Filtration and manganese removal

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ABSTRACT

Manganese removal through a filter bed is generally carried out and accepted by practitioners and researchers as occurring through catalytic oxidation at the surface of MnO_2 coated media, although manganese passage through a coated media filter has been little investigated. To better understand the kinetics of Mn removal through a naturally coated filter, a pilot plant consisting of four filter columns packed with various sand and coal media was used to investigate manganese removal using different chlorine species, viz. chlorine, calcium hypochlorite and sodium hypochlorite, in water of pH 6.6–8.0. Outcomes of the investigation were a clearly observed association of the bulk of Mn removed with the build-up of carbonaceous material in the filter column, and the observation that while Mn was removed through the filter column, 75–85% of such removal took place in the top 20–40 mm of the media column of 0.9–1.0 m overall depth. This investigation suggests that commonly held beliefs regarding the design of catalytic filters should be revisited and the actual removal mechanisms contributing to the overall removal be reassessed. Considerable savings in operation/pre-conditioning of filters may be possible with an improved understanding of the Mn removal through the filter column.

Key words | catalysis, chlorine, filtration, greensand, manganese removal

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INTRODUCTION

The removal of soluble manganese in a water treatment plant (WTP) is commonly attempted by dosing chlorine into the treated water stream just before it enters the filter cell (Faust & Aly 1983). This process has been termed by Knocke et al. (1988, 1990) as a modified manganese greensand process, or as it is colloquially referred to among those in the water industry as catalytic filtration of manganese.

The underlying assumption in the modified greensand process is that naturally occurring soluble manganese is adsorbed onto the filter media and oxidized at the surface, in the presence of a chlorine residual. This yields an active MnO_x layer on the media, that will adsorb and oxidize further Mn species, thereby adding potential for increasing capacity to *catalyse* further oxidation and removal of Mn(II) species. As distinct from the synthetic greensand process, where the media is deliberately coated with MnO_2, the modified process requires no initial manganese addition as the process is self-seeding (Knocke et al. 1988; Carlson &

Knocke 1999). The aim of the project was not to determine how much catalytic activity was or was not occurring, but rather to gain a better understanding of the fate of Mn species throughout the filtration process under different sets of operating conditions for unconditioned media, i.e., no deliberate pre-coating of the media with manganese oxide species.

In a report to the American Water Works Association Research Foundation (AwwaRF) on this process, Knocke et al. (1990) summarised five important conclusions from their investigations:

1. The ability of Mn oxide-coated media to adsorb Mn(II) is a function of surface oxide concentration and of pH.
2. Oxide surface uptake of Mn(II) ions is first order in rate.
3. There is no auto-oxidative reaction between the oxide surface and adsorbed Mn(II) below pH of 9 in the absence of chlorine.

4. In the presence of chlorine, oxidation of Mn(II) takes place at the oxide surface, but not in the pre-filter water.
5. For a number of WTPs, the presence of surface manganese oxide deposits appears not to change the characteristic behaviour of the filter media.

Most of Knocke *et al.*'s work, and certainly that leading to the conclusions noted above, was, however, carried out with lower pH water (typically in the range 5–6.5), in which chlorine oxidation of Mn(II) is, if it takes place, very slow (White 1972). At these pH values, Hargette & Knocke (2001) claim that manganese removal in the presence of chlorine is due to Mn(II) surface adsorption followed by catalytic oxidation on the MnO_x surface. More recent work by this group of workers has shown that for both coal and sand media, desorption and sequestration of manganese can take place (Gabelich *et al.* 2006). Attempts to identify the nature of the manganese-containing deposit have met with limited success (Cerrato *et al.* 2010). Further findings, in what has been a detailed and comprehensive study by Knocke and co-workers, are more completely reviewed by Chiswell & Huang (2006).

Although not seen in the pre-filter water in the work described above, we believe that at pH >7 the chlorine may lead to Mn(II) oxidation in solution, followed by precipitate formation which is then captured on the filter media. If this occurs, the possibilities of catalytic oxidation will be substantially reduced. It would appear likely from the results described here, that both precipitation and catalytic oxidation of manganese may occur simultaneously depending upon the pH of the water, with precipitation predominating as pH is raised above 7.1.

