

Improving remineralization and manganese-removal of soft waters using a mixed CaCO_3/MgO contactor

Authorship

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Abstract

The aim of this study was to investigate the role of MgO on the long-term operation of a mixed media contactor. Specifically, the simultaneous removal of aqueous manganese and the remineralization of soft waters using pure calcite is limited by a remineralization breakthrough after 600h of operation in the presence of high Mn concentrations (5 mg Mn/L). The introduction of as little as 5% (m/m) MgO was able to improve the Mn removal kinetic, while maintaining remineralization objectives over 720 hours of operation. After treating elevated concentrations of Mn, both media exhibited an Mn-coated layer which contributed to limiting the mass transfer from the media core to the liquid phase. X-ray photoelectron spectroscopy (XPS) identified this superficial layer as 10% Mn oxides (MnOx) on MgO media compared to 1.4% MnOx on calcite, suggesting the MgO acts as the preferred reaction surface during Mn removal. Therefore, it is postulated that in the presence of MgO, Mn removal is impacted by high pH conditions (pH = 10.5) which introduces a significant precipitation mechanism as Mn^{2+} is oxidized. For all the examined conditions, the formation of this coating improved Mn removal due to the autocatalytic nature of the

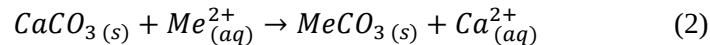
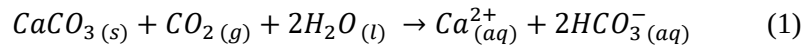
adsorption/oxidation of dissolved manganese by MnOx. MgO is therefore thought to contribute to a complex sorption-coprecipitation process in the operation of a mixed media contactor.

Keywords: Mn removal, Soft water demineralization, Calcite contactor, Sorption-co-precipitation, Sorption media coating

1.0 Introduction

Drinking water with low mineral content or which has been softened during a treatment process often requires remineralization in order to avoid corrosion. Also called water conditioning or stabilization, the remineralization process typically aims to achieve bicarbonate equilibrium as well as to increase pH and alkalinity. At the municipal level, various post-treatment options are available, including the direct dosage of chemicals, blending of hard water with a soft effluent, and mineral dissolution (Shemer, Hasson, & Semiat, 2015). For residential and small-scale installations, the application of a passive mineral dissolution step at the point-of-entry (POE) is preferred (Letterman, Driscoll, Haddad, & Hsu, 1987). As such, calcite (CaCO₃ or limestone) contactors are a common residential POE technology, due to the wide availability of the media, simple design and capacity to treat soft waters without requiring continuous chemical addition (Shemer et al., 2015). Due to increased pollution of aquatic environments, there is also a demand for improved and novel treatment techniques which are simultaneously capable of removing contaminants (organic, inorganic or pharmaceutical). Among these, the removal of heavy metals are of particular interest due to their associated health risks, and the fact that they may naturally occur at high concentrations depending on the water source.

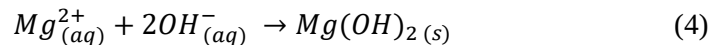
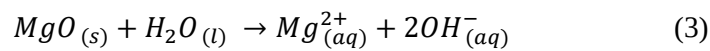
The benefit of a CaCO₃ based treatment is two-fold; the mineral provides calcium (Ca²⁺) hardness and bicarbonate alkalinity (equation 1), as well as having been found effective in reducing aqueous metal concentrations by sorption/ion exchange (equation 2).



Several researchers have studied the advantage of CaCO₃ surface sorption of divalent metals (Me²⁺) in both wastewater and drinking water applications and have found the media to be especially effective for manganese (Mn) removal (Aziz & Smith, 1996; Franklin & Morse, 1983; Pourahmad et al., 2019). In a drinking water context, the occurrence of Mn causes aesthetic and operational issues and Mn removal is thus a common treatment objective (Tobiason, Bazilio, Goodwill, Mai, & Nguyen, 2016). As of 2019, Canada has introduced a health-based regulation of Mn (0.12 mg/L) due to increasing evidence of

manganese neurotoxicity, especially for infants and children (Bouchard et al., 2011; Dion et al., 2018; Health Canada, 2019). Currently, POE catalytic filtration with intermittent regeneration or POE cationic ion exchange (IX) coupled with point-of-use reverse osmosis are two of the most common domestic installations to remove Mn (Carrière, Brouillon, Sauvé, Bouchard, & Barbeau, 2011). In an effort to address the shortcomings of these methods (such as the risk of Mn leaching and the high consumption of salts and production of spent brine), we previously proposed an alternative Mn removal method using a novel backwashable hollow fiber nanofiltration (HFNF) membrane (Haddad, Ohkame, Bérubé, & Barbeau, 2018). The soft permeate which is produced by the HFNF membrane process requires remineralization, and it was determined that coupling the treatment with a calcite contactor polishing step increased hardness as well as reduced remnant levels of Mn which were not completely rejected by the membrane (Haddad & Barbeau, 2019). Further work led to the conclusion that although effective for the simultaneous remineralization and removal of Mn from soft waters, the lifespan of the pure calcite contactor was limited by the formation of a solid Mn-coating on the media surface. While this coating improved the Mn-removal capacity of the media due to the autocatalytic nature of the adsorption/oxidation of dissolved manganese by MnOx, it also caused a significant decrease in remineralization after 600 hours of operation when treating high concentrations of influent manganese (5 mg Mn/L) (Pourahmad et al., 2019). The performance of a contactor can be improved by acidification at the inlet (i.e. injection of CO₂) (Shemer et al., 2015); however, the initial aim of implementing a mineral dissolution step was to simplify the treatment chain and to minimize operational costs. Hence, it becomes interesting to investigate whether the contactor media can be adapted to extend the remineralization capacity in the presence of dissolved divalent metals such as Mn without adding an acidification step.

The dissolution of magnesium oxide (MgO) media introduces magnesium (Mg²⁺) hardness to the water. This is of particular interest as the World Health Organisation (WHO) recommends a baseline of 20 mg/L of calcium and 10 mg/L of magnesium in drinking water for the health benefit of the consumer. As such, several researchers have studied Mg²⁺ based remineralization using MgO (Hasson, Semiat, Shemer, Priel, & Nadav, 2013; Schwartz, Shemer, Hasson, & Semiat, 2015). Notably, the MgO surface rapidly hydrates upon contact with water. The long-term addition of Mg²⁺ hardness and hydroxide (OH⁻) alkalinity are therefore widely considered to be controlled by the hydration surface, or Mg(OH)₂ (Rocha, Mansur, & Ciminelli, 2004):



MgO is also known to be an effective media in the removal of divalent metals when treating contaminated groundwater or acid mine drainage (Caraballo, Rötting, & Silva, 2010; de Repentigny, Courcelles, & Zagury, 2018; Tobias Stefan Rötting, Cama, Ayora, Cortina, & De Pablo, 2006). This is due to the oxidation of divalent metals at the high pH (up to 12) produced by the dissolution of MgO. Consequently, MgO is an appealing media choice to integrate with a calcite contactor. In fact, mixed CaCO₃/MgO filters are already commercially available, with the recommendation of limiting the MgO fraction to 10-20% due to its high reactivity. However, to the best of our knowledge, the application of a mixed CaCO₃/MgO contactor with the dual objective of introducing Ca²⁺/Mg²⁺ hardness and reducing divalent metal concentrations has not yet been investigated. Table 1 provides a summary of the processes expected to contribute to remineralization and Mn removal in a mixed CaCO₃/MgO contactor.

