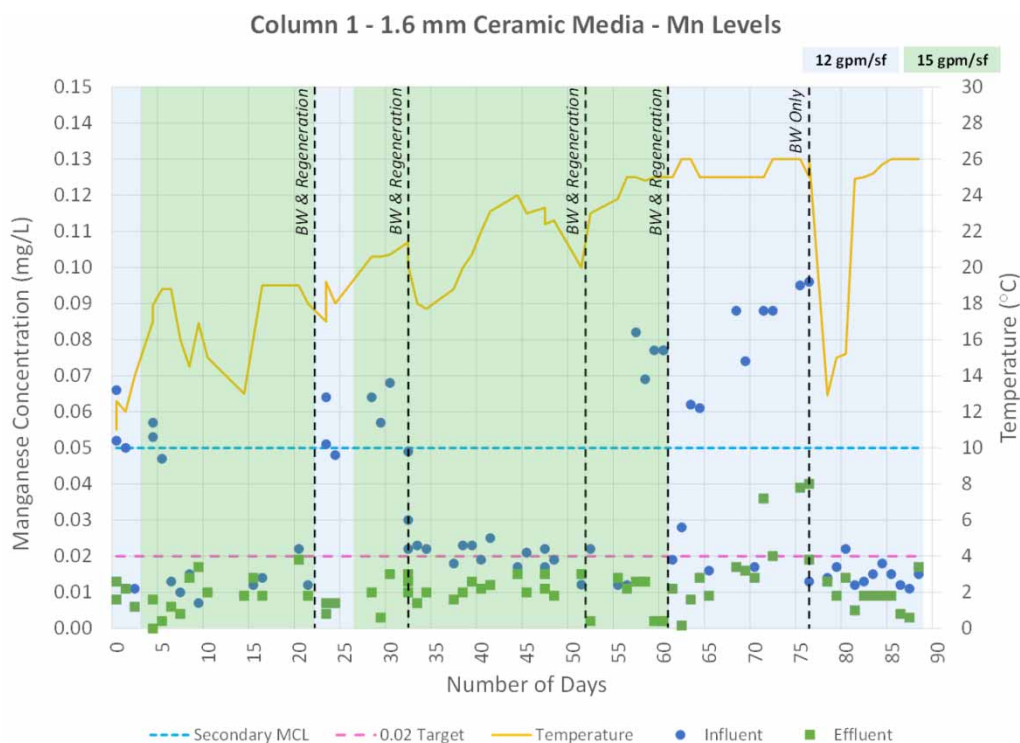
depending upon the influent soluble Mn level in a given test. Instead, the observed  $\text{NH}_2\text{Cl}$  demand across the contactors was in the 0.5–0.7 mg/L range, more than double the theoretical value. No mechanistic explanation could be developed to address the larger-than-expected  $\text{NH}_2\text{Cl}$  demand. It is important to note that actual  $\text{NH}_2\text{Cl}$  demand was occurring across the Mn contactors receiving  $\text{NH}_2\text{Cl}$  in the applied water. This further reinforced the hypothesis that  $\text{NH}_2\text{Cl}$  was promoting at least partial regeneration of the  $\text{MnO}_{x(s)}$  present on the contactor media surface.

