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Start-up of non-bioaugmented pumice biofilters in flow-through and recirculating flow regime for Mn removal

José Andrés Araya-Obando [a,*], Luuk C. Rietveld[b], Daniel E. Kelly-Coto[c], Andrea Quesada-González[c], Andrey Caballero-Chavarría[c] and Luis G. Romero-Esquivel [c]

[a] Centro de Investigación en Vivienda y Construcción (CIVCO), Escuela Ingeniería en Construcción, Instituto Tecnológico de Costa Rica (ITCR), Cartago, Costa Rica
[b] Department of Water Management, Delft University of Technology (TU Delft), Delft, The Netherlands
[c] Environmental Protection Research Center (CIPA), School of Chemistry, Instituto Tecnológico de Costa Rica (ITCR), Cartago, Costa Rica
*Corresponding author. E-mail: jobando@tec.ac.cr

JAA-b, 0000-0002-6440-5483

ABSTRACT

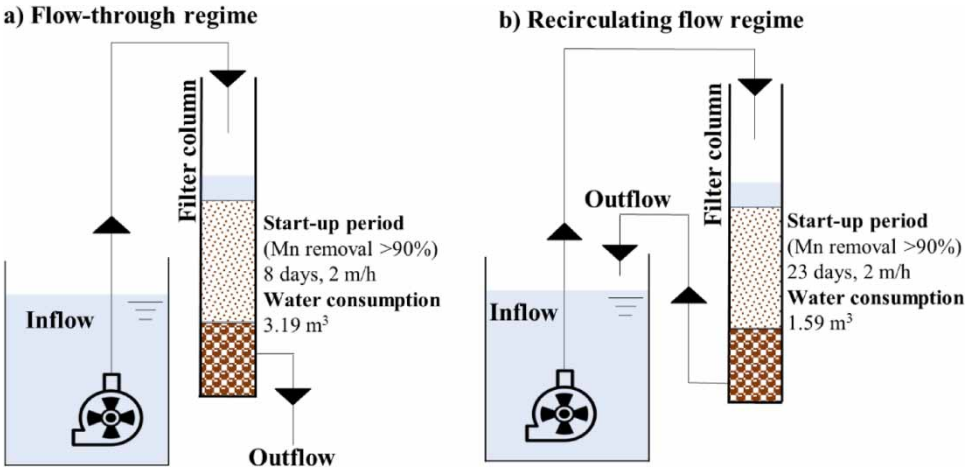
Biofilters are effectively used for drinking water treatment. However, the long ripening time of virgin media for manganese (Mn) removal is a major concern. In this study, the influence of the flow regime on the ripening time of virgin pumice medium was investigated. For this purpose, pilot-scale experiments were performed to compare the start-up of flow-through and recirculating filter columns using inherent inoculation with the same groundwater source. The systems were operated at 2 $m{\cdot}h^{-1}$ with gradual flow increments up to 5 $m{\cdot}h^{-1}$ and avoiding Fe-loading. Effective Mn removal (>90%) in flow-through and recirculating columns was achieved after 8 and 23 days, respectively. Flow-through columns reached compliance with a local drinking water criterion ($Mn < 0.1$ $mg{\cdot}L^{-1}$) at 15 cm filter depth in 11 days. Recirculating filter columns required 32 days to reach compliance at 30 cm depth. The start-up in recirculation regime resulted in a water consumption reduction of about 50% compared with flow-through regime. The intermittent provision of the Mn-loading in recirculating regime impacted the Mn-oxidizing bacteria (MOB) concentration in the pumice stone medium. Both flow regimes required a similar total Mn-loading (0.16 and 0.11 $kg{\cdot}Mn{\cdot}m^{-2}$, respectively), suggesting that Mn-loading was the limiting factor for the ripening of pumice.

Key words: flow-through, groundwater, manganese-removal, pumice media, recirculating, start-up

HIGHLIGHTS

- Flow-through filter columns reached effective Mn removal (>90%) in only 8 days.
- Recirculating flow regime required 23 days, however, with 50% less water consumption.
- Both flow regimes registered a similar total Mn-loading (0.11–0.16 $kg{\cdot}Mn{\cdot}m^{-2}$).
- Intermittent Mn-loading provision impacted the Mn-oxidizing bacteria concentration in the pumice stone medium.
- Mn-loading was the limiting factor for the ripening of pumice stone medium.

GRAPHICAL ABSTRACT



1. INTRODUCTION

Biofiltration is considered a cost-effective and suitable technology for manganese (Mn) removal from groundwater (Marsidi *et al.* 2018). Compared to conventional physicochemical treatments, a significant advantage of biofiltration is that the use of chemicals is not necessary, representing lower operation and maintenance costs (Pacini *et al.* 2014; Cai *et al.* 2015). Mn removal in biofilters involves both biological and physicochemical processes (Bruins *et al.* 2017; Breda *et al.* 2019b). Particularly, Mn removal in a non-coated virgin medium is initiated biologically (Bruins *et al.* 2015a; Breda *et al.* 2019b). Mn^{2+} is oxidized by Mn-oxidizing bacteria (MOB) and deposited gradually as Mn oxide ($MnO_{x(s)}$) (Mouchet 1992). Subsequently, more Mn^{2+} is adsorbed in the $MnO_{x(s)}$-coated filter medium and is autocatalytically oxidized (Sahabi *et al.* 2009; Bruins *et al.* 2015a). Previous research confirmed that biological Mn^{2+} oxidation occurred mainly at the top of the non-inoculated biofilters during the start-up (Breda *et al.* 2019b). Finally, the start-up period is considered complete when the biofilter becomes functional in compliance with a drinking water criterion (Breda *et al.* 2016) or with a high Mn uptake (>90%) (Bruins *et al.* 2017). However, filter ripening typically continues even when high Mn^{2+} removal efficiencies have already been observed (Dangeti *et al.* 2017; Breda *et al.* 2019a).

Bioaugmented methods and inherent inoculation are used to start up the biofilters. The first one involves the following steps: biofilters are inoculated using a concentrated source of microorganisms, isolated, and grown in the laboratory (Ramsay *et al.* 2018; Zeng *et al.* 2019), backwash sludge (Štembal *et al.* 2004; Cai *et al.* 2015; Cheng 2016), or matured filter media (Zeng *et al.* 2010; Bruins *et al.* 2015b; Breda *et al.* 2019b), which are taken from other active Mn biofilters. These methods have been demonstrated to be effective, reporting rapid start-up periods for Mn removal from 2 up to 4 weeks (Štembal *et al.* 2004; Zeng *et al.* 2010; Cai *et al.* 2015; Breda *et al.* 2019b). The success of these methods relies on the proper selection and acclimatization of the biomass used as inoculum (Tekerlekopoulou *et al.* 2013). However, these resources may not be available, especially in zones where biofiltration technology is just emerging. In such cases, inherent inoculation of non-bioaugmented biofilters by autochthonous MOB present in raw water should be used. However, an important drawback is the long start-up period, required for virgin filter media, to achieve effective Mn removal (Ramsay *et al.* 2018). Typically, it takes between 1 and 4 months (Bruins *et al.* 2015b). Bruins *et al.* (2017) affirmed that several factors such as groundwater quality, iron (Fe) loading, type of filter media, and operational parameters (e.g. filtration velocity and backwash strategy) seem to influence the start-up of non-bioaugmented biofilters for Mn removal (Bruins *et al.* 2017). According to the authors, some strategies could be applied to reduce the ripening time of virgin filter media for Mn removal using inherent inoculation, such as to avoid or previously reduce the presence of other contaminants (e.g. Fe) and/or temporarily operating filters at a low filtration velocity.