Table 1. Summary of principal processes occurring in mixed media contactor.

Processes	CaCO ₃	MgO
Dissolution ¹	+ Ca ²⁺ hardness + CO ₃ ⁻² alkalinity	+ Mg ²⁺ hardness + OH ⁻ alkalinity
MnCO ₃ formation by ionic exchange ²	↓ Mn _(aq) concentration	Not applicable
Recrystallization of MnCO ₃ into MnO _x ²	+ Mn diffusion barrier	Not applicable
Oxidation of Mn ²⁺ /precipitation	Not significant	↓ Mn _(aq) concentration
Surface sorption of precipitates and recrystallization into MnO _x ^{2,3}	+ Mn diffusion barrier	+ Mn diffusion barrier
Autocatalytic sorption of Mn _(aq) by MnO _x ^{2,3}	↓ Mn _(aq) concentration	↓ Mn _(aq) concentration

1. (Shemer et al., 2015)

2. (Pourahmad et al., 2019)

3. (Hövelmann, Putnis, & Benning, 2018)

1.1 Objectives

The primary aim of this work is to improve the overall performance of a calcite contactor by blending MgO with calcite and to confirm the role of MgO in the Mn removal process by discriminating some of the mechanisms at play in a mixed media system (Table 1). The hypothesis is that the addition of a MgO fraction will increase the remineralization capacity of the filter and will help mitigate the impact of the solid Mn-coating which was previously determined to limit the long-term operation of a pure calcite contactor. Introducing a MgO fraction, therefore, aims to extend the operational longevity of the contactor with the following treatment targets: 1) introducing ≥ 30 mg CaCO₃/L total hardness 2) reducing Mn concentrations to below the Health Canada recommended aesthetic objective of 0.02 mg Mn/L (Health Canada, 2019).

110 2.0 Materials and methods

111 2.1 Media and synthetic feedwater

112 The synthetic feed water (SFW) was prepared by dilution of a stock solution (1000 mg Mn/L) into ultra-
113 pure (Milli-Q™), resulting in a final Mn concentration ranging from 0.5 to 5.0 mg/L. The stock solution
114 was prepared by dissolving powdered reagent grade (>99% pure) MnSO_4 (Fisher Scientific, NJ, USA) in
115 Milli-Q™ water. Both the stock solution and SFW remained stable at a pH of ~6. The SFW was maintained
116 at room temperature ($23 \pm 2^\circ\text{C}$) in 60 L tanks, open to the atmosphere.

117 2.2 Experimental design

118 The experimental design was adapted from previous work done by Pourahmad and co-workers (2019). Two
119 experimental phases were performed, including 1) a continuous sorption-dissolution column experiment
120 investigating soft water remineralization and Mn removal; and 2) batch test experiments investigating the
121 effect of the MgO fraction and Mn-loading on Mn removal.

122 2.3 Continuous sorption-dissolution experiments

123 The first experimental phase aimed to assess the performance of a mixed CaCO_3/MgO contactor in attaining
124 both remineralization and Mn removal targets. A schematic of the column installation is illustrated in Figure
125 1. In order to compare the data obtained from these assays with our previous study of a pure calcite column,

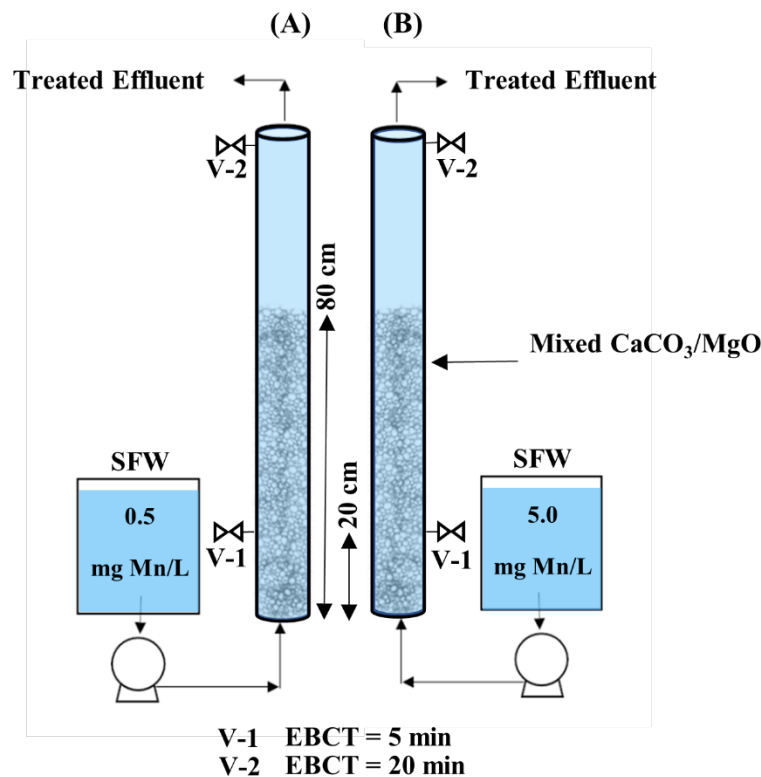


Figure 1. Schematic of laboratory column installation.

the design and operation of the column experiments was replicated and can be found in greater detail in our previous study (Pourahmad et al., 2019). Two columns were filled to an 80 cm bed height with ratios of media prepared by weight and were backwashed with a pure water feed for 2 hours prior to switching to the SFW feeds. The filters were operated upflow at 2.27 m/h and water samples were taken at 5 and 20 minutes of empty bed contact time (EBCT), the latter being equivalent to the fully treated water exiting the column. The first column was fed with SFW with 0.5 mg Mn/L while the second one treated SFW with 5 mg Mn/L.

Several different mass ratios of calcite/MgO media (100%/0%, 90%/10%, 80%/20%) were first tested for 72 hours, upon which the ratio of 95%/5% was selected for a 720-hour installation to observe the column operation over longer term. This paper presents the results of the 720-hour column experiment, as well as batch test results using media of the various ratios produced after 72 hours.