### Pilot-scale Mn contactor trials in Orangeburg

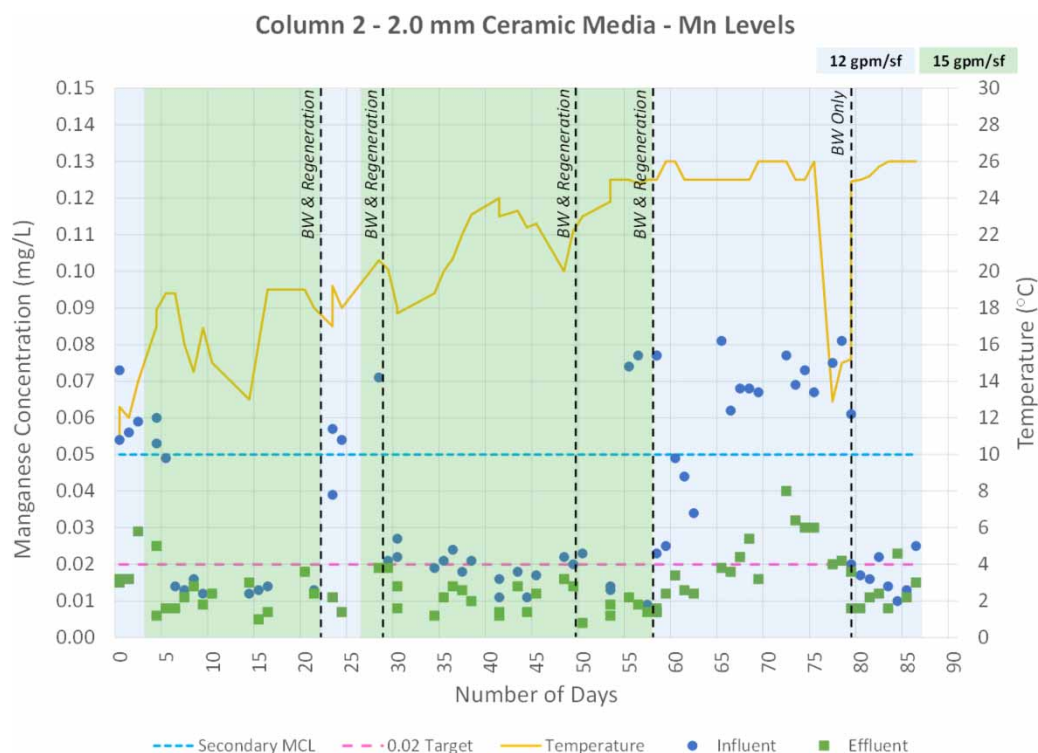
Based upon the positive results obtained at the bench-scale level, pilot-scale testing of the Mn contactor concept was undertaken at the Orangeburg water treatment plant. There was an initial roughly 2-month period of operations when plant personnel were becoming familiar with pilot column operations as well as formulating the offline media regeneration process with free chlorine. Following that period, data collection began in earnest; results for Mn removal are shown in Figures 5 and 6 for the two media sizes employed in the pilot study.

Both contactors performed well in terms of lowering the treated Mn concentration to values at or below 0.02 mg/L; only a few observed values exceeded 0.02 mg/L, and even in those instances, the EPA secondary MCL of 0.05 mg/L was achieved. The contactor performance data for Mn removal are summarized in Tables 1 and 2. Both contactor media configurations yielded average effluent Mn concentrations that were below the 0.015 mg/L threshold to protect against aesthetic concerns (Brandhuber *et al.* 2013).

The smaller media size (1.6 mm ES) yielded improved Mn removal as evidenced by a lower average treated water Mn concentration (0.010 versus 0.014 mg/L) and slightly a higher percent removal performance for a given HLR. This would be explained by the fact that the smaller media size would yield a higher media-specific surface area (and, hence, the greater density of Mn adsorptive sites on the media) as a function of contactor media depth. Also, operating at a higher HLR did negatively impact the observed Mn removal for both media sizes, a result that was expected. Higher HLRs effectively reduce the residence time of the liquid within the contactor, decreasing the time available for soluble Mn adsorption to the media surface.



**Figure 5** | Pilot-scale Mn contactor performance data when employing  $\text{MnO}_{x(s)}$ -coated ceramic media (media effective size = 1.6 mm).



**Figure 6** | Pilot-scale Mn contactor performance data for  $\text{MnO}_{x(s)}$ -coated anthracite coal media (media effective size = 2.0 mm).

