

Reduction of ripening time of full-scale manganese removal filters with manganese oxide-coated media

Jantinus H. Bruins, Branislav Petrusevski, Yness M. Slokar, Koen Huysman, Koen Joris, Joop C. Kruithof and Maria D. Kennedy

ABSTRACT

Effective manganese removal by conventional aeration-filtration with virgin filter media requires a long ripening time. The aim of this study was to assess the potential of manganese oxide-coated media to shorten the ripening time of filters with virgin media under practical conditions. A full-scale filter filled with virgin sand and a full-scale filter filled with anthracite/sand were operated at two groundwater treatment plants, in parallel with (full-scale) test filters, with an additional layer of manganese oxide-coated sand (MOCS) or manganese oxide-coated anthracite (MOCA). Significantly different ripening times were observed to achieve an effective manganese removal: 55 days for a filter with virgin sand and 16 days for a filter with virgin anthracite/sand. The observed differences could be attributed to different feed water quality, different iron loading, and backwashing intensity and frequency. In batch experiments fresh MOCA and MOCS showed good manganese adsorptive properties. Addition of a shallow layer of fresh MOCA in test filters eliminated the ripening time, while a layer of aged MOCS did not significantly shorten the ripening period. The poor performance of the aged MOCS was probably caused by changed properties of aged and dried MOCS, that had lost its adsorption capacity, auto-catalytic activity and biological activity.

Key words | filter media, filter ripening, groundwater treatment, manganese oxide coating, manganese removal

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INTRODUCTION

Worldwide, groundwater is the predominant source for drinking water production (UNEP 2008). In addition to naturally occurring compounds, such as Fe^{2+} , NH_4^+ , CH_4 , groundwater frequently contains dissolved manganese in excess of drinking water standards (Katsoyiannis *et al.* 2008), which should be removed for both health and aesthetic reasons. In some countries (e.g. the USA, and Central and Eastern Europe) an efficient manganese removal is commonly achieved by pre-oxidation with strong oxidants, such as O_3 , Cl_2 , ClO_2 , KMnO_4 , followed by rapid sand filtration. Use of strong oxidants for manganese removal is not desirable due to the potential formation of harmful oxidation by-products, as well as costs and risks associated with the usage and handling of chemicals. In some cases pre-oxidation is combined

with filtration through a filter bed with a manganese adsorbent, most frequently manganese green sand. This treatment can be very effective, but it requires continuous or intermittent regeneration typically with potassium permanganate (Knocke *et al.* 1991). In view of the above-mentioned disadvantages, the removal of manganese from groundwater in the Netherlands and Belgium is commonly achieved with conventional aeration-filtration treatment, also called contact filtration. Under common groundwater conditions (e.g. low pH), manganese removal may be initiated by bacterial activity during aeration-filtration (Diem & Stumm 1984; Burger *et al.* 2008). Aeration-filtration is efficient and cost effective, but in practice it is frequently associated with a number of drawbacks, such as the following:

- Very long ripening times of virgin filter media; several weeks to more than a year (Figure A1, Annex A, available online at <http://www.iwaponline.com/jws/064/117.pdf>) are required to achieve an efficient manganese removal (Cools 2010; Krull 2010).
- Occasional manganese breakthrough of filters may occur after some years of operation, requiring filter media replacement associated with additional costs for filter media disposal and replacement (Buamah *et al.* 2009a).

Ripening of filter media (for manganese removal) is defined as the development of properties to auto-catalytically adsorb and subsequently oxidise Mn^{2+} , without the use of strong oxidants, such as Cl_2 , O_3 and KMnO_4 .

From Figure A1 (Annex A), it can be seen that efficient manganese removal in a filter with virgin sand was not achieved until after almost 1 year of continuous filter operation. However, such a long ripening time is exceptional, typically it takes 1–4 months to achieve an efficient manganese removal.

Many authors (Hu *et al.* 2004a; Kim & Jung 2008; Kim *et al.* 2009) have described the potential of manganese oxide-coated sand (MOCS) to adsorb dissolved manganese from (ground)water. It was also reported that removal of Mn^{2+} in filters with anthracite is enhanced by development of ‘catalytic oxide layers’ on aged anthracite, due to formation of manganese oxide-coated anthracite (MOCA) (Sahabi *et al.* 2009). Buamah *et al.* (2008) have suggested that the performance of conventional manganese removal plants could be improved by introducing manganese and/or iron (hydro-)oxide-rich filter media into rapid sand filters.