The oxidation rates of Fe^{2+} and Mn^{2+} by oxygen, at neutral pH and above, are different, being Fe^{2+} relatively rapid oxidized, whereas the Mn^{2+} oxidation is orders of magnitude slower (Singer & Reckhow 2011). Therefore, simple aeration is commonly used for the oxidation of Fe^{2+}, forming Fe (hydr)oxide precipitates. Even though the produced Fe oxides can adsorb Mn^{2+} and catalyze its oxidation, they can block the active sites in the filter media avoiding Mn^{2+} adsorption

(Buamah 2009; Bruins *et al.* 2014). Moreover, Fe^{2+} can compete with Mn^{2+} for adsorption sites (Hu *et al.* 2004), and Mn^{2+} adsorption on Fe (hydr)oxide is lower than manganese (hydr)oxides (Buamah *et al.* 2008). Consequently, Mn removal is commonly better when Fe is previously removed or the Fe-loading prefilter run is lower (Bruins *et al.* 2014). According to Bruins *et al.* (2015b), the effect of a lower Fe^{2+} concentration in the feed water, combined with appropriate operational conditions (e.g. lower filtration velocities and backwash frequency intensity), plays an important role to accelerate the ripening of virgin filter media for Mn removal. In addition, Bruins *et al.* (2017) found that backwashing prolongs the ripening time of a virgin filter and therefore recommended to recirculate part of the filtrate or lower the filtration velocity to reduce the Fe-loading and subsequent backwashing. Regarding matured filters, Bruins *et al.* (2014) found from a statistical analysis of 100 drinking water plants that efficient Mn removal in matured aerated-rapid filters was guaranteed when Fe^{2+} was previously removed or when the Fe-loading per filter run was lower than 2.7 kg $Fe{\cdot}m^{-2}$. Araya-Obando *et al.* (2022) also found that matured rapid sand filters exhibited effective Mn removal during 10 years of operation using an up-flow roughing filter (URG) as Fe pretreatment (removing 68% of the total Fe).

A lower filtration velocity enhances the settling and association of bacterial cells with the media surface (Donlan 2002). Slow velocities from around 1.5 $m{\cdot}h^{-1}$ (Zeng *et al.* 2010) up to 5 $m{\cdot}h^{-1}$ (Breda *et al.* 2016; Bruins *et al.* 2017) are commonly adopted during the start-up, with a constant velocity or by gradually increasing the velocity when the filter effluent reaches the treatment goal (speed-up stage) (Zeng *et al.* 2019). Other studies have recommended to operate the flow-through biofilters at half or one-third of the designed hydraulic load (Štembal *et al.* 2004; Li *et al.* 2005; Ramsay *et al.* 2018). Backwashings with a low-flow intensity ($<$30–35 $m{\cdot}h^{-1}$) (Bruins *et al.* 2015b; Breda *et al.* 2016) have been recommended during the start-up to prevent bacterial detachment.

A novel approach, for inherent inoculation, could be to recirculate (between the effluent and influent of biofilter) the flow to improve the effect of inoculation of biofilters. Cheng (2016), in a bioaugmented method, recirculated the supernatant water of the sedimented backwashing sludge through a pilot-scale biofilter for 3 days and repeated it for 2 more days to improve the effect of inoculation. Then, the filters were operated in a flow-through regime at 2 $m{\cdot}h^{-1}$ and reached the water quality criteria after 44 days. Subsequently, the velocity was increased to 3, 4, and 6 $m{\cdot}h^{-1}$. This approach seems promising, as effective start-up of the degradation of organic compounds in bench-scale (pumice) biofilters by autochthonous microorganisms has been reported (Börnick *et al.* 2001; Worch *et al.* 2002). However, to the best of our knowledge, the influence of the recirculating flow regime, using only inherent inoculation, on the ripening time of virgin media for Mn removal, has not been reported.

In the previous work with the same groundwater source used in this study, the presence of autochthonous culturable MOB in raw water was confirmed (Calderón-Tovar *et al.* 2020). In addition, the feasibility of biofiltration for Mn removal using non-bioaugmented virgin pumice, anthracite, and sand media was demonstrated at bench-scale (Araya-Obando *et al.* 2021). Although, a long start-up period of about 80 days for Mn removal was required for the three materials, it was concluded that pumice has great potential for Mn biofiltration because it is a low-cost, porous, low-density medium and exhibited similar performance compared to sand and anthracite (commonly used in biofiltration). Therefore, to obtain further insight into the efficacy of the start-up of Mn removing in non-bioaugmented biofilters, using groundwater with relatively high temperatures (~23 °C), this study focuses on the influence of the regime of operation on the ripening time of virgin pumice media. For this purpose, pilot-scale experiments were performed in duplicate to analyze the start-up of flow-through and recirculating gravity filter columns, with low Fe-loading and increasing filtration velocities.

2. MATERIALS AND METHODS

2.1. Experimental procedure

To study the influence of the flow regime during the start-up for Mn removal of non-bioaugmented biofilters, two experiments were conducted in duplicate. In *experiment 1* (flow-through regime), feed water passed continuously through virgin pumice columns until ripening (Mn removal $>$90%). In *experiment 2* (recirculating flow regime), feed water was recirculated through biofilter columns until ripening, then the system was switched to flow-through regime. Both experiments were compared in terms of the start-up period, the Mn^{2+} concentration profiles registered over the depth of filter columns, the Mn-loading, and the water consumption.

2.2. Pilot-scale setup

A pilot-scale biofilter system (Figure 1) was installed at a physical – chemical drinking water plant, which is located in La Hacienda Condominium, Cartago, Costa Rica (9°50′28″N; 83°58′26″W). Raw water from the well, used for drinking