2.3 Analytical determinations on water samples

Water samples were analyzed to determine pH (Electrometric Method 4500-H⁺ B, HQ30D Portable meter), dissolved inorganic carbon (DIC) (Sievers 2310 TOC Analyzer, Suez Water Technologies & Solutions) and alkalinity (Standard Method 2320B) immediately after collection. Manganese concentrations were also periodically verified by the porphyrin colorimetric method (T(4-CP)P) (Hatat-Fraile & Barbeau, 2019). A duplicate of each sample was stabilized by acidification for later ICP-MS analysis of Ca²⁺, Mg²⁺, and Mn²⁺ concentrations (NexION 300x, Perkin Elmer, USA). Total hardness was then calculated using the measured concentrations of dissolved Ca²⁺ and Mg²⁺ (Calculation Method 2340 B).

2.4 Characterization of Mn-loaded media

After 720 hrs of operation (and following an additional 72 hours switched to an ultra-pure water feed), used media was collected from the column treating 5 mg Mn/L at a range of column depths for surface analysis using Scanning Electron Microscope (SEM), Energy Dispersive X-ray Analysis (EDX) and X-ray Photoelectron Spectroscopy (XPS). SEM images were taken at 1000X magnification using a field emission gun electron microscope (JMS-7600 FEG-SEM, Jelo, USA). An energy dispersive spectrometer (Oxford X-Max silicon drift detector, Oxford Instrument, UK) was connected to the microscope to perform the elemental analysis of the surface of the media (EDX) at the same magnification as the SEM analysis (1000X), using a 15-kV accelerating voltage and a 12mm working distance. XPS was performed using the Al K α micro-focused monochromator as an X-ray source (Thermo-Scientific K-Alpha, ThermoFisher, USA), with a 400 μ m spot size and standard lens mode. These analyses served to characterize the media after Mn-loading to compare the nature of the deposits on the MgO surfaces to those found on calcite. The quantity of Mn-loading was determined after digesting 1g of pre-weighted rinsed, dried media (Standard

Method 3050B) by progressive heating and the addition of HNO₃ and HCl. Manganese concentrations were measured using ICP-MS following the digestion.

2.5 Batch sorption-precipitation experiments on Mn-loaded media

The effect of MgO ratio and Mn-loading on media dissolution and sorption was investigated using batch experiments at 23 ± 2°C. The batch tests were operated with 10 g/L of Mn-loaded media and were flushed with N₂ gas before being closed to the atmosphere. Tests were repeated with increasing aqueous manganese concentrations (0.0, 0.1, and 1.0 mg Mn/L) and were continuously shaken at 175 rpm for a duration of 48 hours. Samples were taken periodically with a syringe (0.25h, 1h, 8h, 24h and 48h) and analyzed to determine pH, DIC, alkalinity, Mn, Ca, and Mg using the methods described previously. Additionally, pH and dissolved oxygen (DO, Hach, USA) were measured continuously online to capture the rapid pH response upon introduction of the media to the solution, and to monitor the effect of DO on MnO_x species.

3.0 Results and discussion

3.1 Effect of MgO on the pH of the effluent and Mn removal kinetic

Our results confirm that the addition of only 5% (w/w) MgO in the media blend increases the pH response significantly. Over 720 hours of operation, the pure calcite column produced treated water with pH values

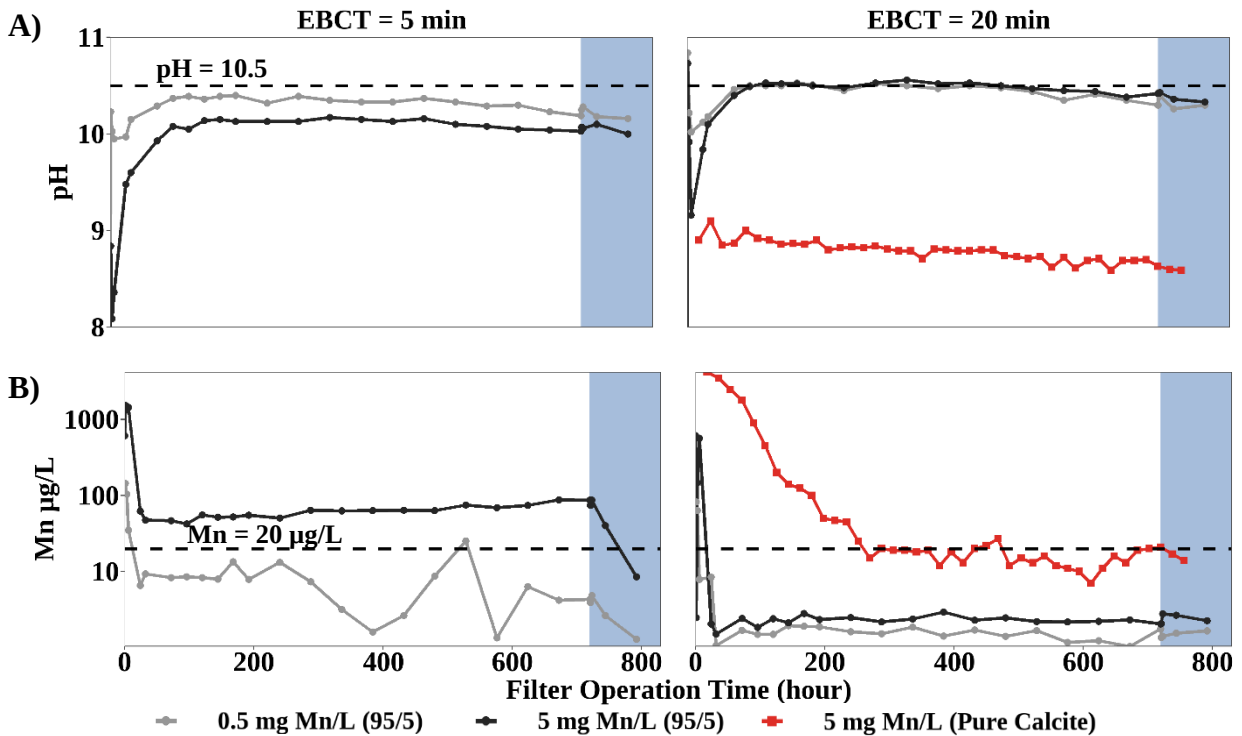


Figure 2. Evolution of pH (a) and aqueous manganese concentrations (b) over 720 hours using a 95/5 ratio of CaCO₃/MgO (23 ± 2 °C). Samples were taken at 20 cm column depth (5 min EBCT) and at the effluent (20 min EBCT). Data in red is incorporated from previous work investigating the operation of a pure calcite (100/0 ratio) contactor (Pourahmad et al., 2019). After 720 hours the feed was switched to ultrapure Milli-Q™ water (indicated in blue).

between 8.6 and 8.8 (Pourahmad et al., 2019) whereas the columns containing 5% MgO produced effluents with a pH around 10.5 (Figure 2).