The primary aim of the study reported in this paper was to examine if the long ripening time typically required to achieve an effective manganese removal with virgin filter media, in full-scale conventional aeration-filtration treatment plants, could be substantially reduced by addition of a MOCS or MOCA layer.

MATERIALS AND METHODS

MOCS and MOCA

The manganese oxide-coated filter media used in this research were obtained from two full-scale groundwater treatment

plants (GWTPs). MOCS was obtained from GWTP De Punt (water supply company, Groningen, Glimmen, The Netherlands), and MOCA was obtained from GWTP Grobbendonk (Pidpa water supply company, Antwerp, Belgium). It was shown that both MOCS and MOCA coatings contain a Birnessite type of manganese oxide (Bruins *et al.* 2015).

For all batch adsorption experiments and full-scale filter experiments fresh MOCA or MOCS were taken directly from an operating, ripened full-scale manganese removal filter. However, MOCS was stored in the open air for several months prior to the full-scale filter experiments.

Physical and chemical properties of MOCS and MOCA

Chemical composition of the MOCS and MOCA coating was determined by boiling the media in 3 M HNO_3 , followed by analysis for Fe, Mn, Ca, Si and Al with inductively coupled plasma mass spectrometry according to NEN-EN-ISO 17294-2 (NEN 2004).

The pH of point of zero charge (pH_{PZC}), i.e. the surface charge of coated filter media depending on structural deficits, unbalanced bonds and the presence of protons (Appelo & Postma 2005), was determined by a mass titration method (Fiol & Villaescusa 2009).

Batch adsorption experiments

To determine the MOCS and MOCA manganese adsorption capacity, batch adsorption isotherm experiments were carried out. Model water used in these experiments contained 1 mmol/L HCO_3^- and 2 mg/L Mn^{2+} in demineralised water; the pH was adjusted to 7 with 0.1 M HCl. The bottles containing model water and five different concentrations of either MOCS or MOCA in granular form were agitated on an Innova 2100 shaker at 100 rpm for 48 hours. Prior to measuring the final concentration of manganese, the samples were filtered through a 0.45 μm membrane filter, and acidified to preserve them for the analyses. The manganese concentration was measured, and results were plotted as a Freundlich adsorption isotherm.

The results obtained from the batch adsorption experiments of the two manganese-coated filter media were compared with those obtained with a commercial manganese adsorbent Aquamandix (Aqua-techniek, Hellevoetsluis, The Netherlands).

Full-scale filter runs (FRs)

Full-scale FRs were conducted at GWTPs where the manganese-coated filter media were obtained. In total, six different combinations of filter media were used (Figure 1). Two filters were operated at GWTP De Punt (Figure 1(A) and 1(B)), and the other four (Figure 1(C)–1(F)) at GWTP Grobbendonk.

Of the two filters at GWTP De Punt, one filter (Figure 1(A)) was filled with virgin quartz sand, commonly applied at this plant. This filter served as a reference filter. The second filter (Figure 1(B)) was filled with the same virgin sand; however, a 15 cm layer of sand was replaced by MOCS. The MOCS was aged and dried prior to use in the full-scale FR. Based on practical experience, the MOCS layer was placed at the level where manganese removal in ripened filters is observed at this facility.

The effect of the MOCA layer on the ripening of virgin filter media was studied at GWTP Grobbendonk. This plant utilises filters with dual media – anthracite and sand – which is how the reference filter was prepared (Figure 1(C)). In the other three (full-scale) test filters (Figure 1(D)–1(F)), part of the top anthracite layer was replaced by 10, 20 and

30 cm MOCA, respectively. MOCA was placed on the top of the anthracite layer, because at this level manganese removal is observed at this water treatment plant.

The composition of the feed water for the full-scale experiments at the two GWTPs is given in Table A1 (Annex A, available online at <http://www.iwaponline.com/jws/064/117.pdf>). At GWTP De Punt, groundwater was aerated prior to the test filters. At GWTP Grobbendonk the treatment consists of a first stage rapid sand filtration (aeration and biological adsorptive iron removal), a pH correction with milk of lime and a second stage dual media filtration. The feed water for the experiments at GWTP Grobbendonk was the water after pH correction.