In the work described here, we have undertaken pilot plant studies on manganese removal on various coal and sand filter media using three different chlorine species, viz. chlorine, calcium hypochlorite and sodium hypochlorite. We have also used treated waters with pH values in the range of 6.8–7.4, which we believe are more commonly encountered in contemporary WTPs, and are values somewhat higher than those present in Knocke's work.

The aim of this section of the investigation was to examine the abiotic process in detail and determine whether manganese removal efficiency was affected by different media, commonly used in WTPs, and by the species of chlorine added, using a pilot plant that approximated closely to a

full scale WTP. Of the four test columns, one was always retained as a control.

MATERIALS AND METHODS

The pilot plant, located at the Mudgeeraba WTP on the Gold Coast, Queensland, Australia, was based on a conventional WTP, and consisted of four filters each approximately 5 m tall and 100 mm in diameter, and containing a filter bed depth of 0.9–1.0 m. Filter columns were operated at constant head and constant flow with loadings between 8 and 10 m/hour through each column. These conditions were controlled by maintenance of column overflow and use of a proportional outlet valve. The configuration of the pilot columns has demonstrated strong correlation with full scale performance following adoption of the recommendations from these studies at Gold Coast WTPs.

Two different filter media protocols were used:

1. Media #1 protocols (initial experimental runs with chlorine in all columns), in which filter 1 contained sand of 0.7 mm nominal size, filter 2 contained 1.25 mm coal and filters 3 and 4 contained 1.33 mm coal. These media are commonly used in filtration plants.
2. Media #2 protocols, in which all previous filter media were removed from the columns, the filters cleaned, and all four filters filled with 1.33 mm coal.

Media #1 runs allowed comparisons to be drawn between the performance of sand and coal of different sizes, while Media #2 runs allowed filter 1 to be used as a control, while filters 2, 3 and 4 were dosed with three different chlorine species, viz. chlorine, calcium hypochlorite and sodium hypochlorite.

The 'dose water' used as the feed for the pilot plant originated from the clarifier launder of an operating full scale WTP by use of a small pump placed in the clarifier launder. This water underwent typical preliminary treatment with the addition of lime, polyelectrolyte and aluminium sulphate coagulant to remove colour and settle some solids. Turbidity, pH and true colour for this dosed water were as recorded for the full scale plant on SCADA and manually sampled at the top and bottom of each column and measured with a hand-held pH meter and the operating

plant's laboratory spectrophotometer. The turbidity of dosed water was normally between 0.4 and 2 NTU and true colour <7 PtCo. The feed water entered the pilot plant columns approximately 30 cm from the top of the filters, with a detention time between addition and top of the media of 39 min. Three runs were carried out with a detention time shortened to 2.6 min via a deeper injection into the column, to test sensitivity to reaction rates for oxidation, coagulation and flocculation on Mn removal rates. Filtered water from the bottom of the filters flowed into a balance tank containing a flow control device. Sample points were located at 180 mm above media and 20, 220, 420, 620 and 820 mm below the top of the media down the column. Pressure sensors were also located at 20, 420 and 820 mm depths through the filter media to determine head loss profiles. Figure 1 shows a schematic diagram of the pilot plant column.

Sampling of all online filters occurred at regular intervals each day; typically, one set in the morning and one in the afternoon for periods of 1 to 5 days of continuous operation. Samples were collected from each filter and analysed, on site, for pH, turbidity, colour and chlorine residual. The samples were then filtered through 0.45 μm membranes, stored in 15 mL flasks containing 1 mL of 5 M nitric acid and sent to the Gold Coast Water (GCW) laboratory or Entox for manganese analysis. All results shown in this work were analysed using carbon furnace atomic absorption spectrometry with a detection limit of 0.001 mg/L Mn at GCW or by inductively coupled plasma mass spectrometry with a detection limit of 0.0001 mg/L at EnTox. The ambient temperature range tested was 19–25 °C.