In preliminary column tests, the addition of greater than 5% MgO at 2.27 m/h (EBCT= 20 min) produced an ‘over-corrected’ pH, thereby exceeding the Health Canada recommended maximal pH of 10.5 for potable water. In the industry, MgO media is advertised as capable of neutralizing up to 5 times more acidity than CaCO_3 (Clack Corporation, 2002). Upon introducing an MgO fraction, an initial ‘spike’ is also observed in the total alkalinity, total hardness and to a lesser extent, pH data. This is despite performing a backwash of the filter with 6-bed volumes prior to the start of the assay. Notably, results for the pure calcite contactor did not exhibit the same trend. We might therefore expect these high values to be the result of MgO impurities, such that pH, alkalinity, and hardness are initially controlled by a small percentage of more soluble fractions (i.e., CaO) at the beginning of column operation. A similar observation was made by Rötting and co-workers, who documented a pH spike above 12 before decreasing to 11 using a column containing 25% MgO (Tobias S. Rötting, Ayora, & Carrera, 2008).

Interestingly, compared to a pure calcite filter, the addition of MgO also accelerated Mn removal kinetics such that effluent manganese concentrations were reduced from 5 mg Mn/L to below 0.02 mg Mn/L within the first 24 hours of operation (Figure 2B). In comparison, the 100% calcite contactor required 10 days of operation to achieve this objective.

3.2 Effect of MgO on hardness addition

Previously, the pure calcite column treating 5 mg Mn/L experienced a remineralization breakthrough after 600 hours due to the build-up of a diffusion barrier caused by Mn-coating. In the mixed media contactor,

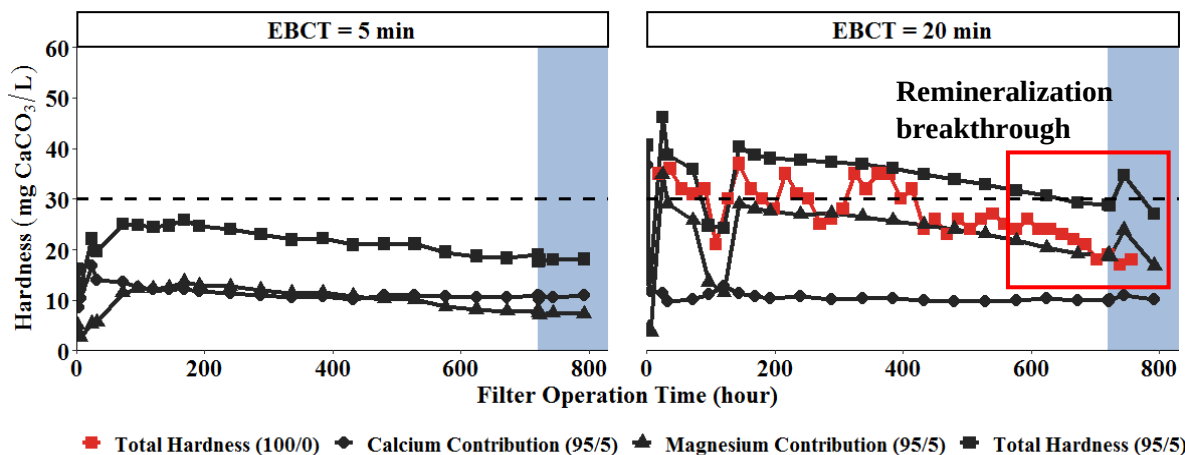


Figure 3. Total hardness addition and $\text{Mg}^{2+}/\text{Ca}^{2+}$ contribution over 720 hours treating 5 mg Mn/L using a 95/5 ratio of CaCO_3/MgO ($23 \pm 2^\circ\text{C}$). Samples were taken at 20 cm column depth (5 min EBCT) and at the effluent (20 min EBCT). Data in red is incorporated from previous work investigating the operation of a pure calcite (100/0 ratio) contactor (Pourahmad, Haddad, Claveau-Mallet, & Barbeau, 2019). After 720 hours the feed was switched to ultrapure Milli-QTM water (indicated in blue).

effluent hardness remained close to 30 mg CaCO₃/L at the end of operation despite a gradual decrease after 144 hours (Figure 3).

Figure 3 illustrates that this decrease is due to a decrease in aqueous Mg²⁺, whereas the contribution of the Ca²⁺ to total hardness remains relatively stable throughout the duration of the operation. This suggests that MgO acts as a preferred reaction surface in the mixed media column, and consequently experiences more Mn-loading than calcite. This hypothesis is further investigated in section 3.5 when we discuss media characterization.

3.3 Effect of initial Mn concentration on long-term operation of a mixed media contactor

Column experiments treated feedwaters of 0.5 and 5 mg Mn/L, respectively. For both tested conditions, the pure calcite contactor and the mixed media contactor were able to remove over 95% of dissolved Mn from the SFW, producing an effluent concentration below the target value of 0.02 mg Mn/L. However, as Pourahmad et al., mentioned, treating high concentrations of Mn causes a decrease in remineralization for the pure calcite column after ~600 hours of operation (Pourahmad et al., 2019). The observed hardness decline was proposed to be due to the effect of MnO_x present on the calcite surface, a statement supported by EDX analysis. Consequently, it was determined that after the long-term operation of the contactor, the accumulation of solid-phase Mn at the calcite surface impeded calcite dissolution through a diffusion barrier at the mass transfer boundary layer.

However, with the addition of MgO the negative impact of high influent Mn concentrations is diminished. In fact, the mixed media filter was able to reduce both influent concentrations to below target levels within 24 hours while maintaining the total hardness addition close to the target value of 30 mg CaCO₃/L (Figures 2B and 3). This suggests that the high pH induced by the dissolution of MgO favours a higher kinetic rate or a different removal mechanism (i.e., direct precipitation vs sorption on preformed MnO_x deposits). Furthermore, this leads to an interrogation of the importance of homogeneous precipitation (precipitation by nucleation) or heterogeneous precipitation (precipitation by crystal growth) in the mixed media filter. The latter occurs at a higher supersaturation index and has been hypothesized to help limit the effect of media coating, which is often accompanied by a decrease in hydraulic conductivity (Claveau-Mallet & Comeau, 2020).