**Table 1** | Summary of contactor performance data for manganese removal

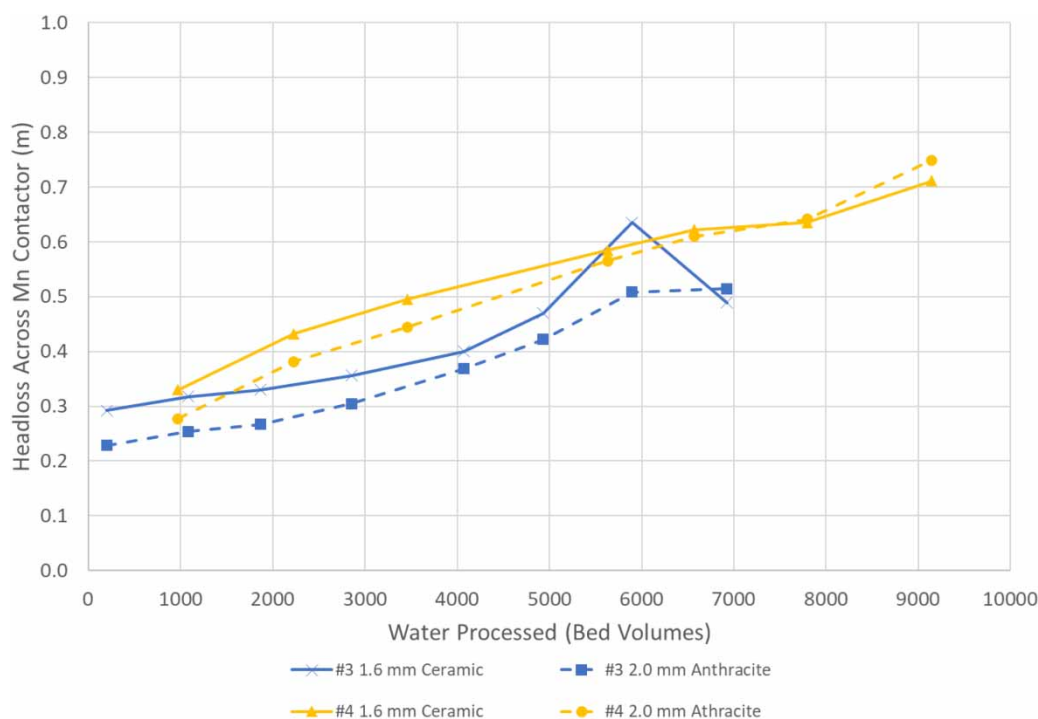
Media type	Influent Mn (mg/L) Minimum–Maximum (average)	Effluent Mn (mg/L) Minimum–Maximum (average)	Average percent reduction in Mn
1.6 mm ES ceramic	0.007–0.096 (0.044)	0.004–0.040 (0.010)	61
2.0 mm ES anthracite coal	0.009–0.081 (0.037)	0.004–0.040 (0.014)	55

**Table 2** | Impacts of hydraulic loading rate on Mn removal across pilot-scale contactors

Hydraulic loading rate, m/hr (gpm/ft <sup>2</sup> )	Mn removal for 1.6 mm ES ceramic media (%)	Mn removal for 2.0 mm ES anthracite coal media (%)
29.4 (12)	61	60
37.8 (15)	57	48

A tradeoff regarding media size and observed head loss was seen when comparing the results for the two media sizes studied. Head loss accumulation was monitored across both pilot-scale contactors during each trial period (between backwash and regeneration cycles); typical results are shown in Figure 7 for two of the trial periods (Trial #3 with the HLR = 29.4 m/hr (12 gpm/ft<sup>2</sup>) and Trial #4 with the HLR = 36.8 m/hr (15 gpm/ft<sup>2</sup>)). As expected, there was a lower head loss for the same volume of water processed in the contactor that experienced a slightly lower HLR. Likewise, the smaller media size did generate a slightly higher head loss value, with much of that difference attributed to the ‘clean bed’ head loss. In general, the rate of head loss buildup over the course of a trial was not extensive. Typically, the contactor columns required backwashing approximately every 2 weeks; furthermore, the total amount of head loss experienced was related to the amount of soluble Mn removal observed across the contactor (data not shown).





**Figure 7** | Representative head loss across contactor media.

It is important to note that the observed head loss generation in the contactors was not associated with any type of particulate matter capture (since the water fed to the contactors had been previously treated by dual-media filtration in the full-scale plant). Instead, the uptake of soluble Mn coupled with the surface-based oxidation of the Mn does yield some observed head loss. This same phenomenon has been reported when Mn contactors employ free chlorine as the media regeneration process (Subramaniam 2010). Backwashing the contactor media removed accumulated head loss associated with Mn removal and restored the hydraulic behavior of the media.