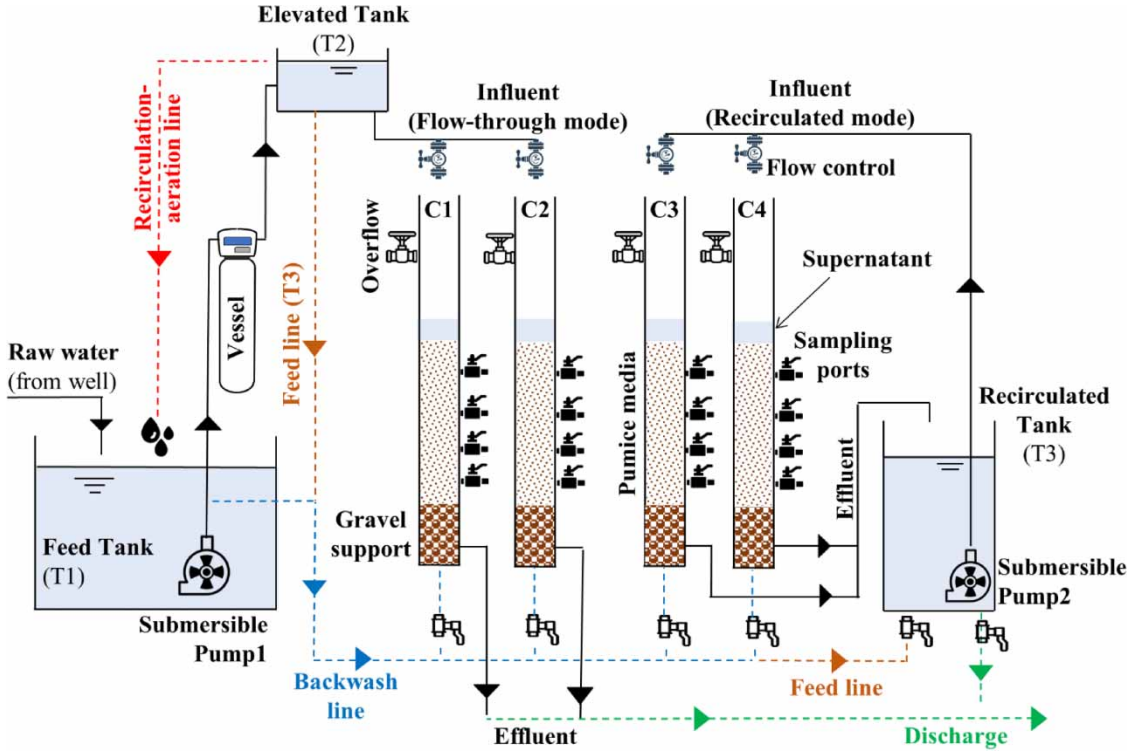


Figure 1 | Configuration of the pilot-scale unit.

water production, was used to perform the experiments. Because the well was operated intermittently (~12 h/day), a feed raw water tank (T1) of 750 L was installed to continuously provide water to the pilot-scale experiments (24 h/day). During T1 filling, raw water was aerated, changing its redox condition. Besides, a preliminary pilot-scale test indicated that Fe pretreatment was needed (further details in Section 3.1). Thus, to prevent the effect of Fe-loading on the start-up of the biofilters, a prefilter using a pressure vessel (Structural FRP, Pentair Company) with a silica sand (0.8–1.3 mm) filter bed height of 60 cm and a diameter of 18 cm was installed after T1 (Figure 1). The prefilter was operated with an empty bed contact time (EBCT) of ~1 min, according to hydraulic tests done before the experiments, to ensure a minimal removal of Mn in the prefilter. The pretreated water was pumped to an elevated tank (T2) of 60 L and used as feed water for the experiments. Raw and feed water quality (collected from the groundwater well and at the effluent of T2, respectively) are depicted in Table 1. In Costa Rica, maximum Fe and Mn concentration levels (MCL), stipulated in the local regulation, are 0.3 and 0.5 $mg{\cdot}L^{-1}$, respectively

Table 1 | Chemical composition of the raw and feed water used in the pilot-scale experiments

Parameter	Unit	Raw water	Feed water
Mn^{2+}	$mg{\cdot}L^{-1}$	0.55[a] ± 0.05[b]	0.49 ± 0.05
Fe	$mg{\cdot}L^{-1}$	0.29 ± 0.16	<0.10[c]
pH	–	7.15 ± 0.23	7.91 ± 0.16
Temperature	°C	22.99 ± 0.56	23.29 ± 0.55
ORP[d]	mV	−21.25 ± 26.15	177 ± 31
DO[e]	$mg{\cdot}L^{-1}$	0.61 ± 0.35	6.52 ± 0.22

[a]Average.
[b]Standard deviation.
[c]Detection limit.
[d]Oxidation–reduction potential.
[e]Dissolved oxygen concentration.

(Decreto Ejecutivo No. 41499-S 2019). Besides, this regulation sets an alert value (AV) for Mn of 0.1 mg·L^{-1} intended to minimize aesthetic concerns.

The biofilter columns consisted of four identical polyvinyl chloride (PVC) columns with a diameter of 10 cm and a filter bed height of 70 cm. Each column was composed of virgin pumice with a grain size between 0.88 and 1.16 mm. To obtain further in-depth information on the start-up of the pilot-scale biofilters, four sampling points were distributed from the top of the media to the bottom at 15, 30, 45, and 70 mm (Figure 1). Filter columns were operated as downflow filters. The filtration velocity was controlled in the inlet of the columns (Figure 1), using a flowmeter rotameter with valve fit (LZM-6T, Sorekarain Company), with a flow range of 100–1,000 mL·min^{-1}. Specifically, two columns were used for the flow-through regime (*experiment 1*) and the other two for the recirculating flow regime (*experiment 2*). In both cases, the start-up period was defined as the ripening time required for the biofilters to achieve Mn removal efficiencies greater than 90% (Bruins *et al.* 2017).

2.2.1. Flow-through regime (experiment 1)

In *experiment 1*, feed water from T2 flowed continuously in parallel through column 1 (C1) and column 2 (C2), and the effluents from both columns were discarded. The filtration velocities used during the experiment were determined according to Zeng *et al.* (2019), with slight modifications. Specifically, a low filtration velocity of 2 m·h was initially used to promote the attachment of autochthonous bacteria present in the raw water (inherent inoculation). The authors also proposed a speed-up stage. Hence, increments of about 1 m·h were performed when the Mn removal remains higher than 90%. Once the Mn removal reached 90%, the velocity was increased in steps of about 1 m·h until reaching a final filtration velocity of 5 m·h, keeping the desired removal percentage. In total, the filtration velocities of 2, 3, 4, and 5 m·h were used, resulting in empty bed contact times (EBCT) of 21, 14, 10.5, and 8.4 min, respectively. Besides, an initial supernatant water level of about 2 cm was provided above the filter media, as also used by Gude *et al.* (2018). Backwashing was performed using water from T1 when supernatant water level rose to 30 cm, using a filter expansion of about 10–20% for 10 min, similar to the pilot-scale study for Mn removal of Bruins *et al.* (2017).

2.2.2. Recirculating flow regime (experiment 2)

Following a similar protocol used in biodegradation studies for organic compounds (Börnick *et al.* 2001; Worch *et al.* 2002), in *experiment 2* (recirculating flow regime), column 3 (C3) and column 4 (C4) were also fed in parallel, but with water from the recirculation tank (T3) (177 L) that was previously filled with feed water from T2. Subsequently, the water from T3 was recirculated at 2 m/h (EBCT of 21 min) through the filter columns until Mn^{2+} concentration in water was not detectable at $<$0.03 mg L^{-1}. Afterward, feed water in T3 was discarded, repeating this protocol. In practice, feed water was renewed every 2–3 days. Consequently, feed water in T3 was renewed nine times in total. Then the columns were switched to flow-through regime and the speed-up stage procedure was applied until both columns operated at 5 m·h with a Mn removal higher than 90%. Initial supernatant water level and backwashing procedures were the same as described in *experiment 1*.