3.4 Effect of Empty Bed Contact Time on Contactor Performance

In the contactor process, the dissolution reaction ideally reaches equilibrium before leaving the bed in order to maximize effluent remineralization. For this purpose, the recommended EBCT for a calcite contactor ranges from 10 to 30 minutes (Voutchkov, 2012). At an EBCT of 20 minutes, the column design presented in this work was able to produce an effluent that met the treatment target values. In practice, it is

recommended to adjust the contactor flow conditions such that the EBCT is reduced, and pH over-correction is avoided when using MgO. For the tested conditions, EBCT does not appear to have a significant impact on pH or DIC. The dissolution of media at the entrance of the column rapidly ‘corrects’ the pH of the soft influent water and the MgO fraction which explains why we reduced MgO to 5% by weight to further constrain the pH response. Upon closer investigation, total alkalinity measurements exhibited a visible increase from 5 minutes of EBCT to the effluent measurement when operating with 5% MgO. If the total alkalinity is considered to be the sum of $[HCO_3^-]$, $[CO_3^{2-}]$ and $[OH^-]$ species, this increase can be attributed to the presence of a significant fraction of hydroxide alkalinity due to high pH given that at pH = 11, the concentration of OH^- is equivalent to 50 mg $CaCO_3/L$ of alkalinity (Figure 4). In contrast, if we associate carbonate alkalinity primarily with the dissolution of calcite and therefore the introduction of calcium ions into solution, both varied minimally with EBCT. One possible explanation for this is that calcite dissolution is most significant at the entrance of the column prior to the increase in pH, whereas the progression of the dissolution reaction for MgO is less impeded by the high column pH after 5 minutes of EBCT. Based on dissolution theory, it was expected that a mixed media column would be unable to attain equilibrium for both minerals. Inevitably, the mixed media column will produce water that is under-saturated with respect to either $CaCO_3$ or MgO due primarily to the impact of pH on their respective equilibrium dynamics.

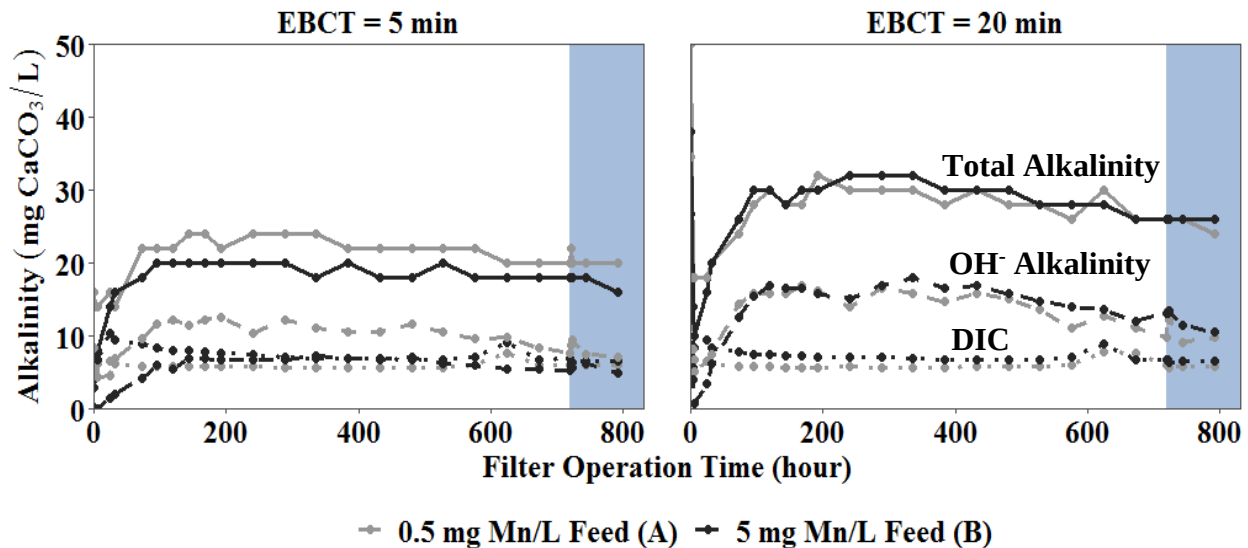


Figure 4. Evolution of total alkalinity, hydroxide alkalinity and DIC ($HCO_3^- + CO_3^{2-}$ alkalinity) over 720 hours using a 95/5 ratio of $CaCO_3/MgO$ (23 ± 2 °C). After 720 hours the feed was switched to ultrapure Milli-QTM water (indicated in blue).

3.5 Media characterization

Fresh $CaCO_3$ and MgO media were analyzed by SEM, EDX and XPS, as well as one sample of mixed media collected after long-term operation with a 5 mg Mn/L influent. In comparison to fresh media surfaces

(0 mg Mn/L), we can see that used media surfaces exhibit distinct crystals and precipitates (Figure 5A). For both media, the decrease in Mn-phases corresponds to samples taken at increasing EBCT (or higher up the column), confirming that Mn-removal occurs primarily at the entrance of the contactor. This also corresponds well with the distinct colour change that was seen during the operation of the contactor, where the media at the entrance of the column turned brown-black. Most manganese oxide minerals are brown-black and identifying the particular mineral can be a challenge. High resolution XPS analysis confirms the presence of Mn2p spectra which implies the presence of MnO₂, Mn₂O₃ and/or MnO(OH), as seen in Figure 5B. Mn-loaded surfaces also produce O1s and Mg1s spectra, which correspond to the MgO surface and the crystallization of magnesium carbonates (Table 2). Previously, comparable surface analyses of media from a pure CaCO₃ column led to the hypotheses that Mn sorption is initiated by an ion exchange reaction between aqueous Mn²⁺ and Ca²⁺ from the CaCO₃ matrix, followed by the slow recrystallization of MnCO₃ into MnO₂ (Pourahmad et al., 2019). Manganese removal using MgO has been suggested to be controlled by the rapid oxidation of Mn²⁺ at high solution pH and subsequent precipitation of Mn³⁺ phases (Caraballo et al., 2010; Cortina, Lagreca, De Pablo, Cama, & Ayora, 2003; Tobias S. Rötting et al., 2008). The authors used pH-based calculations which predicted MnO(OH) and MnO₂ phases as oversaturated or close to equilibrium, and Cortina and co-workers successfully identified Mn₃O₄ and MnO(OH) precipitates by XRD (Cortina et al., 2003).

Table 2. High resolution XPS spectra for fresh and Mn-loaded media.