From Table A1 (Annex A), it is evident that the feed water quality at the two test locations differed significantly. In particular the difference in water quality parameters that are known to influence manganese removal (Fe^{2+} , NH_4^+ concentrations, pH and redox potential) should be noted (Bruins *et al.* 2014).

Table A2 (Annex A, online at <http://www.iwaponline.com/jws/064/117.pdf>) depicts an overview of process design parameters and operational conditions applied during the test FRs at both locations. From this table, it is

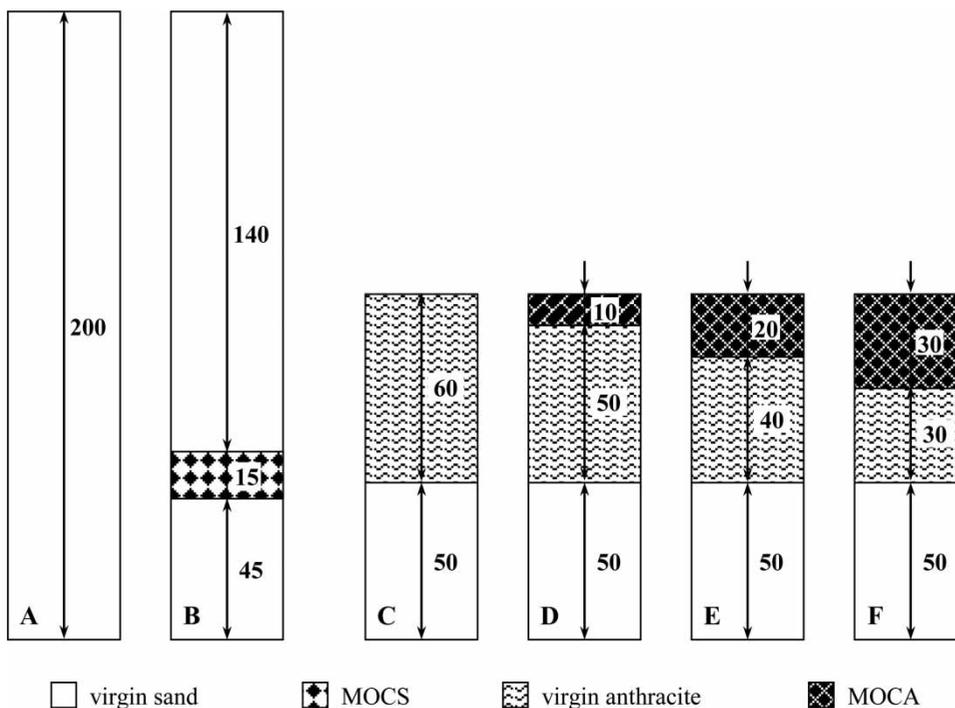


Figure 1 | Schematic presentation of filter media layers in the six full-scale filters included in the study (all values in cm).

evident that especially ‘Iron loading per FR’ is substantially different (De Punt: 2.5 kg Fe/m².FR and Grobbendonk: <0.1 kg Fe/m².FR). Iron loading is known to influence manganese removal (Bruins *et al.* 2014). In Table A3 (Annex A, online at <http://www.iwaponline.com/jws/064/117.pdf>) backwash procedures at both GWTPs are listed.

RESULTS AND DISCUSSION

Ripening of virgin filter media in reference filters

In Figure 2, the ripening times of the two full-scale reference filters filled with virgin sand (GWTP De Punt) and anthracite/sand (GWTP Grobbendonk) are shown.

As seen from Figure 2, the ripening time required to reach >90% manganese removal of the single media reference filter at GWTP De Punt was about 3.5 times longer (55 days) than that of the dual media reference filter at GWTP Grobbendonk (16 days). The observed difference was attributed to both the different feed water quality and the difference in applied operational conditions (e.g. backwashing pattern, intensity and frequency).