2.3. Sampling and analytical methods

Raw water and filter column inlet and outlet samples were collected approximately two times a week. Water sampling along the filter bed was conducted weekly. Non-filtered samples were immediately acidified to pH $<$ 2 with nitric acid and stored at 4 °C. A preliminary test showed no difference between filtered and non-filtered samples; hence, it was assumed that any Mn present was soluble Mn^{2+} (Cooley & Knocke 2016). Fe was referred here as total Fe. Mn and Fe concentrations were measured using an Analyst 800 atomic absorption equipment (Perkin Elmer, Waltham, USA) according to the Extraction/Air-Acetylene Flame Method 3111 C (APHA *et al.* 2005). The detection limits for Fe and Mn were 0.10 and 0.03 mg·L^{-1}, respectively. Dissolved oxygen (DO), pH, and oxidation–reduction potential (ORP) measurements were conducted using the Hach HQD30 equipment following the methods recommended by the manufacturer (Hach, USA).

2.4. Microbiological analysis

Similar to Araya-Obando *et al.* (2021), 10 g of matured filter media were taken (in quadruplicate) from the top 10 cm of each filter column at the end of the experiments. The samples were diluted in 90 mL sterile 0.1% (w/v) peptone water isotonic solution and stomached for 1 min. Serial dilutions were made, up to 10^{-4}, and 1 mL of each dilution was plated in duplicate on modified R2A agar with 17 mg·L^{-1} $MnSO_4$ and incubated for 5 days at room temperature ($<$28 °C). The ability of isolated bacterial strains to oxidize Mn^{2+} was confirmed with the leucoberbelin blue (LBB) dye assay. Specifically, two drops of the LBB reagent (0.04% (w/v) dissolved in 45 mM acetic acid) were added to the colonies after an incubation period of 20 days.

LBB dye is oxidized by Mn oxides (with Mn oxidation states of +3 and higher) producing a blue color (Piazza *et al.* 2019). MOB is referred to here as the isolated strains that resulted positive in the LBB test.

2.5. Data analysis

Data analysis was performed in R (R Core Team 2021). Summary descriptive statistics for all variables were done using stat.desc (library pastecs). Time series and concentration profiles were done using packages R Graphics.

3. RESULTS AND DISCUSSION

3.1. Start-up of filter columns operated in flow-through regime (*experiment 1)*

Figure 2 shows the registered Mn removal efficiencies and the performed filtration velocities during the start-up period of filter columns C1 and C2 operated in a flow-through regime. In 8 days, 90% removal of Mn was already reached using filtration velocities of 2 m·h, resulting in a Mn-loading of 0.16 kg·Mn·m^{-2}. Afterward, the filtration velocity was increased up to 3 and 4 m·h on days 8 and 11 of filter operation, respectively. A final filtration velocity of 5 m·h was adopted, which is similar to a typical mid-speed value used in rapid biofilters (Cai *et al.* 2014). The fact that Mn removal efficacy in the flow-through columns remained constant after 8 days of operation, even with the flow increments, indicates effective inoculation of the filters, following Zeng *et al.* (2019).

Figure 3 shows the average Mn^{2+} concentration profiles registered over the depth of filter columns C1 and C2, indicating the ripening progress of the pumice media and the most active sections of the biofilters. The profiles show that the flow-through columns reached $Mn^{2+} < 0.1$ mg·L^{-1} (compliance with the local drinking water criterion) already at 15 cm depth after 11 days of operation. It can therefore be concluded that ripening of the filters was more rapid than some others reported in the literature (Ramsay *et al.* 2018; Breda *et al.* 2019a). For instance, Breda *et al.* (2019b) studied the start-up of a non-bioaugmented pilot-scale biofilter for Mn removal and reported that virgin sand media required 41 days to achieve Mn^{2+} concentrations below the MCL (0.05 mg·L^{-1}). However, the filter columns needed 72 days of filter operation to reach compliance at 30 cm depth.

Figure 3 also shows that Mn^{2+} concentration profiles after day 11 remained constant, locating the active zone for effective Mn removal at the top (<15 cm) of the pumice media bed. Inspection of the pumice medium after completion of the experiments showed dark Mn oxides, mainly deposited in the top 15 cm of the filter bed.

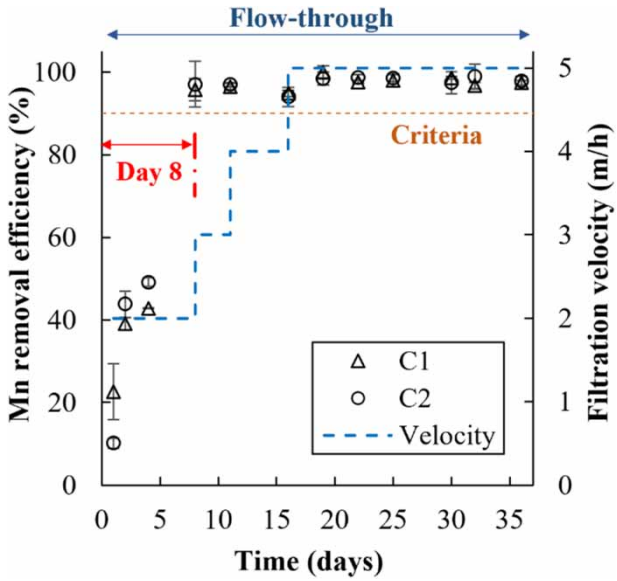


Figure 2 | Mn^{2+} removal efficiencies and filtration velocities over time in biofilter columns C1 and C2 in the flow-through regime. Blue dotted line: filtration velocity increments. Horizontal dashed line: start-up criterion (>90%). Please refer to the online version of this paper to see this figure in colour: http://dx.doi.org/10.2166/ws.2023.045.

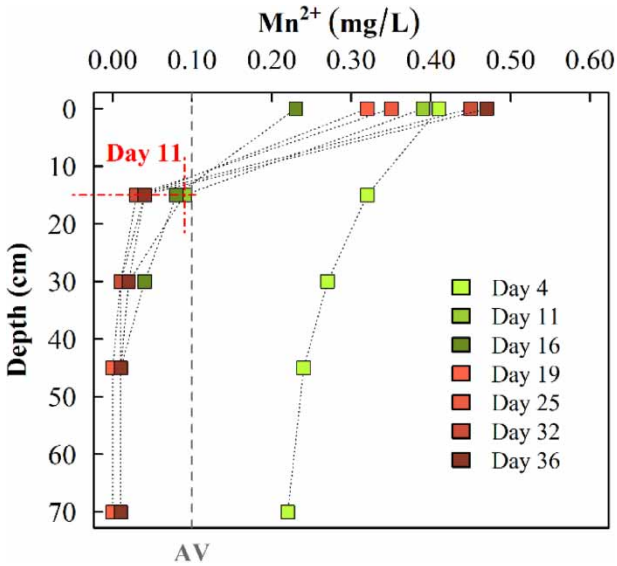


Figure 3 | Average Mn^{2+} concentration profiles over time in columns C1 and C2 in the flow-through regime. Vertical dashed line: acceptability threshold value (AV) for Mn stipulated in the local regulation (Decreto Ejecutivo No. 41499-S 2019). Standard deviation of Mn^{2+} concentration lower than 0.03 mg·L^{-1} in all points (error bars not shown). Please refer to the online version of this paper to see this figure in colour: http://dx.doi.org/10.2166/ws.2023.045.