Chlorine solutions

Sodium hypochlorite

Operational parameters were initially determined using sodium hypochlorite as the chlorine species, with the Media #1 protocol. Sodium hypochlorite solution was dosed into each of the filters, with three different concentrations being

Figure 1 │ Schematic of pilot plant.

used: 3, 4 and 5 mg/L chlorine. After determining the chlorine demand through the filter for each dose concentration, 5 mg/L chlorine was chosen as the standard chlorine concentrations to be dosed for Media #1; later work using Media #2 protocol used a dosing concentration of 4 mg/L chlorine, to more closely approximate that used in practice.

Gaseous chlorine and calcium hypochlorite

Both were dosed in aqueous solution at concentrations of 5 mg/L (Media #1 protocol) or 4 mg/L chlorine (Media #2 protocol). Gaseous chlorine solution was taken from the chlorine dosing line for filtered water disinfection of the full scale plant and placed in a 20 litre batch tank for dilution and dosing via a positive displacement metering pump. Chlorine residual was determined using a DPD kit provided at the WTP laboratory. Calcium hypochlorite was prepared using 68% dry chlorine powder dissolved in a 20 litre batch dosing tank, while sodium hypochlorite was prepared from a 12% liquid diluted to provide the required batch concentration.

The batch concentration for chlorine dosing required approximately 5 g/L free chlorine concentration for the dosing pumps to deliver the necessary residual chlorine levels. A new batch was necessary prior to each trial run given the losses experienced over each run. Most runs were supervised throughout and adjustments made to the dosing based on residual chlorine measurements in the filtered water.

Manganese

Manganese chloride (LR grade) solution of the required concentration was prepared as a batch solution and dosed into the feed water to the filter at a point upstream in the feed pipe to provide at least 1 min hydraulic retention time prior to chlorine dosing. Filterable manganese dose concentrations ranged between 0.1 and 0.5 mg/L based on filtration through a 0.45 μm filter.

Graphical presentation and statistical methods

A large number of filter runs have been incorporated into single graphs to both summarise and emphasise the more important results, and to reduce the volume of data obtained. It should be kept in mind that a total of 16 runs was undertaken, and that the number of analysis results for manganese alone was of the order of >1,100. The number of individual results (N) for a given parameter is shown along the x-axis of the graphs, as are the six bed depths (viz. 180 mm above filter bed, and 20, 220, 420, 620 and 800 mm from surface) for sampling. Each graphical box plots the minimum, interquartile range, median and maximum on the y-axis parameter, while outliers are identified by circles and extremes are shown by an asterisk.

For all statistical analyses comparing the effect of a particular factor (e.g., chlorine species, bed depth, filter media, etc.) on the manganese removal efficiency of the filter, the General Linear Model (GLM) Repeated Measures procedure has been used (Rao 1998).

Hypotheses

The hypotheses tested were as follows:

1. The chlorine residuals down through both sand and coal media are not different.
2. The chlorine residual through the filter bed is not different when dosing with different chlorine species.
3. The manganese removal efficiency of the filter bed is not different when dosing with different chlorine species.
4. The manganese removal efficiency of the filter bed is not different at different sample depths.
5. Retention time between water entering the filtration column and reaching the media has no effect upon manganese removal.

RESULTS AND DISCUSSION

pH and temperature changes

Statistical analysis of results of monitoring of ambient temperature (18–24 °C) and pH (6.8–7.4) of influent and effluent waters indicated that there was no statistically significant change in either parameter during the experiments conducted upon the adsorption columns of the pilot plant under the selected set of operating conditions (results not shown).

Chlorine loss through media

Figure 2 illustrates chlorine decay through both sand and crushed coal media. It is apparent that filter coal reacts with chlorine significantly more than does the sand; the results for the sand media indicating that it is not soluble carbon present in the feed water that is reacting. This result has been observed previously by Eley & Nicholson (1993), although little work appears to have been undertaken on the nature of chlorinated organic species that may be formed from the coal. This marked chlorine removal during passage through the coal column is in line with our contention that manganese removal due to addition of chlorine occurs close to the top of the filter or either sand or coal. Thus, some chlorine chemical input facilitates such initial removal, but at least some subsequent chlorine interaction is with species other than manganese, as seen in the coal column, but not for the sand. The rapid reaction of aqueous chlorine (hypochlorous acid) with activated carbon has been previously documented by Snoeyink *et al.* (1982). These workers found that in the presence of carbon, adsorbed humic substances produced less chloroform per unit mass of HOCl than in the absence of activated carbon, indicating, as we have found, that the chlorine is reacting with the carbon. Snoeyink *et al.* (1982) do not report on any chlorinated

products formed by this interaction; our work, also, did not lend itself to analysis of any such products.

