

Manganese removal in groundwater treatment: practice, problems and probable solutions

R. Buamah, B. Petrusevski, D. de Ridder, T. S. C. M. van de Wetering and J. C. Shippers

ABSTRACT

Most drinking water production plants use rapid sand filters for the removal of manganese from groundwater. The start-up of manganese removal on newly installed sand media is slow, taking several weeks till months. Reducing this period in order to prevent the loss of water during this phase has become an issue of concern. In this study pilot and bench scale experiments were conducted to investigate the mechanism, influence of operational conditions (e.g. filtration rate, manganese loading) and measures that enhance manganese removal capacity of the sand media. Other filter media were investigated with the objective of finding suitable substitutes for the sand. The development of the adsorptive/catalytic coating the sand media in a pilot plant was very slow, notwithstanding the relatively high pH of 8. Low manganese concentration and more frequent backwashing resulted in a longer start up period of the manganese removal. It can not be excluded, that nitrite has a negative effect as well. Measurements in the lab and bench scale tests show that the rate of adsorption/oxidation of manganese in the top layer of the filter bed is too low to explain the complete manganese removal in the filters. It is likely that the adsorptive catalyst in the top layer has partly been covered with ferric hydroxide. From the Freundlich's isotherms determined for 6 different filter media, a crushed medium consisting of mainly manganese dioxide and some silica, iron and aluminium (Aquamandix) followed by iron oxide coated sand, containing some manganese, demonstrated highest adsorption capacities at pHs 6 and 8. These materials can therefore be potential substitutes for sand in situations of slow start-up of manganese removal.

Key words | adsorption, catalytic, filter media, manganese, oxidation

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INTRODUCTION

Groundwaters generally contain one or more contaminants like iron, manganese, ammonium, methane and natural organic matter e.g. humic acid. For drinking water supply purposes, these contaminants need to be removed or reduced to acceptable levels. High manganese levels in drinking water can give rise to aesthetical and health problems. Together with dissolved iron, manganese (II) could flocculate and form sediments in distribution lines. If the flow in the distribution lines increases (daily peak

demand), the sediment can become re-suspended and may result in customer complaints of incidents of 'black' or 'brown' water. These 'black water' incidents may occur when manganese concentrations in treated water is as low as 0.02 mg/L (Sly *et al.* 1990; MWH 2005). To exclude the possible health hazard as a result of chronic exposure to manganese, a health-based guideline of 0.4 mg/L for the occurrence of manganese in drinking water has been recommended by WHO (2006).

Many groundwater treatment plants (GWTP) aerate the raw water to remove methane and oxidize dissolved Fe (II) and Mn (II) to their respective oxides. Ammonium can be removed biologically in a following one or two-stage sand filtration. The oxidized iron is removed by physical filtration and the dissolved Fe (II) and Mn (II) are adsorbed on the filter media and subsequently get oxidized. Humic acids may combine with Fe (II) and Mn (II) to reduce the rate of oxidation. The extent and rate of oxidation in a filter is dependent on the pH, the dissolved oxygen content, presence of iron and manganese oxide coatings on the filter media, the GWTP design and the operational conditions (i.e. the backwashing regime employed).

Frequently, it has been observed that, the manganese removal capacity of the sand filters reduces after a couple years in operation. As part of the measures to solve this problem, the filter media has to be regularly replaced with new sand. After replacements, a slow start-up of manganese removal has frequently been observed. This study is focused on the manganese removal problems with the aim to get insight in the mechanisms governing the start up of manganese removal in rapid sand filters. For this purpose a pilot plant study has been conducted at the GWTP Haaren of the Water Supply Company Brabant. Pilot rapid sand filters were operated at different filtration rates and manganese concentrations in the influent.

Laboratory and bench scale investigations were done to determine manganese adsorption capacities of the media after several months of operation. These tests were done under oxic and anoxic conditions to differentiate between adsorption capacity and adsorption/catalytic oxidation capacity.

In addition adsorption isotherms for several filter media were determined to get an indication of their potentiality as alternate filtration media.

Theoretical background

During the operation of rapid sand filters, the influx of Fe (II) and Mn (II) ions from the raw water facilitates formation of iron oxide coating on the sand grains. The coatings formed normally have manganese oxides embedded within. These iron and manganese oxides (e.g. Fe_2O_3 , FeOOH , MnO_2) in the sand mineral coating enhance adsorption of in-coming

Fe (II) and Mn (II) ions. Certain oxides in the mineral coating especially MnO_2 , catalyses the oxidation of adsorbed Mn (II) in the presence of dissolved oxygen and favourable pH (Stembal *et al.* 2004). Consequently new adsorption sites are created thus preventing saturation of adsorption capacity. The presence of high amount of these catalytic oxides on the sand grains is therefore paramount for the rapid start-up of manganese removal in the sand filters. Literature informs that the iron content of the raw water, pH and length of time in use contribute to the rate of growth of the iron oxide coating (Sharma *et al.* 1999). Despite these findings, the precise length of time required to achieving adequate oxidation of the adsorbed iron and manganese to subsequently create new adsorption sites on the filter media still remains to be determined.

Manganese can exist in eleven oxidative states; the most environmentally and biologically important manganese compounds are those that contain Mn (II), Mn (IV), or Mn (VII) (US EPA 1994). The equilibria between the various forms of Mn are determined mainly by pH and redox potential as illustrated in Figure 1. At low pH and redox potential, Mn (II) prevails whereas at high pH and low redox potential, the formation of MnCO_3 is favoured. Manganese cannot be oxidised and removed from water as readily as iron, so in some cases aeration-filtration alone is not very effective.