Virgin filter media typically take between 1 and 4 months to achieve effective Mn removal (Bruins *et al.* 2015b). Similar to Bruins *et al.* (2015b), the rapid ripening of virgin pumice could be explained by a combination of factors that combined favorable feed water quality and operational conditions. First, the pH and Eh of feed water during the experiments were within the field of action of MOB reported by Mouchet (1992) (Figure 4). Besides, as shown in Table 1, the average water temperature during experiments was relatively high (around 23.29 ± 0.55 °C). This condition is quite different than the observed in cold winter temperatures (~3–17 °C), where functional oxidizing bacteria typically require a longer start-up to be effectively acclimated (Cai *et al.* 2014; Pacini *et al.* 2014; Lauderdale *et al.* 2016; Ciancio *et al.* 2020; Evans *et al.* 2021). Second, the presence

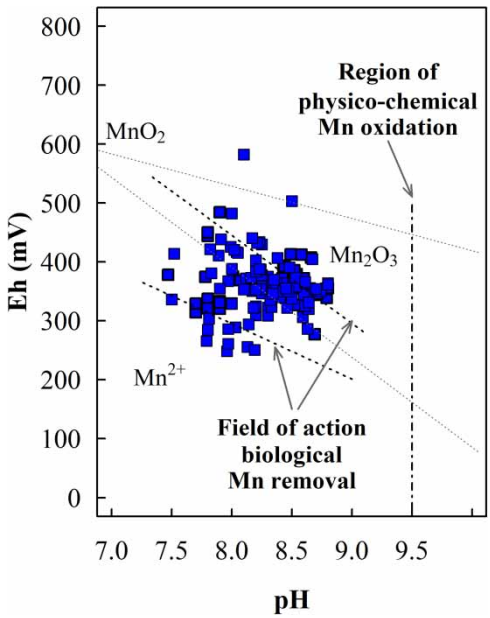


Figure 4 | pH–Eh diagram of experimental feed water quality data showing the field of action of the MOB. Adapted from Mouchet (1992). Eh: standard ORP. Please refer to the online version of this paper to see this figure in colour: http://dx.doi.org/10.2166/ws.2023.045.

of Fe and the subsequent Fe-loading were avoided using a sand filter as pretreatment (pressure vessel in Figure 1); therefore, backwashing was not required, avoiding detachment of biofilms during operation. In preliminary experiments using the same column setup and without the sand filter, pumice filter maturation was not reached, even after 130 days of the experiment, probably due to the high Fe-loading (average 0.5 ± 0.1 kg·Fe·m^{-2} per filter run) (see Supplementary Material S1). Previous studies have also found that Fe-loading and more frequent backwashing prolong the ripening time of virgin media for Mn removal (Bruins *et al.* 2015b, 2017). Besides, Fe oxides can block the active sites in the filter media avoiding Mn^{2+} adsorption (Buamah 2009; Bruins *et al.* 2014), Fe^{2+} can compete with Mn^{2+} for adsorption sites (Hu *et al.* 2004), and Mn^{2+} adsorption on Fe (hydr)oxide is lower than in manganese (hydr)oxides (Buamah *et al.* 2008). Finally, the adoption of a low initial filtration velocity of 2 m·h and the applied speed-up stage, suggested by Zeng *et al.* (2019), is appropriate to enhanced bacteria attachment. However, in our previous study at the bench scale using the same feed water and similar temperature, a filtration velocity of 0.45 m·h resulted in 80 days of ripening (Araya-Obando *et al.* 2021). Thus, it seems that at such lower velocity, bacteria attachment depends mainly on cell size and mobility, reducing the association with the material surface (Donlan 2002).

3.2. Start-up of filter columns operated in recirculating flow regime (*experiment 2*)

Figure 5 shows the registered Mn removal efficiencies and the filtration velocities performed during the start-up period of filter columns C3 and C4. Inherent inoculation using the recirculating flow regime was started using a constant filtration velocity of 2 m·h to enhance the bacterial growth. As can be observed in Figure 5, at this filtration velocity, the filter columns required a start-up period of 23 days to achieve effective Mn removal (>90%). Afterward, both columns were switch to the flow-through regime on day 33, and only a slightly reduced removal efficiency to approximately 80% during the first 2 days of filter operation was observed in column C4; but it was rapidly recovered above 90%, as observed in column C3 (Figure 5). Once the removal efficiencies in both columns remained constant, the filtration velocity was increased to 3, 4, and 5 m·h (on days 40, 47, and 54, respectively) and stable operation was observed (Figure 5). As mentioned earlier, it can be concluded that recirculating filter columns required 15 days longer ripening time, compared to the start-up time of the flow-through filter columns, to reach effective removal (>90%). However, compared to earlier studies, the start-up can still be considered as rapid, since effective Mn removal with virgin filter media typically takes between 1 and 4 months (Bruins *et al.* 2015b), as mentioned previously. Similar to the flow-through system, the feed water characteristics (Table 1) and the relatively low filtration velocity may have played an important role to accelerate the ripening of virgin pumice.

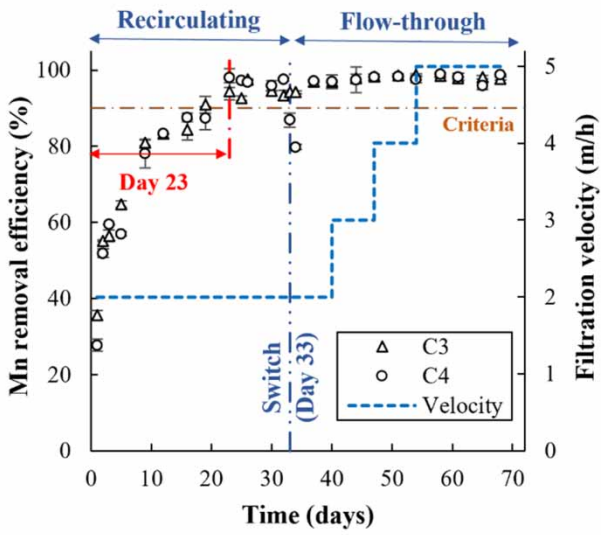


Figure 5 | Mn^{2+} removal efficiencies and filtration velocities over time in biofilter columns C3 and C4 in recirculating the flow regime. Blue dotted line: filtration velocity increments. Horizontal dashed line: start-up criterion (>90%). Please refer to the online version of this paper to see this figure in colour: http://dx.doi.org/10.2166/ws.2023.045.

Figure 6 shows the average Mn^{2+} concentration profiles registered over the depth of columns C3 and C4, using (a) recirculating and (b) flow-through regime. As shown in Figure 6(a), $Mn^{2+} < 0.1$ mg·L^{-1} (local AV) was reached on day 23 (after start-up). Subsequently, the operation of the filter columns in recirculating flow regime continued for 1 week (until day 32) to study the development of the ripening of the pumice media. However, after 30 days of operation, effective Mn removal only occurred at a depth of 30 cm (Figure 6(a)). A similar Mn^{2+} concentration profile was reported by Breda *et al.* (2019b) during the start-up of non-inoculated sand filters.

As shown in Figure 6(b), after filter columns were switched to the flow-through regime (day 33) and operated for 1 week, the active Mn removal zone was in the first 15 cm of then filter bed depth. As shown in Figure 5, column C4 also reduced removal efficiencies up to about 80% but recovered the higher Mn capacity uptake in only 2 days. This finding suggests that the biologically active zone in the filter columns required a short time of acclimatization to the new flow regime conditions (see Section 3.3). Full ripening, and thus effective Mn removal at 15 cm depth, was finally registered on day 40. Besides, the speed-up stage following Zeng *et al.* (2019), which was carried out after day 40 (Figure 5), did not affect the Mn^{2+} concentration profiles patterns, indicating that the virgin pumice media was also fully inoculated with the autochthonous groundwater bacteria.