The percentage of chlorine remaining at the different depths of the filter bed is not significantly different for the three chlorine species used; this is clearly seen by the results presented in Figure 3. As might be expected, however, the higher the dose concentration of chlorine, the greater is its penetration down the column. This is clearly seen by reference to Figure 4 showing cumulative chlorine removals down the coal media columns for sodium hypochlorite dosing regimes. It is obvious that chlorine removal by reaction with the coal media is occurring. These results were obtained using Media #2 protocol.

Manganese removal

The study of manganese removal upon the addition of various species of chlorine used yielded interesting results once statistical analysis was applied to the large amount of data obtained. The benefit of using such an approach is evidenced in the results shown in Figure 5 for the percentage of manganese remaining in solution down filter 1 containing sand when dosed with the three different species of chlorine.

The analysis shows that the percentage of total manganese remaining in solution for the sand filter 1 is
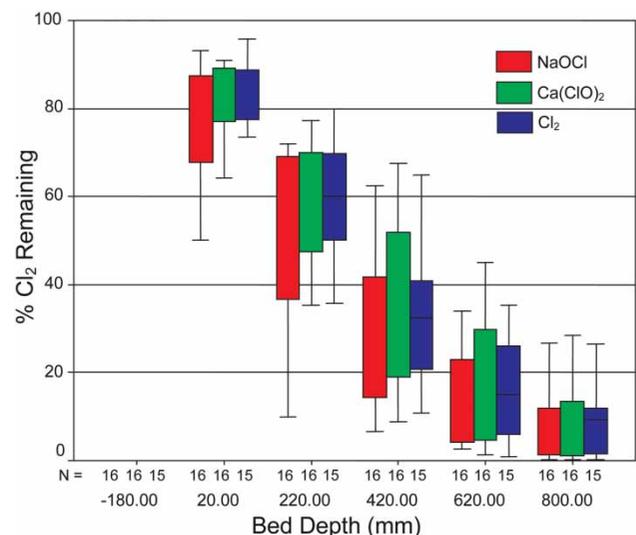
Figure 2 | Percentage chlorine remaining through the filter column using Media #1 protocol; filter #1, 0.7 mm sand; filter #3, 1.33 mm coal.

Figure 3 | Percentage chlorine remaining down filter bed using Media #2 protocol (coal) when dosing with various chlorine species (4 mg/L).
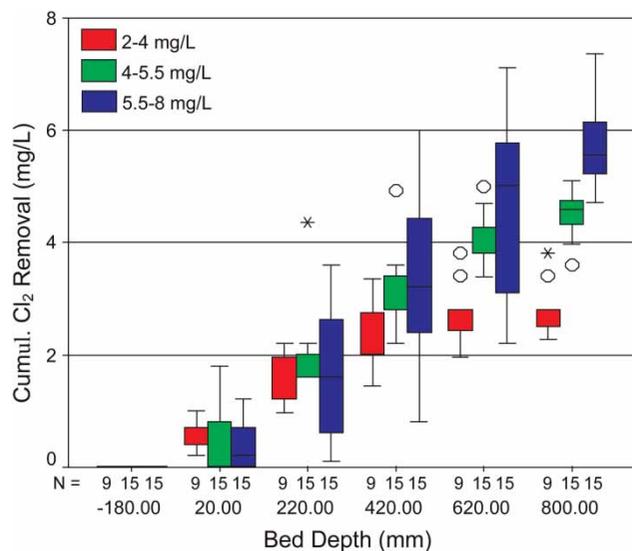
Figure 4 | Cumulative chlorine removal with bed depth using Media #2 protocol for 1.33 mm coal with addition of various concentrations of sodium hypochlorite.
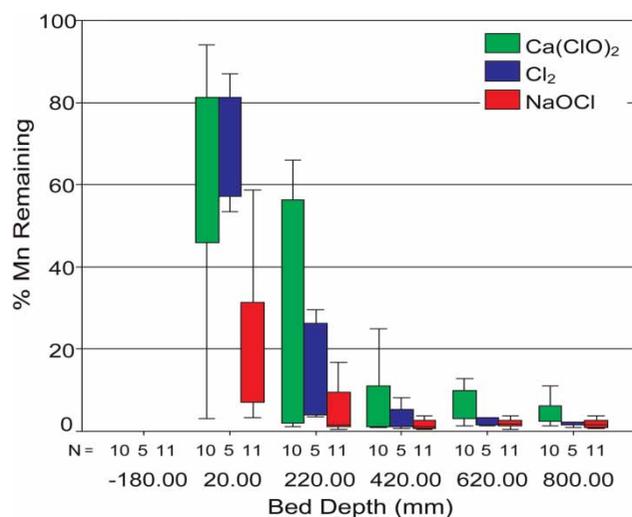