Effect of water quality parameters

It has been reported that ferrous iron competes with Mn²⁺ for adsorption sites on filter media (Hu *et al.* 2004a, b). Feed water at GWTP De Punt had a 50–150 times higher Fe²⁺

concentration than the GWTP Grobbendonk feed (Table A1, online at <http://www.iwaponline.com/jws/064/117.pdf>). At GWTP De Punt (in combination with a slightly lower feed water pH), the high Fe²⁺ concentration caused a more pronounced competition for available adsorption sites by Mn²⁺. It has been reported that the presence of iron hydro-oxide layers in the filter media coating could support the Mn²⁺ adsorption (Buamah 2009). However, iron hydro-oxide has a much lower Mn²⁺ adsorption capacity than manganese (hydro-)oxides (Buamah *et al.* 2008). Therefore, formation of iron hydro-oxide layers in the filter bed zone where manganese is removed should be prevented in practice.

The feed water concentration of Fe²⁺ also determines an important operational condition for manganese removal, i.e. iron loading per FR. Feed water at GWTP De Punt contained a significantly higher Fe²⁺ concentration, resulting in much higher iron loading per FR than at GWTP Grobbendonk (2.5 and <0.1 kg Fe/m², respectively). In addition, this much higher iron loading at GWTP De Punt required approximately four times more frequent backwashing than at GWTP Grobbendonk. Backwashing results in a partial removal of MnO_x from the coating, while the presence of MnO_x is essential for an effective manganese removal. Intensive backwashing can also cause a substantial removal of the biological activity (e.g. by removal of bacteria from filter media), which may play an important role in the process of manganese adsorption and oxidation (Vandenabeele *et al.* 1992; Katsoyiannis & Zouboulis 2004; Tebo *et al.* 2004). Partial loss of MnO_x and biological activity is even more pronounced for backwashing with combined water and air flushing. Both the frequency and intensity of the backwashing at GWTP De Punt were more detrimental for the filter media, resulting in a longer ripening time of the filters at this location.

Another water quality parameter playing an important role in manganese removal is the pH. To achieve an effective manganese removal the pH should preferably be above 7.1 (Bruins *et al.* 2014). In general, the higher the pH, the better the manganese removal. From the pH values of feed water at both GWTPs it can be concluded that Grobbendonk water (pH 7.5–7.6) provided slightly better conditions for an effective manganese removal than GWTP De Punt water (pH 7.3–7.5).

NH₄⁺ removal efficiency is another parameter that shows a strong positive correlation with manganese removal

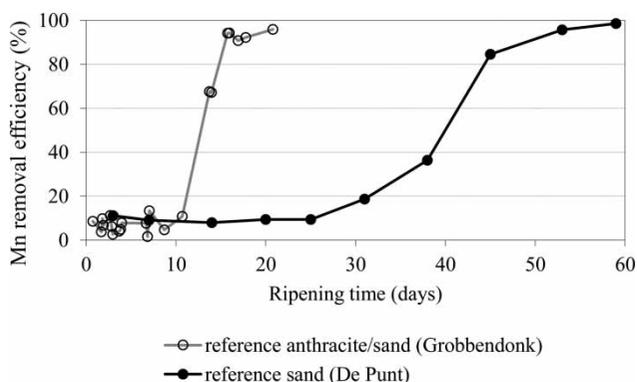


Figure 2 | Comparison of the Mn removal efficiency (%) as a function of the filter ripening time for the two reference full-scale filters: (virgin) anthracite/sand, at GWTP Grobbendonk (pH: 7.5 to 7.6; redox potential: +200 to +300 mV; filtration rate: 5.0 m³/m².h) and (virgin) sand, at GWTP De Punt (pH: 7.3 to 7.5; redox potential: –50 to +50 mV; filtration rate: 4.8 m³/m².h).

(Bruins *et al.* 2014). The presence of NO_2^- (due to incomplete NH_4^+ removal) may not only prevent effective Mn^{2+} removal, but may even cause manganese leaching, by reducing already adsorbed and oxidised MnO_x back to Mn^{2+} (Vandenabeele *et al.* 1995). The NH_4^+ concentration in the filtrate of the two filters at GWTP De Punt was substantially higher than at GWTP Grobbendonk especially during the filter start-up, which could explain the much longer ripening time of filters at the De Punt location.