Name	BE (ev)	Identification	Relative atomic %			
			Fresh ≈ 0 mg/g		Mn-loaded 15 mg/g	
			CaCO ₃	MgO	CaCO ₃	MgO
Mg1s	1304.5	MgO	1.22	11.64	ND	10.55
	1305	MgCO ₃	ND	ND	5.66	ND
O1s	530.5	MeO _x	ND	ND	ND	52.79
	531.9	R-CO ₃ , Me-OH, Si-O	49.5	54.45	47.1	ND
Mn2p3	641.7	MnO₂, Mn₂O₃ or MnO(OH)	ND	ND	1.39	10

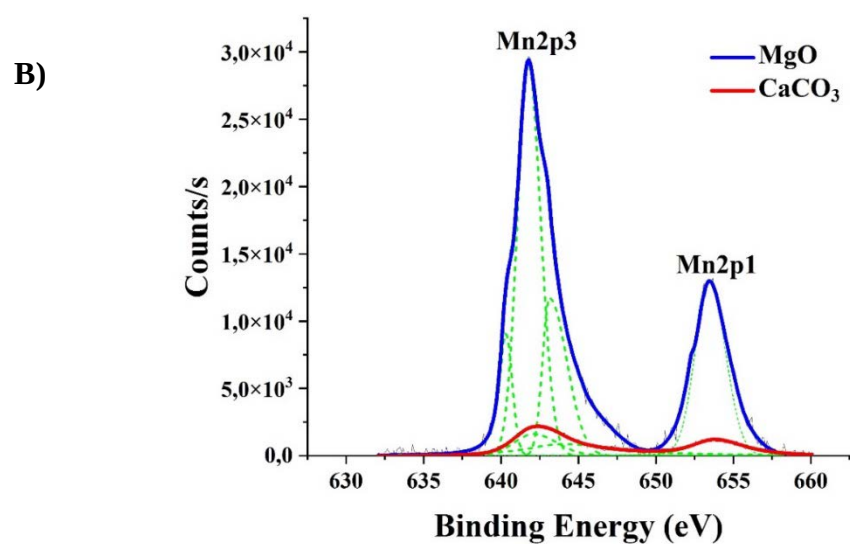
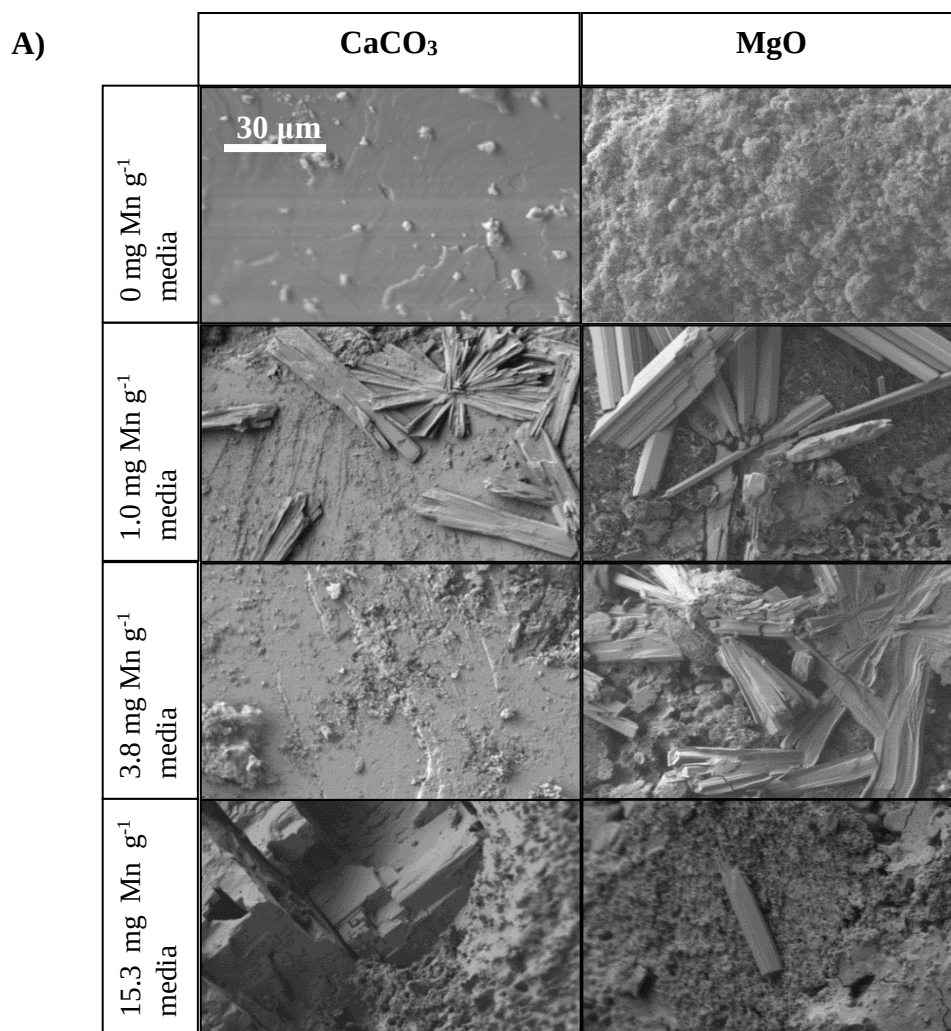


Figure 5. SEM images (x 1000 magnification) of Mn-loaded media surfaces **(a)** and XPS analysis of Mn-loaded (15 mg/g sample) MgO in blue and CaCO_3 in red for the region of Mn oxides **(b)**.

3.6 Mn sorption isotherm and kinetics

Figure 6A compares the Mn removal kinetics in a batch reactor containing fresh or Mn-loaded media from the 72-hour column experiments. In the absence of MgO, Mn-loading on calcite media (5 mg Mn/g sample) improved the reaction kinetics as well as increasing Mn removal by 36% over 48 hours. However, both fresh and Mn-loaded calcite displayed slower reaction kinetics than either fresh MgO or Mn-loaded mixed media (5 mg Mn/g sample) which attained a stable sorption regime within the hour. The convergence of different MgO fractions with Mn-loaded calcite at 76% removal suggests that the presence of Mn-phases on the used media surfaces contributes to long-term Mn removal regardless of varying MgO content.