Figure 5 | Percentage of Mn remaining in filter 1 (sand) against bed depth when dosing with various chlorine species (5 mg/L); initial Mn concentration 0.1–0.4 mg/L.

significantly different at the different bed depths and significantly very different when dosing with different chlorine species. The range of analyses indicated that initial manganese concentration (0.1–0.4 mg/L) and initial chlorine concentration (4–5 mg/L) do not have an effect on the percentage of manganese remaining (data not shown). It is obvious that manganese removal is greatly enhanced using sodium hypochlorite when compared with the removal achieved by either chlorine gas solution or calcium

hypochlorite solution. Any initial judgement might then suggest that chlorine gas is more effective than is calcium hypochlorite, but upon further study of the results shown in Figure 5, this is only likely to be true at the final two deepest bed depths, where the % Mn remaining in solution is very low.

What is clear is that:

1. sodium hypochlorite removes manganese much more rapidly than either of the other two chlorine compounds;
2. all three chlorine compounds will remove soluble manganese on the sand filter, given enough bed depth; even calcium hypochlorite will reduce an input level of 0.4 to approximately 0.02 mg/L.

Visual observation of the black deposits at the top of the filter column supports the view that manganese oxide formation when using sodium hypochlorite is very rapid (Kim & Jung 2008). We surmise that the very high pH of this liquid chlorine (approximately 13) at the point of the injection plume leads to extremely rapid formation of manganese oxides upon interaction with the solution above the filter media; effectively, it is the sodium hydroxide present in this solution which is promoting manganese oxide deposition. Even though no marked increase in pH could be measured in the dosed water solution above the media, we believe that the microenvironment at the injection plume raises the pH sufficiently to initiate rapid oxide formation and subsequent 'seeding' of oxide precipitation (von Weimarn 1925; van Hook 1961). If the precipitation of MnO_x is promoted as suggested here, it should be expected that the dark deposit clearly seen at the topmost levels of the filter bed would contain other metal (hydr)oxides than manganese. This is supported by other work which has shown the presence of Mn, Fe and Al deposits on filter media.