Finally, oxidation of (adsorbed) manganese takes place more easily at a higher redox potential (Stumm & Morgan 1996; Scherer & Wichmann 2000; Flemming *et al.* 2004). The redox potential of the feed water at GWTP De Punt was much lower compared to that of the feed water at GWTP Grobbendonk ($-50/+50$ mV and $+200/+300$ mV, respectively), partly caused by the presence of NH_4^+ in the filtrate, which was much higher at the De Punt location. As a consequence, even if Mn^{2+} was adsorbed it was not as effectively oxidised and therefore possibly desorbed, resulting in a longer ripening time at the De Punt location.

Although the feed water quality at both locations is suitable to achieve effective manganese removal in a conventional aeration-filtration system once the filters are ripened, the conditions to achieve shorter filter ripening times were found to be more favourable at the Grobbendonk location.

In summary, much faster ripening of virgin filter media with respect to complete manganese removal at GWTP Grobbendonk can be attributed to the combined effect of the following parameters crucial for manganese removal:

- More favourable feed water quality (lower Fe^{2+} and NH_4^+ concentrations, higher pH and redox potential).
- More favourable operational conditions (lower iron loading per FR, lower backwash frequency and intensity).

MOCS and MOCA characterisation and batch adsorption experiments

Table A4 (Annex A, available online at <http://www.iwaponline.com/jws/064/117.pdf>) depicts the physical characteristics of MOCS, MOCA and Aquamandix (AQM), and coating composition of MOCS and MOCA.

From Table A4 (Annex A) it can be seen that the grain size of MOCA is considerably smaller than that of MOCS.

As a consequence, MOCA has a larger geometric surface area, enhancing the adsorption capacity. Another characteristic indicating a better adsorption capacity of MOCA is the coating composition. The most pronounced difference in chemical composition of the two media is the iron content. Iron is present as iron (hydro-)oxide, whereas manganese is present as manganese oxide (MnO_x). Although both oxides can absorb Mn^{2+} , iron (hydro-)oxide has a significantly lower manganese adsorption capacity (Buamah *et al.* 2008). Therefore, it was expected that MOCA with a more than 70 times lower iron content, would adsorb Mn^{2+} better. On the other hand, the pH_{PZC} of MOCS was significantly lower compared to MOCA. This suggests that MOCS will have better adsorptive properties over a wider pH range for positively charged ions such as Mn^{2+} .

In Table 1, the Freundlich adsorption isotherm constants for manganese adsorption on MOCS, MOCA and AQM are given.

From Table 1 it can be seen that manganese adsorption capacities, q_e expressed per unit weight of adsorbent (ads.), for MOCS and MOCA are very different (0.132 mg/g ads. and 0.276 mg/g ads., respectively, at C_e of 0.2 mg/L Mn^{2+}). When expressed per unit volume, however, adsorptive capacities of MOCS and MOCA were found to be similar (0.155 mg Mn^{2+} /L and 0.179 mg Mn^{2+} /L of MOCS and MOCA, respectively, at C_e of 0.2 mg Mn^{2+} /L). A much higher adsorption capacity per volume of adsorbent was found for AQM. However, this commercial adsorbent has no auto-catalytic oxidation properties, thus once the adsorption capacity is exhausted, manganese removal stops (Buamah 2009).

Based on the adsorption capacities, q_e , reported in Table 1, the (calculated) theoretical manganese adsorption capacities of the MOCS and MOCA layers, placed in the full-scale test

Table 1 | Freundlich adsorption isotherm constants for Mn^{2+} adsorption on MOCS, MOCA and AQM

Constant	Adsorbent		
	MOCS	MOCA	Aquamandix (AQM)
K [(mg/g)/(mg/L)]	0.45	0.91	0.90
$1/n$	1.31	1.34	1.38
r^2	0.91	0.91	0.96
q_e (mg/g) at $C_e = 0.2$ mg/L	0.132	0.276	0.280
q_e (g/L) at $C_e = 0.2$ mg/L	0.155	0.179	0.560

filters are calculated (Table A5, Annex A, online at <http://www.iwaponline.com/jws/064/117.pdf>). This table also shows the expected operational times of the filters before manganese breakthrough, assuming that adsorption was the only manganese removal mechanism ignoring the catalytic effect associated with adsorption and oxidation of adsorbed manganese. For a 15 cm MOCS layer (De Punt), the Mn^{2+} adsorption capacity is approximately 0.29 kg, with an expected breakthrough after 24–48 hours, whereas these values for a 10 cm layer of MOCA (Grobendonk) are respectively 0.67 kg Mn^{2+} and breakthrough also after 24–48 hours.