3.3. Comparison of the start-up of the filter columns in flow-through and recirculating flow regimes

As shown in Figure 4, both experiments were conducted using feed water with pH and Eh values within the field of action of MOB (Mouchet 1992). In addition, considering that non-catalyzed, homogeneous Mn^{2+} oxidation (by oxygen only) is very slow at pH < 9 (Granger *et al.* 2014) (feed water pH ~7.9, Table 1), and biological Mn^{2+} oxidation is supposed to occur at the top of the non-inoculated sand filter during the start-up (Breda *et al.* 2019b), it can be concluded that Mn removal by the virgin pumice media was probably dominated by biological processes in both cases. This finding is in line with the previous studies that have also reported that Mn removal in a non-coated virgin medium was initiated biologically (Bruins *et al.* 2015a; Breda *et al.* 2019b) Furthermore, in the active zone on top of the columns, microbiological analysis showed that during flow-through experiments, MOB count was 1.9×10^6 CFU·g^{-1}, whereas in the recirculating regime, the MOB concentration was 4.0×10^3 CFU·g^{-1} and was reduced to 2.9×10^3 CFU·g^{-1} after switching to flow-through regime. As explain later, the intermittent Mn-loading impacted the MOB population in the recirculated biofilters and probably slowed down the acclimation time in this system. More information about MOB diversity detected in the same well water and in a bench-scale experiment can be found in the previous studies (Calderón-Tovar *et al.* 2020; Araya-Obando *et al.* 2021).

During the start-up period in the flow-through regime (Figure 2), the Mn^{2+} concentration was always around 0.50 mg·L^{-1}. In contrast, in the recirculating experiment, the average initial Mn^{2+} concentration in T3 was around 0.52 mg·L^{-1} but was typically reduced to less than 0.1 mg·L^{-1} in 7–8 h (see Supplementary Material S2). The water replacement was conducted

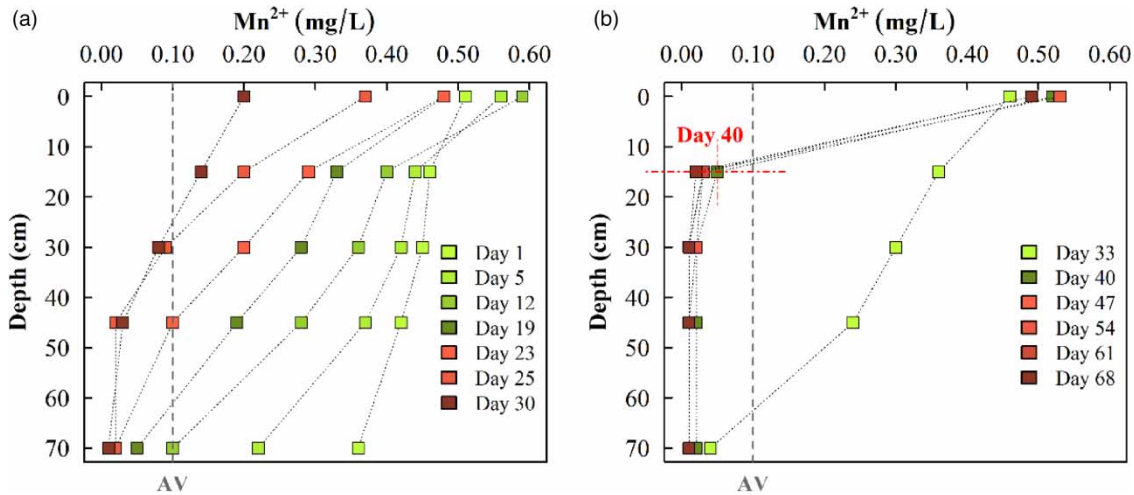


Figure 6 | Average Mn^{2+} concentration profiles over time in columns C3 and C4 in (a) recirculating flow regime and (b) after switching to flow-through regime. Vertical dashed line: acceptability threshold value (AV) for Mn stipulated in the local regulation (Decreto Ejecutivo No. 41499-S 2019). Standard deviation of Mn^{2+} concentration lower than 0.03 mg·L^{-1} in all points (error bars not shown). Please refer to the online version of this paper to see this figure in colour: http://dx.doi.org/10.2166/ws.2023.045.

two times a week; therefore, during 48–64 h of operation, the recirculated water did not contain Mn^{2+}. Therefore, the flow-through columns, through the experiment, registered a Mn-loading of about 0.16 kg $Mn{\cdot}m^{-2}$ in total (until day 8 of operation, $>$ 90% removal). During the recirculating flow experiment, the columns had a total Mn-loading of 0.11 $kg{\cdot}Mn{\cdot}m^{-2}$ to reach the 23 days of ripening time, comparable to the loading of the flow-through columns. The difference between both experiments was mainly associated with the intermittent provision of the Mn-loading in the recirculating regime in contrast with the continuous Mn-loading in the flow-through regime. It suggests that the total Mn-loading, in this case, 0.11 kg $Mn{\cdot}m^{-2}$, was a limiting factor during the start-up of the non-bioaugmented Mn biofilters.

Comparing the Mn^{2+} concentration profiles (Figures 3 and 6), it can be observed that flow-through columns reached $Mn^{2+} < 0.1$ $mg{\cdot}L^{-1}$ (compliance with the local drinking water criterion) at 15 cm depth in only 11 days, while recirculating filter columns required 32 days to reach $Mn^{2+} < 0.1$ $mg{\cdot}L^{-1}$ at 30 cm depth. The latter case was probably affected by the intermittent provision of the Mn-loading that impacted the MOB population at the top of the filter columns. The ripening of filter media gradually rises from the bottom to the top of the filter depth likely due to the accumulation of inorganic precipitates and biomass on top of filter media (Dangeti *et al.* 2017). Usually, filter ripening continues even when high Mn removal efficiencies have already been observed (Dangeti *et al.* 2017; Breda *et al.* 2019a).

Under the present conditions, inherent inoculation using a recirculating flow regime required more time for ripening than a flow-through regime. However, an advantage of the recirculating system is that it consumed less feed water. During the first 8 days of filter operation, the flow-through column registered a water consumption of 3.19 m^3, whereas the recirculating column consumed only 1.59 m^3 in the 23 days of filter operation (see estimations in Supplementary Material S3). It represents a water consumption reduction of approximately 50%, thus making it a suitable strategy for groundwater applications, where spillage of water should be minimized. However, there are still chances to improve the performance of the recirculating system. For example, Worch *et al.* (2002) applied the recirculating approach for the biodegradation of synthetic organic chemicals (SOCs) and found that the adaptation of microorganisms depended on the contact time with the SOCs. Thus, the authors recommended stimulating the microorganisms by maintaining the SOC concentration in the recirculated water. In that sense, a more frequent refreshment of water in T3 (e.g. 1.5 or 2 days) and/or even supplementing dissolved Mn^{2+} into the recirculated water could help to reduce the ripening time in the recirculating system.