The results summarised in Figures 6–8 indicate that the bulk of manganese is being removed in the very top levels of the filter media, particularly when using sodium hypochlorite as the chlorine source. The data presented in Figure 6 show that the percentage of manganese remaining in filter 3 (1.33 mm coal) is significantly different through the depth of filter and also at different bed depths when dosing with different chlorine species. As found with sand media before, initial chlorine and initial manganese
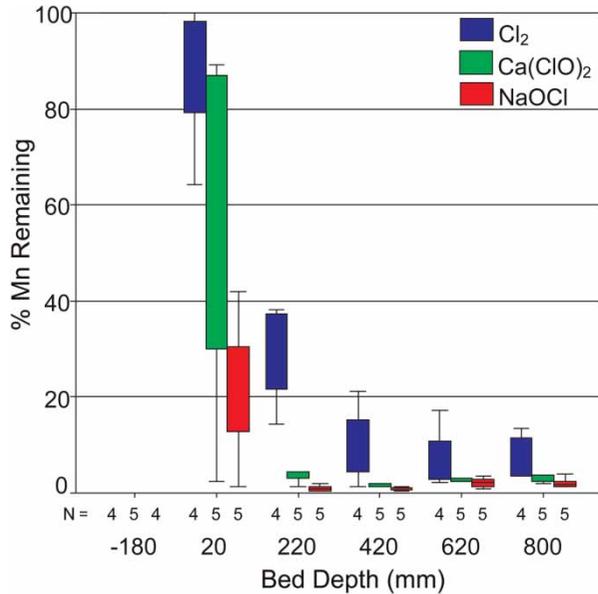
Figure 6 │ Percentage Mn remaining at various 1.33 mm coal bed depths (Media #2 protocol) when using different chlorine species. Initial chlorine and Mn concentrations were 5 and 0.1–0.4 mg/L, respectively.
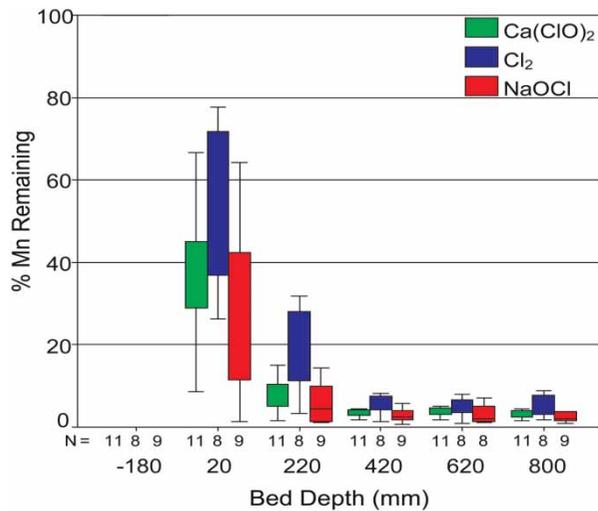

Figure 7 │ Percentage Mn remaining through bed depth when dosing 1.33 mm coal with various chlorine species (4 mg/L). Initial Mn 0.25 mg/L (Media #2 protocol).

concentrations did not make a difference to the percentage of manganese remaining through the filter bed.

The rapid removal of dosed manganese seen in Figures 6 and 7 when using 5 and 4 mg/L sodium hypochlorite, respectively, is clearly emphasised in the results shown in Figure 8, in which manganese remaining at increasing media bed depths is plotted for results for filter 2 (Media
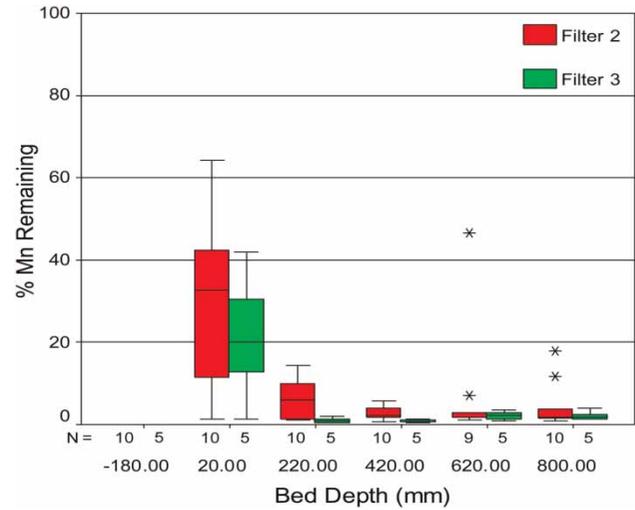

Figure 8 │ Percentage Mn remaining with bed depth using 1.33 mm coal when dosing with NaOCl (4–5 mg/L). Initial Mn concentration 0.1–0.4 mg/L.

#2 protocol) and filter 3 (Media #1 protocol), both of which contain 1.33 mm coal.

The experimental findings that the bulk of manganese was removed in the very top layers of the media were confirmed by visual observation of the filter media, in which an obvious dark brown stain is observed within the top 20–40 mm of the columns. This result correlates with those of Eley & Nicholson (1993), although those workers were using water at pH 9 compared with a pH range of 7.0–7.2 used in this study across all runs.