Ripening of full-scale filters with the addition of MOCS and MOCA layers

Manganese removal during the ripening time of the two full-scale filters at GWTP De Punt are shown in Figure 3(a). Based on batch adsorption experiments conducted with fresh MOCS (Table 1 and Table A5, Annex A), it was expected that the MOCS layer in the full-scale filter would effectively remove Mn^{2+} at least during the first 24–48 hours. However, the addition of 15 cm of MOCS did not have a significant impact on the ripening time of the filter with respect to the manganese removal. The reason for the poor Mn^{2+} removal is probably attributed to the difference in adsorptive properties of MOCS used in the batch adsorption experiments (freshly taken from a running ripened filter), and in the FRs (dried and stored for several months before use). The layered structure of Birnessite may have irreversibly collapsed, decreasing the number of available adsorptive sites (Post

1999). Furthermore, long exposure to air may have resulted in (complete) oxidation of the auto-catalytically active Birnessite into not auto-catalytically active Pyrolusite (MnO_2). Storage of the MOCS could also have resulted in a loss of biological activity (e.g. by dying of bacteria present on MOCS), which may play an important role in initiating oxidation of manganese adsorbed on filter media (Vandenabeele *et al.* 1992; Katsoyiannis & Zouboulis 2004; Tebo *et al.* 2004). Drying and storage of the MOCS used in the full-scale filter most probably caused loss of a substantial part of its original adsorption capacity. Besides, it is most likely that the stored MOCS had lost its auto-catalytic and biological activity.

In Figure 3(b), the results of the experiments with four full-scale test filters at GWTP Grobendonk are shown. At this location the filter ripening time of the reference anthracite/sand filter was compared to the ripening times of three test filters containing MOCA layers of different thicknesses (Figure 1(D)–1(F)).

Results obtained with the test filters containing a layer of MOCA showed a very high (>90%) manganese removal from the start of the FR, irrespective of the thickness of the MOCA layer. As a comparison, the manganese removal efficiency in the reference filter without a MOCA layer was approximately 10% during the first 10 days of operation.

Assuming that the manganese removal in the test filters was achieved only by adsorption on MOCA, the filter with a 10 cm layer should display breakthrough after 24 hours of filter operation (Table A5). However, no breakthrough was observed during more than a month of continuous operation of the test filters, most probably due to the presence of

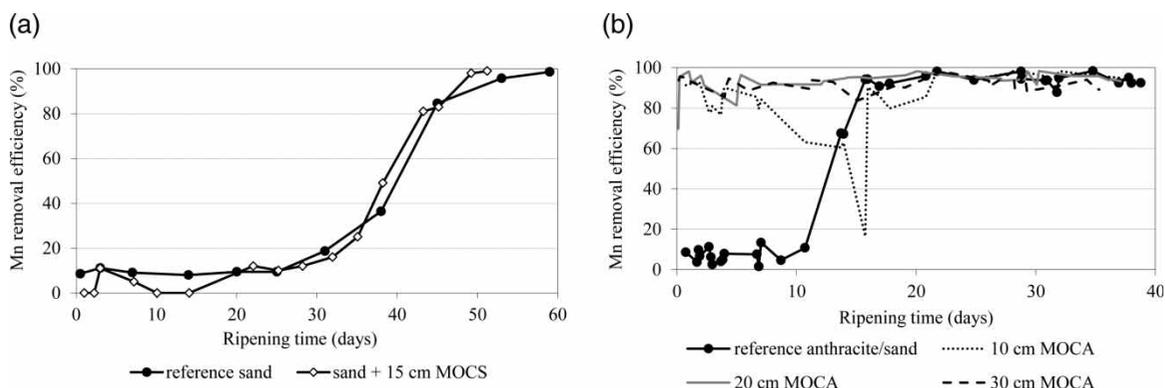


Figure 3 | Mn removal efficiency (%) as a function of the ripening time of two (full scale) test filters at GWTP De Punt (a) – (pH: 7.3 to 7.5; redox potential: –50 to +50 mV; filtration rate: $4.8 \text{ m}^3/\text{m}^2\cdot\text{h}$) and four full-scale test filters at GWTP Grobendonk (b) – (pH: 7.5 to 7.6; redox potential: +200 to +300 mV; filtration rate: $5.0 \text{ m}^3/\text{m}^2\cdot\text{h}$).