4. CONCLUSIONS

This study aimed to investigate the influence of the flow regime (flow-through and recirculating) on the ripening time of virgin pumice media in non-bioaugmented biofilters. For this purpose, pilot-scale experiments using the same tropical groundwater (~23 °C) were performed to compare the start-up of flow-through and recirculating filter columns. The flow-through filter columns exhibited a Mn removal above 90% after 8 days of filter operation and reached Mn $<$0.1 $mg{\cdot}L^{-1}$ (compliance with the local drinking water criterion), whereas the recirculating filter columns registered a start-up of 23 days. These exceptional rapid start-ups were probably obtained due to the favorable feed water characteristics (temperatures ~22–24 °C, pH $>$ 7.5, DO $>$ 6 $mg{\cdot}L^{-1}$, redox potential (Eh) ~300–400 mV, and low Fe), and the initial filtration velocity of 2 m·h.

In addition, results suggest that inherent inoculation using the recirculating mode was less effective than using a flow-through regime in terms of the ripening time. However, an advantage of this operational strategy was that it consumed less feed water during the start-up (approximately 50%) than using a flow-through regime, making it still a suitable strategy for groundwater applications, where spillage of water should be minimized.

Finally, the start-up of the non-bioaugmented biofilters in both flow regimes was reached under comparable conditions, using the same feed water and adopting an initial low filtration velocity of 2 m·h. Both the flow-through and the recirculating flow regime required a similar total Mn-loading (0.16 and 0.11 $kg{\cdot}Mn{\cdot}m^{-2}$, respectively). In that sense, differences between the start-up periods through both regime flows could be attributed to the intermittent Mn-loading of the recirculating system. It seems that the intermittent Mn-loading impacted the MOB populations formed in the pumice stone medium during the start-up of biofilters operated in the recirculating flow regime. Therefore, it was concluded that the total Mn-loading, in this case, 0.11 $kg{\cdot}Mn{\cdot}m^{-2}$, was a limiting factor during the start-up of the non-bioaugmented Mn biofilters.

In summary, an optimal start-up protocol for recirculating flow regime should be: appropriate feed water characteristics, initial filtration velocity of 2 m·h (EBCT of 21 min); once the Mn removal reach 90%, velocity increase in steps of about 1 m·h until reaching a final filtration velocity of 5 m·h (~ EBCT of 8.4 min). Fe-loading should be prevented using a prefilter (Fe concentrations in the influent $<$0.10 $mg{\cdot}L^{-1}$).

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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, & WEF 2005 Metals by flame atomic absorption spectrometry. Extraction/air-acetylene flame method – 3111 C. In: A. Eaton, E. Rice & L. Clesceri (eds.) *Standard Methods for the Examination of Water and Wastewater*, 21st edn. American Public Health Association, American Water Works Association and Water Environment Federation, Washington, DC, USA, pp. 3.22.

Araya-Obando, J. A., Rietveld, L. C., Quesada-González, A., Caballero-Chavarría, A., Pacini, V. & Romero-Esquivel, L. 2021 Start-up of bench-scale biofilters for manganese removal under tropical conditions: a comparative study using virgin pumice, silica sand, and anthracite filter media. *Environmental Science: Water Research & Technology* **7** (8), 1504–1515. http://dx.doi.org/10.1039/D1EW00093D.

Araya-Obando, J. A., Pacini, V., Fernández, R. G. & Romero-Esquivel, L. G. 2022 Long-term monitoring of Mn and Fe removal in biofilters from a converted plant. *Water Supply* **22** (6), 6059–6069. https://doi.org/10.2166/ws.2022.209.

Börnick, H., Eppinger, P., Grischek, T. & Worch, E. 2001 Simulation of biological degradation of aromatic amines in river bed sediments. *Water Research* **35** (3), 619–624. https://doi.org/10.1016/S0043-1354(00)00314-6.

Breda, I. L., Ramsay, L. & Søborg, D. A. 2016 The role of backwash in start-up of full-scale drinking water biofilters. *Journal of Water Supply: Research and Technology-Aqua* **65** (3), 234–243. https://doi.org/10.2166/aqua.2016.093.

Breda, I. L., Ramsay, L., Søborg, D. A., Dimitrova, R. & Roslev, P. 2019a Manganese removal processes at 10 groundwater fed full-scale drinking water treatment plants. *Water Quality Research Journal* **54** (4), 326–337. https://doi.org/10.2166/wqrj.2019.006.

Breda, I., Søborg, D. A., Ramsay, L. & Roslev, P. 2019b Manganese removal processes during start-up of inoculated and non-inoculated drinking water biofilters. *Water Quality Research Journal* **54** (1), 47–56. https://doi.org/10.2166/wqrj.2018.016.

Bruins, J. H., Vries, D., Petrusevski, B., Slokar, Y. M. & Kennedy, M. D. 2014 Assessment of manganese removal from over 100 groundwater treatment plants. *Journal of Water Supply: Research and Technology-Aqua* **63** (4), 268–280. https://doi.org/10.2166/aqua.2013.086.

Bruins, J., Petrusevski, B., Slokar, Y. M., Huysman, K., Joris, K., Kruithof, J. C. & Kennedy, M. D. 2015a Biological and physico-chemical formation of Birnessite during the ripening of manganese removal filters. *Water Research* **69**, 154–161. https://doi.org/10.1016/j.watres.2014.11.019.

Bruins, J., Petrusevski, B., Slokar, Y. M., Huysman, K., Joris, K., Kruithof, J. C. & Kennedy, M. D. 2015b Reduction of ripening time of full-scale manganese removal filters with manganese oxide-coated media. *Journal of Water Supply: Research and Technology-Aqua* **64** (4), 434–441. https://doi.org/10.2166/aqua.2015.117.

Bruins, J., Petrusevski, B., Slokar, Y. M., Huysman, K., Joris, K., Kruithof, J. C. & Kennedy, M. D. 2017 Factors controlling the ripening of manganese removal filters in conventional aeration-filtration groundwater treatment. *Desalination and Water Treatment* **72**, 22–29. https://doi.org/10.5004/dwt.2017.0306.

Buamah, R. 2009 *Adsorptive Removal of Manganese, Arsenic and Iron From Groundwater*. PhD-Thesis, UNESCO-IHE Delft/Wageningen University, The Netherlands.

Buamah, R., Petrusevski, B. & Schippers, J. C. 2008 Adsorptive removal of manganese(II) from the aqueous phase using iron oxide coated sand. *Journal of Water Supply: Research and Technology-Aqua* **57** (1), 1–11. https://doi.org/10.2166/aqua.2008.078.

Cai, Y., Li, D., Liang, Y., Zeng, H. & Zhang, J. 2014 Operational parameters required for the start-up process of a biofilter to remove Fe, Mn, and NH_3-N from low-temperature groundwater. *Desalination and Water Treatment* **57** (8), 3588–3596. https://doi.org/10.1080/19443994.2014.986203.

Cai, Y., Li, D., Liang, Y., Luo, Y., Zeng, H. & Zhang, J. 2015 Effective start-up biofiltration method for Fe, Mn, and ammonia removal and bacterial community analysis. *Bioresource Technology* **176**, 149–155. https://doi.org/10.1016/j.biortech.2014.11.025.