Given that the length of residence time (either 39 or 2.6 min) between manganese dosing, chlorine addition and the water entering the media had no effect upon manganese removal (data not shown), it is concluded that the media is capturing already formed MnO_x, and that no substantial auto-oxidation or microbial mediation contributes significantly to the removal process. Sodium hypochlorite clearly removes more manganese which suggests that a micro-scale pH effect during dosing may be involved. NaOCl solution has a very high pH, which when added to a Mn-containing solution will initiate instantaneous nucleation of MnO_x (Stumm & Morgan 1996). Such nucleation may 'seed' further deposition. $Ca(OCl)_2$ solution is lower in pH, but would be expected to produce a somewhat similar effect. Solutions of gaseous chlorine are acidic, and thus would not be expected to initiate precipitation of MnO_x as rapidly as does NaOCl. These conclusions fit well with the
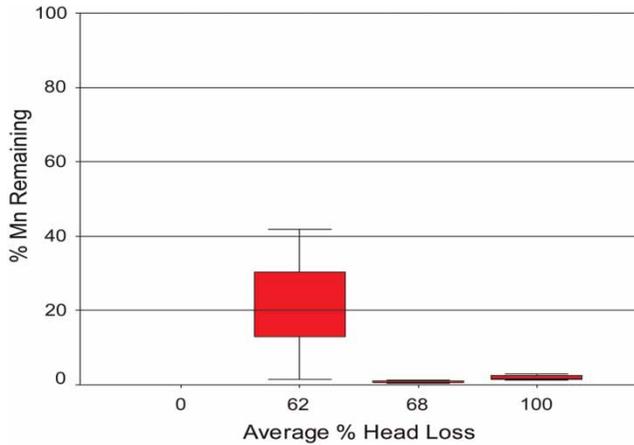
Figure 9 | Percentage manganese remaining in solution against average percentage head loss using 1.33 mm coal filtration (Media #1 protocol), for five repeat runs. Samples were taken at −180, 20, 420 and 800 mm down the filter.

statistical analysis of the results as shown in the preceeding graphs.

One of the more interesting results of this work has been the ability to find a very close correlation between manganese removal and head loss in the filters. Figure 9 illustrates very clearly that head loss and manganese removal are both greater than 60% after the first 20 mm depth through filter media. These results are the product of five repeat experiments ($N = 5$), with manganese samples and head loss being taken at four points down the column. The correlation suggests that manganese removal is strongly associated with the material presence that is causing the head loss.

CONCLUSIONS

The main findings of the work described here regarding manganese removal using the modified greensand process are as follows:

1. Sand media has little to no chlorine demand while coal filter media have a marked and prolonged chlorine demand, regardless of the species of chlorine being used, viz. NaOCl, $Ca(OCl)_2$ or Cl_2. This finding has implications for attempts to avoid or reduce organo-chlorine species in potable water. At this time when so much attention is being given to the concentration and nature of any chlorinated organics formed within the WTP, it

is surprising that so little research appears to have been conducted on this topic. The size of coal used (1.25 or 1.33 mm) has no effect upon manganese removal.

2. The percentage of chlorine remaining at the different depths of the filter bed is not significantly different for the three chlorine species used.

3. Sodium hypochlorite solution appears in all cases to be more successful at removing manganese than calcium hypochlorite or gaseous chlorine, for both sand and coal media at the same dosed water environment of pH, turbidity, true colour, temperature, etc. We attribute this to the high pH micro plume created by the addition of the sodium hypochlorite solution which leads to instantaneous initiation of MnO_x production created by the addition, even though an overall pH change in the water above the media could not be measured/observed.

4. Manganese removal, on sand or coal media, takes place in the very top 20–40 mm layer of the media at the pH values normally encountered in municipal water treatment processes (usually pH >7 and <8). The observation that there is a well-defined dark layer at the very top of the filter media bed indicates that particulate or colloidal MnO_x is being accumulated in association with or mediated by other materials removed through coagulation/filtration. This observation is confirmed by the head loss gradient through the filter.

5. There was no evidence of a first order rate through the filter given 60–80% removal in the first 20–40 mm.

6. Little to no manganese removal takes place in the absence of chlorine at the ambient pH ranges trialled (6.6–8.0).

7. There is a direct and significant relationship between manganese removal on sand or coal and head loss down the filter depth, regardless of the chlorine species used.

8. Retention time between inflow into the filter column and passage onto the media has no significant effect upon manganese removal when using sodium hypochlorite.

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