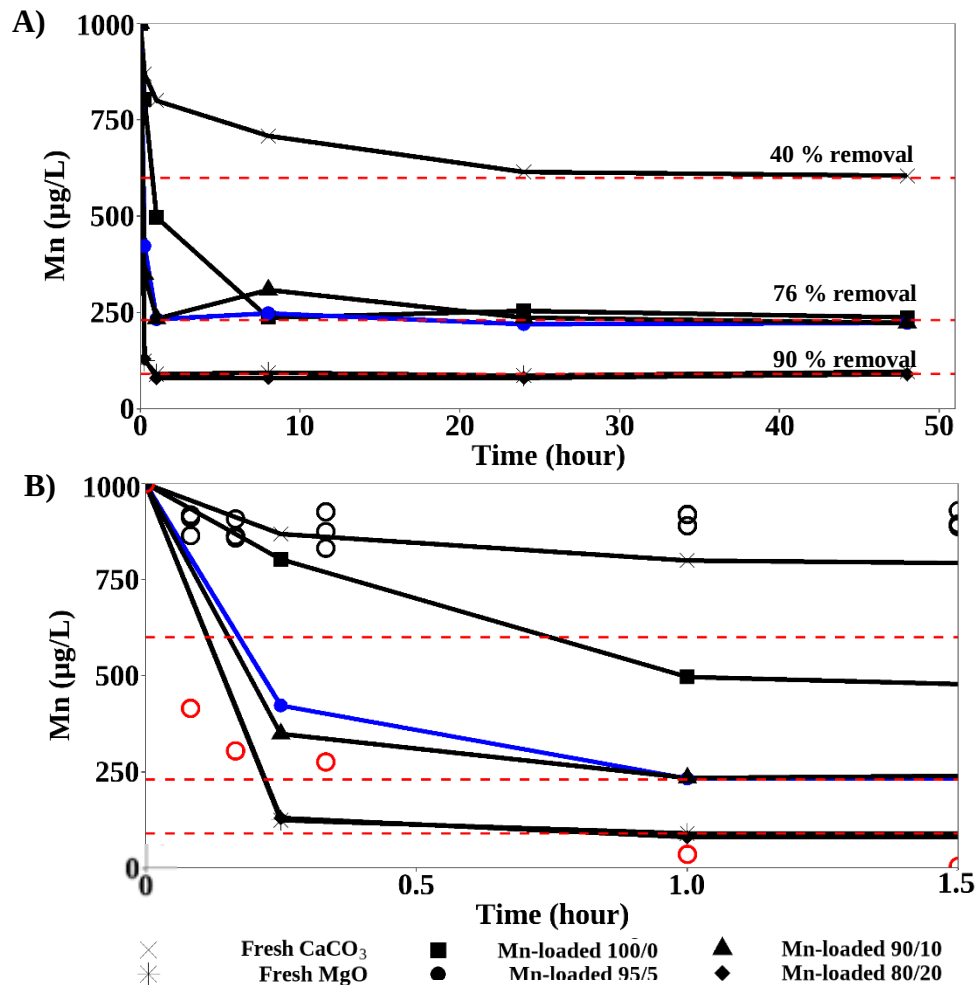


Figure 6. a) Impact of fresh and Mn-loaded media (5 mg Mn/g sample) with increasing MgO content on Mn²⁺ removal in batch tests (red dashed lines indicate sorption isotherms with associated percent removal of aqueous Mn) and **b)** Impact of pH on Mn-removal in the first 1.5 hours of operation in the presence (solid lines) or absence (empty symbols) of Mn-loaded media with increasing MgO ratio (23 ± 2 °C). Empty symbols in black represent final pH conditions between 7–9.2, empty symbols in red represent a final pH of 10.2. Initial Mn²⁺ = 1 mg/L.

Nevertheless, the ratio of MgO available for dissolution and the corresponding increase of solution pH likely remains an important kinetic factor. In fact, figure 6B illustrates that increasing the MgO fraction from 5% to 20% accelerates the removal of Mn within the first 15 minutes of operation.

With the aim of further investigating the effect of pH on Mn removal, a negative control test was performed in which the pH of the batch test solution was increased without the addition of media. Figure 6B illustrates that Mn precipitation is minimal within the pH range 7.0-9.6 (black open symbols), but that 99% removal is achieved within 1.5 hours when the pH is increased to 10.2 (red open symbols). In the presence of media, we can, therefore, assume that pH-induced precipitation from the aqueous phase does not significantly impact Mn removal for either fresh or Mn-loaded CaCO_3 (final pH = 9.5-10). In comparison, fresh MgO and the Mn-loaded mixed media containing 5-20% MgO buffer the solution to a final pH which is above 10.2. At these conditions, we would predict an almost complete removal of aqueous Mn by precipitation. Instead, the batch tests stabilize at 90% and 76% removal, respectively. One possible explanation for this is that the introduction of as little as 5% MgO causes the precipitation of a fraction of the aqueous Mn-phase into Mn hydroxide and carbonate particles due to high solution pH, while solid Mn-phase sorption controls removal kinetics once the aqueous phase has been significantly reduced. This partial precipitation mechanism could account for the increased removal kinetic within the first 8 hours of operation in comparison to pure calcite with the same concentration of solid Mn-phase.

As mentioned, the presence of solid Mn-phases on used media surfaces accelerates the rate of Mn-removal in batch tests. For pure calcite, the formation of this coating was hypothesized to improve Mn removal due to the autocatalytic nature of the adsorption/oxidation of dissolved manganese by MnOx (Pourahmad et al., 2019). It is difficult to distinguish if the precipitation of divalent metals as Me-hydroxides occurs as direct nucleation on the brucite surface (i.e. hydrated MgO surface) or if they are formed within the fluid boundary layer before attaching (Hövelmann et al., 2018). In their work, Hövelmann and co-workers suggested among several possible reaction pathways, the aggregation of metal nanoparticles on the $\text{Mg}(\text{OH})_2$ surface and the consequent crystallization/transformation of these aggregates into a distinct precipitate surface. These precipitation nuclei can then serve to further remove dissolved Me^{2+} species through ion-by-ion growth, or by the sorption of oxidated colloidal particles present in the fluid boundary layer (Hövelmann et al., 2018). In the presence of MgO which rapidly hydrates to $\text{Mg}(\text{OH})_2$, we might therefore expect that Mn removal is not only improved due to pH-induced precipitation, ~~but,~~ -that the removal kinetic is also gradually improving during column operation due to the increased presence of precipitation nuclei on both CaCO_3 and MgO media surfaces.

4.0 Conclusion

This work aimed to determine the role of MgO in a mixed media contactor with the hypothesis that the media improves remineralization and Mn-removal over long-term operation. The main findings are summarized as follows:

- Over 720 hours of operation, the mixed media contactor with a 5% MgO ratio was shown to maintain effluent hardness levels of close to 30 mg CaCO₃/L and to remove aqueous Mn concentrations to below 0.02 mg Mn/L.
- The decrease in remineralization observed at ~600 hours for pure CaCO₃ was mitigated with the addition of MgO.
- When treating high divalent metal concentrations (5 mg Mn/L), the presence of MgO accelerates and improves Mn removal in comparison to treatment with pure CaCO₃.
- The addition of as little as 5% MgO increases the pH up to 10.5, which introduces a significant precipitation mechanism as Mn²⁺ is oxidized. However, batch test results suggest that removal may still be governed by a sorption-coprecipitation reaction over the long-term operation, as the stable sorption regime of Mn-loaded mixed media converges with that of calcite media with the same concentration of Mn coating (5 mg Mn/g media).
- For the tested conditions, surface analyses confirm that Mn-sorption is favoured by the MgO surface, which measured ~10 times higher solid-phase Mn concentrations than found on used CaCO₃ media samples.

Further work is required in order to better understand the numerous reaction pathways in a mixed-media contactor system. It would also be of particular interest to explore the treatment capacity of a mixed media contactor for waters with additional contaminant constituents commonly found in residential groundwater sources (i.e., iron).