Calderón-Tovar, I. L., Rietveld, L. C., Araya-Obando, J. A., Quesada-González, A., Caballero-Chavarría, A. & Romero-Esquivel, L. 2020 Autochthonous tropical groundwater bacteria involved in manganese(II) oxidation and removal. *Environmental Science: Water Research & Technology* **6** (11), 3132–3141. http://dx.doi.org/10.1039/D0EW00704H.

Cheng, Q. 2016 Competitive mechanism of ammonia, iron and manganese for dissolved oxygen using pilot-scale biofilter at different dissolved oxygen concentrations. *Water Supply* **16** (3), 766–774. https://doi.org/10.2166/ws.2015.190.

Ciancio, L., Piazza, A., Masotti, F., Pacini, V. A., Sanguinetti, G., Ottado, J. & Gottig, N. 2020 Manganese removal efficiencies and bacterial community profiles in non-bioaugmented and in bioaugmented sand filters exposed to different temperatures. *Journal of Water Process Engineering* **36**, 101261. https://doi.org/10.1016/j.jwpe.2020.101261.

Cooley, R. & Knocke, W. R. 2016 Low-temperature effects on the removal of soluble manganese in MnOx(s)-coated media systems. *Journal of Water Supply: Research and Technology-Aqua* **65** (8), 626–634. https://doi.org/10.2166/aqua.2016.077.

Dangeti, S., Roshani, B., Rindall, B., McBeth, J. M. & Chang, W. 2017 Biofiltration field study for cold Fe(II)- and Mn(II)-rich groundwater: accelerated Mn(II) removal kinetics and cold-adapted Mn(II)-oxidizing microbial populations. *Water Quality Research Journal* **52** (4), 229–242. https://doi.org/10.2166/wqrj.2017.006.

Decreto Ejecutivo No. 41499-S 2019 *Reforma y adición al Decreto Ejecutivo No.38924-S del 12 de enero del 2015, 'Reglamento para la Calidad de Agua Potable'*. Presidencia de la República y Ministerio de Salud, Costa Rica.

Donlan, R. M. 2002 Biofilms: microbial life on surfaces. *Emerging Infectious Diseases* **8** (9), 881–890. https://doi.org/10.3201/eid0809.020063.

Evans, A. N., Carter, J. T., Kuhnel, B. & Nystrom, V. E. 2021 Seasonal impacts on biofiltration acclimation dynamics and performance. *AWWA Water Science* **3** (3), 1–11. https://doi.org/10.1002/aws2.1225.

Granger, H. C., Stoddart, A. K. & Gagnon, G. A. 2014 Direct biofiltration for manganese removal from surface water. *Journal of Environmental Engineering* **140** (4), 04014006. https://doi.org/10.1061/(ASCE)EE.1943-7870.0000819.

Gude, J. C. J., Rietveld, L. C. & van Halem, D. 2018 Biological As(III) oxidation in rapid sand filters. *Journal of Water Process Engineering* **21**, 107–115. https://doi.org/10.1016/j.jwpe.2017.12.003.

Hu, P., Hsieh, Y., Chen, J. & Chang, C. 2004 Adsorption of divalent manganese ion on manganese-coated sand. *Journal of Water Supply: Research and Technology-Aqua* **53** (3), 151–158. https://doi.org/10.2166/aqua.2004.0013.

Lauderdale, C., Pope, G., Scheitlin, K., Zwerneman, J., Kirisits, M. J. & Woo, S. 2016 *Optimizing Filter Conditions for Improved Manganese Control During Conversion to Biofiltration. (No. #4448)*. The Water Research Foundation (WRF), Denver, CO, USA.

Li, D., Zhang, J., Wang, H., Yang, H. & Wang, B. 2005 Operational performance of biological treatment plant for iron and manganese removal. *Journal of Water Supply: Research and Technology-Aqua* **54** (1), 15–24. https://doi.org/10.2166/aqua.2005.0002.

Marsidi, N., Abu Hasan, H. & Sheikh Abdullah, S. R. 2018 A review of biological aerated filters for iron and manganese ions removal in water treatment. *Journal of Water Process Engineering* **23**, 1–12. https://doi.org/10.1016/j.jwpe.2018.01.010.

Mouchet, P. 1992 From conventional to biological removal of iron and manganese in France. *Journal AWWA* **84** (4), 158–167. https://doi.org/10.1002/j.1551-8833.1992.tb07342.x.

Pacini, V., Ingallinella, A. M., Vidoni, R., Sanguinetti, G. & Fernández, R. 2014 Transformation of an existing physicochemical plant for iron and manganese removal by the application of biological processes. *Journal of Water Supply: Research and Technology-Aqua* **63** (6), 507–517. https://doi.org/10.2166/aqua.2014.145.

Piazza, A., Ciancio, L., Pacini, V. A., Sanguinetti, G., Ottado, J. & Gottig, N. 2019 Environmental bacteria involved in manganese(II) oxidation and removal from groundwater. *Frontiers in Microbiology* **10** (119), 1–13. https://doi.org/10.3389/fmicb.2019.00119.

Ramsay, L., Breda, I. L. & Søborg, D. A. 2018 Comprehensive analysis of the start-up period of a full-scale drinking water biofilter provides guidance for optimization. *Drinking Water Engineering Science* **11** (2), 87–100. https://doi.org/10.5194/dwes-11-87-2018.

R Core Team 2021 *A Language and Environment for Statistical Computing*. The R Foundation for Statistical Computing, Vienna, Austria. Available from: http://www.r-project.org/.

Sahabi, D. M., Takeda, M., Suzuki, I. & Koizumi, J. 2009 Removal of Mn^{2+} from water by 'aged' biofilter media: the role of catalytic oxides layers. *Journal of Bioscience and Bioengineering* **107** (2), 151–157. https://doi.org/10.1016/j.jbiosc.2008.10.013.

Singer, P. C. & Reckhow, D. A., 2011 Chapter 7. Chemical oxidation. In: *Water Quality & Treatment: A Handbook on Drinking Water*, 6th edn. (Edzwald, J. K., ed.). McGraw-Hill Education, New York, NY, USA, pp. 7.1–7.52.

Štembal, T., Markić, M., Briški, F. & Sipos, L. 2004 Rapid start-up of biofilters for removal of ammonium, iron and manganese from ground water. *Journal of Water Supply: Research and Technology-Aqua* **53** (7), 509–518. https://doi.org/10.2166/aqua.2004.0040.

Tekerlekopoulou, A., Pavlou, S. & Vayenas, D. V. 2013 Removal of ammonium, iron and manganese from potable water in biofiltration units: a review. *Journal of Chemical Technology & Biotechnology* **88** (5), 751–773. https://doi.org/10.1002/jctb.4031.

Worch, E., Grischek, T., Börnick, H. & Eppinger, P. 2002 Laboratory tests for simulating attenuation processes of aromatic amines in riverbank filtration. *Journal of Hydrology* **266** (3), 259–268. https://doi.org/10.1016/S0022-1694(02)00169-5.

Zeng, H., Li, D. & Zhang, J. 2010 Rapid start-up of biofilter for removal of iron and manganese from groundwater. *Advanced Materials Research* **113–116**, 1316–1319. https://doi.org/10.4028/www.scientific.net/AMR.113-116.1316.

Zeng, H., Yin, C., Zhang, J. & Li, D. 2019 Start-up of a biofilter in a full-scale groundwater treatment plant for iron and manganese removal. doi:10.3390/ijerph16050698.

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