Birnessite and/or manganese oxidising bacteria in the fresh MOCA, promoting auto-catalytic oxidation, resulting in the immediate formation of a new active MnO_x layer.

After about 2.5 days and in particular after 15 days of operation, a decrease in manganese removal efficiency was observed for the test filter with a 10 cm layer of MOCS. The reason was an operational malfunctioning, caused by a poor distribution of the feed water over the filter surface. In addition, the feed water jet disrupted the top of the MOCA layer, locally thinning the layer to less than 10 cm. As soon as the MOCA layer was restored by a gentle backwash, manganese removal efficiency was re-established.

Based on the results depicted in Figure 3(b), a 10 cm layer of fresh MOCA is sufficient to achieve an efficient manganese removal from the start of a new filter. However, to prevent practical problems (e.g. short circuiting), it is recommended that a MOCA layer of at least 20 cm thickness be applied.

Comparing the results of the full-scale test filters with an added MOCS (Figure 1(B)) and MOCA layer (Figure 1(D)–1(F)), a poor ripening of filters containing MOCS and a fast ripening of filters containing MOCA were observed. The major reason for the poor results achieved with the MOCS layer in a filter was probably, as explained above, attributed to the use of aged (dried) MOCS. The difference in performance could also be caused by the different feed water quality (e.g. redox potential, NH_4^+ removal, pH), difference in MOCS and MOCA composition (coating Fe content) and different operational conditions applied (grain size of MOCS is approximately double that of MOCA, and Fe^{2+} loading and backwashing pattern and frequency were significantly different).

To summarise, this research showed that fresh manganese oxide-coated filter media were able to shorten the filter media ripening time substantially. Drying the MOCS has affected the results dramatically. In addition differences may have been caused by water quality as well as operational conditions. These phenomena must be investigated in more detail under comparable conditions, emphasising also the role of microbiology and the importance and influence of specific bacteria.

CONCLUSIONS

The ripening time required to achieve complete manganese removal with (reference) full-scale filters with virgin sand

and virgin anthracite/sand filter media at two GWTPs – De Punt (The Netherlands) and Grobbendonk (Belgium) – was found to be 55 and 16 days, respectively.

Differences in duration of ripening times between filters of the two GWTPs are caused by a combination of factors including the different composition of feed water (pH, redox potential, concentration of Fe^{2+} and NH_4^+), applied process design and operational conditions (e.g. iron load, intensity and frequency of backwashing, and physical properties and composition of virgin filter media).

Batch adsorption experiments demonstrated that both (fresh) MOCS and (fresh) MOCA adsorb Mn^{2+} . Based on Freundlich adsorption isotherm measurements, the manganese adsorption capacity (q_e) expressed per unit weight of adsorbent of MOCA was approximately twice the capacity of MOCS. However, when expressed per unit volume of adsorbent, which is more relevant for a practical application, the manganese adsorption capacities of MOCA and MOCS were similar. The adsorption capacity of commercial manganese adsorbent (AQM), expressed per unit volume, was found to be approximately three times higher.

Aging and drying of MOCS, most probably resulted in the loss of manganese adsorption capacity. Besides, drying of MOCS may have caused the loss of auto-catalytic activity by changes in its structure and complete manganese oxidation. Finally, the biological activity may have been lost.

The ripening time of a full-scale filter with virgin anthracite/sand filter media, before reaching an effective manganese removal at GWTP Grobbendonk, of typically 16 days could be eliminated if a 0.10–0.30 m deep layer of fresh MOCA were to be placed on top of the virgin anthracite/sand filter bed. Because of operational aspects, it is advisable to apply a MOCA layer with a thickness ≥ 0.2 m.

In follow-up research, based on the results obtained from this study, the effect of water quality and operational conditions, as well as the role of microbiology on filter media ripening, will be investigated in more detail under comparable conditions.

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