Declaration of competing interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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338 References

- 339 Aziz, H. A., & Smith, P. G. (1996). Removal of manganese from water using crushed dolomite filtration
340 technique. *Water Research*, 30(2), 489-492. doi:[https://doi.org/10.1016/0043-1354\(95\)00178-6](https://doi.org/10.1016/0043-1354(95)00178-6)
- 341 Bouchard, M. F., Sauvé, S., Barbeau, B., Legrand, M., Brodeur, M., Bouffard, T., . . . Mergler, D. (2011).
342 Intellectual impairment in school-age children exposed to manganese from drinking water.
343 *Environ Health Perspect*, 119(1), 138-143. doi:10.1289/ehp.1002321
- 344 Caraballo, M. A., Rötting, T. S., & Silva, V. (2010). Implementation of an MgO-based metal removal
345 step in the passive treatment system of Shilbottle, UK: Column experiments. *Journal of*
346 *Hazardous Materials*, 181(1), 923-930. doi:<https://doi.org/10.1016/j.jhazmat.2010.05.100>
- 347 Carrière, A., Brouillon, M., Sauvé, S., Bouchard, M. F., & Barbeau, B. (2011). Performance of point-of-
348 use devices to remove manganese from drinking water. *Journal of Environmental Science and*
349 *Health, Part A*, 46(6), 601-607. doi:10.1080/10934529.2011.562852
- 350 Clack Corporation. (2002). Corosex and Corosex II. In. www.clackcorp.com: Clack Corporation.
- 351 Claveau-Mallet, D., & Comeau, Y. (2020). Chemical Clogging and Evolution of Head Losses in Steel
352 Slag Filters Used for Phosphorus Removal. *Water*, 12(6). doi:10.3390/w12061517
- 353 Cortina, J.-L., Lagreca, I., De Pablo, J., Cama, J., & Ayora, C. (2003). Passive In Situ Remediation of
354 Metal-Polluted Water with Caustic Magnesia: Evidence from Column Experiments.
355 *Environmental Science & Technology*, 37(9), 1971-1977. doi:10.1021/es026018m
- 356 de Repentigny, C., Courcelles, B., & Zagury, G. J. (2018). Spent MgO-carbon refractory bricks as a
357 material for permeable reactive barriers to treat a nickel- and cobalt-contaminated groundwater.
358 *Environmental Science and Pollution Research*, 25(23), 23205-23214. doi:10.1007/s11356-018-
359 2414-3
- 360 Dion, L.-A., Saint-Amour, D., Sauvé, S., Barbeau, B., Mergler, D., & Bouchard, M. F. (2018). Changes
361 in water manganese levels and longitudinal assessment of intellectual function in children
362 exposed through drinking water. *NeuroToxicology*, 64, 118-125.
363 doi:<https://doi.org/10.1016/j.neuro.2017.08.015>
- 364 Franklin, M. L., & Morse, J. W. (1983). The interaction of manganese(II) with the surface of calcite in
365 dilute solutions and seawater. *Marine Chemistry*, 12(4), 241-254.
366 doi:[https://doi.org/10.1016/0304-4203\(83\)90055-5](https://doi.org/10.1016/0304-4203(83)90055-5)
- 367 Haddad, M., & Barbeau, B. (2019). Hybrid Hollow Fiber Nanofiltration–Calcite Contactor: A Novel
368 Point-of-Entry Treatment for Removal of Dissolved Mn, Fe, NOM and Hardness from Domestic
369 Groundwater Supplies. *Membranes*, 9(7). doi:10.3390/membranes9070090
- 370 Haddad, M., Ohkame, T., Bérubé, P. R., & Barbeau, B. (2018). Performance of thin-film composite
371 hollow fiber nanofiltration for the removal of dissolved Mn, Fe and NOM from domestic
372 groundwater supplies. *Water Research*, 145, 408-417.
373 doi:<https://doi.org/10.1016/j.watres.2018.08.032>
- 374 Hasson, D., Semiat, R., Shemer, H., Priel, M., & Nadav, N. (2013). Simple process for hardening
375 desalinated water with Mg²⁺ ions. *Desalination and Water Treatment*, 51(4-6), 924-929.
376 doi:10.1080/19443994.2012.707375
- 377 Hatat-Fraile, M. M., & Barbeau, B. (2019). Performance of colorimetric methods for the analysis of low
378 levels of manganese in water. *Talanta*, 194, 786-794.
379 doi:<https://doi.org/10.1016/j.talanta.2018.11.003>
- 380 Health Canada. (2019). *Guidelines for Canadian Drinking Water Quality: Guideline Technical Document*
381 *– Manganese*. ((Catalogue No H144-39/2017E-PDF).). Ottawa, Ontario.: Health Canada
- 382 Hövelmann, J., Putnis, C. V., & Benning, L. G. (2018). Metal Sequestration through Coupled
383 Dissolution–Precipitation at the Brucite–Water Interface. *Minerals*, 8(8).
384 doi:10.3390/min8080346
- 385 Letterman, R. D., Driscoll, C. T., Haddad, M., & Hsu, H. A. (1987). Limestone bed contactors for control
386 of corrosion at small water utilities. *US EPA. Water Engineering Research Laboratory*.

- Pourahmad, H., Haddad, M., Claveau-Mallet, D., & Barbeau, B. (2019). Impact of media coating on simultaneous manganese removal and remineralization of soft water via calcite contactor. *Water Research*, 161, 601-609. doi:<https://doi.org/10.1016/j.watres.2019.06.037>
- Rocha, S. D. F., Mansur, M. B., & Ciminelli, V. S. T. (2004). Kinetics and mechanistic analysis of caustic magnesia hydration. *Journal of Chemical Technology & Biotechnology*, 79(8), 816-821. doi:10.1002/jctb.1038
- Rötting, T. S., Ayora, C., & Carrera, J. (2008). Improved Passive Treatment of High Zn and Mn Concentrations Using Caustic Magnesia (MgO): Particle Size Effects. *Environmental Science & Technology*, 42(24), 9370-9377. doi:10.1021/es801761a
- Rötting, T. S., Cama, J., Ayora, C., Cortina, J.-L., & De Pablo, J. (2006). Use of Caustic Magnesia To Remove Cadmium, Nickel, and Cobalt from Water in Passive Treatment Systems: Column Experiments. *Environmental Science & Technology*, 40(20), 6438-6443. doi:10.1021/es061092g
- Schwartz, R., Shemer, H., Hasson, D., & Semiat, R. (2015). Design model for magnesium ions remineralization of desalinated water by dissolution of magnesia pellets. *Desalination*, 373, 10-15. doi:<https://doi.org/10.1016/j.desal.2015.06.024>
- Shemer, H., Hasson, D., & Semiat, R. (2015). State-of-the-art review on post-treatment technologies. *Desalination*, 356, 285-293. doi:<https://doi.org/10.1016/j.desal.2014.09.035>
- 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. doi:10.1007/s40726-016-0036-2
- Voutchkov, N. (2012). *Desalination Engineering - Planning and Design*, McGraw Hill, 2012.