Chloramine demand exerted across each Mn contactor was quantified daily based upon analysis of an influent and effluent sample for residual chloramine concentration. The theoretical chloramine demand exerted would have been no more than 0.1 mg/L  $\text{NH}_2\text{Cl}$  based upon an average Mn influent of approximately 0.05 mg/L across the period of pilot testing. As such it would have been difficult to observe a significant change in chloramine concentration across the contactors. Comparing the influent and effluent chloramine concentrations measured daily for the duration of the pilot testing yielded a calculated average chloramine demand across the contactors of 0.08 mg/L, which is comparable to the theoretical demand calculated.

The role of chloramine in media regeneration was also evaluated based upon the amount of free chlorine that was required to fully regenerate the media in an offline manner following backwash. Table 3 presents a summary of the free chlorine regeneration data.

Across the duration of the pilot-scale Mn contactor study, approximately 80% of the oxidant needs to regenerate the  $\text{MnO}_{x(s)}$ -coated media (with respect to oxidation of the previously adsorbed soluble Mn) were being met by the chloramines present in the contactor-applied water. The remaining  $\pm 20\%$  of the media regeneration needs were met by the offline free

**Table 3** | Comparison of total Mn removal and offline chlorine regeneration needs for contactor media

Media type	Total Mn removed (milliequivalents)	Total free chlorine regeneration (milliequivalents)	Media oxidant demand met by free chlorine (%)
1.6 mm ES ceramic	759	164	21.6
2.0 mm ES anthracite coal	682	134	19.6
All media	1,441	298	20.7

chlorine application. From a practical standpoint, the pilot-scale results demonstrated that the contactors could operate for at least the time period between backwashes without requiring free chlorine application and still produce a high-quality effluent with respect to Mn concentration. In fact, the contactors on occasion were not regenerated with free chlorine after backwash and allowed to go until the next backwash before offline regeneration with free chlorine occurred. In one instance, the contactors operated for essentially an entire month without offline free chlorine regeneration. These results confirmed the earlier bench-scale testing, which demonstrated that chloramines were able to achieve a significant level of media regeneration when present during contactor operations.

## CONCLUSIONS AND ENGINEERING SIGNIFICANCE OF RESULTS

Specific conclusions from this applied research study include the following:

- The addition of  $\text{NH}_2\text{Cl}$  to the water applied to the  $\text{MnO}_{x(s)}$  media in the contactor resulted in substantial regeneration of the media coating during contactor operations. This result indicates that  $\text{NH}_2\text{Cl}$  would be a practical means of promoting online contactor media regeneration. In a full-scale treatment situation, this would significantly increase the time period of operation before the contactor would need to be taken offline for free chlorine regeneration of the media.
- Hydraulic loading rates of up to 39.2 m/hr (16 gpm/ft<sup>2</sup>) could be utilized and still produce high-quality contactor effluent with respect to soluble Mn concentrations. An ability to use loading rates this high would be beneficial for decreasing the total amount of contactor surface area required to treat the water at a given treatment facility.
- The ability of  $\text{NH}_2\text{Cl}$  to regenerate the  $\text{MnO}_{x(s)}$  media coating was indirectly related to the contact time of the  $\text{NH}_2\text{Cl}$  with the media surface. A lower hydraulic loading rate promoted a more effective reaction between  $\text{NH}_2\text{Cl}$  and the  $\text{MnO}_{x(s)}$  surface, increasing the amount of Mn that is oxidized per unit time of contactor operation. However, the  $\text{NH}_2\text{Cl}$  was able to promote sufficient rates of media oxidation at high hydraulic loading rates so as to offer a benefit to overall contactor operations.

This study focused on the application of this treatment technique under conditions specific to the Orangeburg situation. Nonetheless, the research findings have relevance to other water treatment scenarios. For example, this study employed pH 8.0–8.3 conditions since (a) that was the pH condition where a Mn contactor would be employed a full scale in the Orangeburg treatment train and (b) this Mn adsorptive contactor process was known to work better at higher pH (Knocke *et al.* 2010). An alkaline pH condition of 8.0–8.3 is routinely employed by many water utilities for corrosion control in the distribution system anyhow. Mn removal via contactor treatment would most likely be less effective if the water applied to a contactor was significantly below pH 8.0.

Likewise, this study focused on  $\text{NH}_2\text{Cl}$  concentrations near 4 mg/L as this was the prevalent situation for a contactor deployment in Orangeburg. This resulted in approximately 80% of the contactor media's regeneration requirements being met by chloramines, with approximately 20% of the media regeneration requirements being met by free chlorine application during offline periods. Using lower applied  $\text{NH}_2\text{Cl}$  concentrations during online operations would most likely result in more offline free chlorine being needed to insure full regeneration of the contactor media for Mn removal.

## DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

## CONFLICT OF INTEREST

The authors declare there is no conflict.

## REFERENCES

- APHA, AWWA, and WEF 1998 Standard Methods for the Examination of Water and Wastewater. American Public Health Association, American Water Works Association, and Water Environment Federation, Washington, DC.
- Barloková, B., Ilavský, J., Kapusta, O., Junstek, M. & Hudec, P. 2017 Removal of iron and manganese from water using filtralite mono-multi. *Desalination and Water Treatment* **78**, 155–165.
- Bazilio, A. A., Nguyen, C., Mai, X., Laren, Y. & Tobiasson, J. E. 2022 Influent of manganese oxide-coated granular media on disinfection byproduct formation. *AWWA Water Science*. <https://doi.org/10.1002/aws2.1282>.

- Bierlein, K. A., Knocke, W. R., Tobiason, J. E., Subramanian, A., Pham, M. & Little, J. C. 2015 Modeling manganese removal in a pilot-scale postfiltration contactor. *Journal of the American Water Works Association* **107** (2), E1–E11.
- Brandhuber, P., Clark, S., Knocke, W. R. & Tobiason, J. E. 2013 *Guidance for the Treatment of Manganese*. Water Research Foundation, Denver, CO.
- Habib, E., Ali, M. A. & Fattah, K. P. 2020 Modified sand for the removal of manganese and arsenic from groundwater. *Journal of Environmental Engineering and Science* **15** (4), 189–196.
- Islam, A. A., Goodwill, J. E., Bouchard, R., Tobiason, J. E. & Knocke, W. R. 2010 Characterization of filter media  $\text{MnO}_{x(s)}$  surfaces and Mn removal capability. *Journal American Water Works Association* **102** (9), 71–83.
- Knocke, W. R., Hamon, J. R. & Palmer, C. C. 1988 Optimization of soluble manganese removal within mixed-media filtration systems. *Journal American Water Works Association* **80** (12), 65–75.
- Knocke, W. R., Occiano, S. C. & Hungate, R. 1991 Removal of soluble manganese by oxide-coated filter media: sorption rate and removal mechanism issues. *Journal of the American Water Works Association* **83** (8), 64–69.
- Knocke, W. R., Zuravnsky, L., Little, J. C. & Tobiason, J. E. 2010 Adsorptive contactors for removing soluble manganese during drinking water treatment. *Journal American Water Works Association* **102** (8), 64–75.
- Subramaniam, A. 2010 *A Pilot-Scale Evaluation of Soluble Manganese Removal Using Pyrolucite Media in a High-Rate Adsorptive Contactor*. MS Thesis available through the Electronic Thesis and Dissertation (ETD) website of the Virginia Tech Graduate School. Available from: <https://vtechworks.lib.vt.edu/handle/10919/5534/browse?type=author&value=Subramaniam%2C+Archana>.
- Tobiason, J. E., Bazilio, A., Goodwill, J., Mai, X. & Nguyen, C. 2016 Manganese removal from drinking water sources. *Current Pollution Reports* **2** (3), 168–177.
- Yang, H. Y., Tang, X. B., Luo, X. S., Li, G. B., Liang, H. & Snyder, S. 2021 Oxidants-assisted sand filter to enhance the simultaneous removals of manganese, iron and ammonia from groundwater: formation of active  $\text{MnO}_x$  and involved mechanisms. *Journal of Hazardous Materials*. doi:10.1016/j.jhazmat.2021.125707.

First received 3 August 2022; accepted in revised form 16 November 2022. Available online 1 December 2022