As a consequence several groundwater treatment plants make use of an additional aeration-filtration stage. In the first stage primarily iron is removed and in the

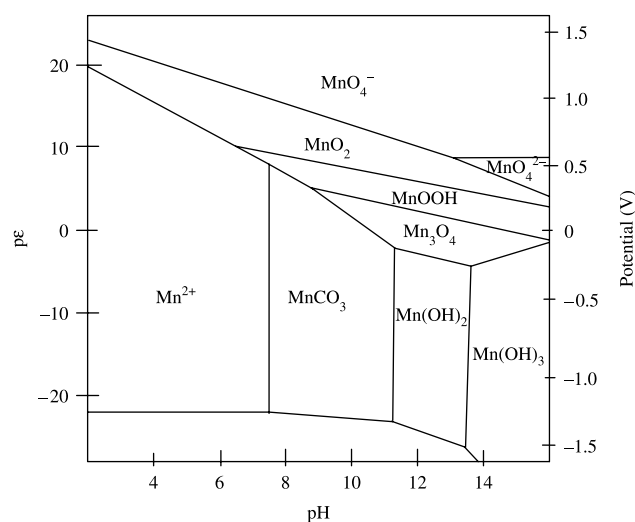


Figure 1 | p_e -pH diagram for aqueous Mn (Stumm & Morgan, 1996).

second stage mainly manganese is removed due to higher pH and absence of iron covering the manganese adsorbant/catalyst.

The manganese oxidation kinetics equation proposed by Stumm & Morgan (1996) is:

$$\frac{d[\text{Mn(II)}]}{dt} = -K_0 [\text{Mn(II)}] + K_1 [\text{Mn(II)}] [\text{MnO}_2]$$

where:

$$K_0 = k\text{PO}_2 \cdot [\text{OH}^-]^2$$

K_0 = reaction rate constant ($\text{l}^2/\text{mol}^2 \cdot \text{atm} \cdot \text{min}$)

K_1 = reaction rate constant ($\text{l}^3/\text{mol}^3 \cdot \text{atm} \cdot \text{min}$)

PO_2 = Partial pressure of oxygen (atm)

So aside the pH, the Mn (II) and oxygen concentrations, the rate depends on the product of the [Mn (II)] and the [MnO₂], implying that the reaction is autocatalytic. At pH values below 9 the rate of oxidation in solutions is very low. In rapid (sand) filters manganese removal has been observed down to pH 6.9. This phenomenon is attributed to the catalytic effect of manganese oxides e.g. Mn₃O₄ and MnO₂.

The mechanisms involved are expected to be as follows:

- Adsorption of Mn (II) on the surface of the media e.g. sand;
- Oxidation of adsorbed Mn (II) to Mn₃O₄ and MnO₂. Oxidation takes place at much lower pH values than 9 (i.e. down to pH 6.9)
- The adsorbed and subsequently oxidized Mn (II) act as a newly created adsorbent. The old and new adsorbents catalyse the subsequently adsorbed Mn (II).

As Mn oxides precipitate, oxidation accelerates in response to the increased surfaces available for selective adsorption of Mn (II) ions.

MATERIALS AND METHODS

Pilot plant experiments

Pilot plant experiments were conducted using three filter columns (Internal diameter of 18 cm) and virgin sand (particle size 0.71–1.25 mm; bed depth of 75 cm) as filter

media at the Haaren GWTP in the Netherlands. The three columns were run with the aerated raw water from the Haaren GWTP containing about 0.04 mg Mn(II)/L, 0.55 mg NH₄⁺/L, 0.4 mg Fe (II)/L, 9.6 mg O₂/L, alkalinity of 183 mgHCO₃⁻/L, and pH 8 (Figure 2). One column (i.e. filter A) was fed with the aerated raw water without any manganese spiking at a filtration rate of 2.8 m/hr. This filter A served as a reference. The feed water of the other two columns (i.e. filters B and C) was spiked with MnCl₂ to increase the manganese concentration to 0.5 mg Mn(II)/L in order to determine the influence of manganese concentration on the start up of manganese removal. The Filters B and C were run at filtration rates of 2.8 m/hr and 0.6 m/hr respectively. The filters were run for 22 weeks and their filtrates periodically sampled and analysed for NH₄⁺, NO₂⁻, NO₃⁻, Mn and Fe.

Lab and bench scale investigations

After 15 weeks of the filter runs, batch reactor experiments (Figure 3) were conducted using the filter media taken from the top segment of the filter bed from each of the three columns. The manganese removal capacities of the various filter media were determined at pH 8 under both oxic and anoxic conditions using filtrate from the Haaren GWTP. Under the oxic and anoxic conditions, the extent to which manganese is removed by only adsorption or adsorption aided by catalytic oxidation could be investigated. In the batch reactor experiments 1 g/L filter media was added and 0.3 mg Mn/L spiked. Nitrogen gas was infused into the reactor to attain and maintain anoxic conditions. Carbon dioxide was introduced for pH adjustment. Mixing was ensured by the gas infusions and continuous stirring. Each batch experiment was run for 7 days and sampled periodically to determine the residual dissolved manganese content. The samples were filtered through a 0.45 μm membrane filter using a polypropylene syringe filter. Manganese analysis on the samples was done using Perkin Elmer 3110 spectrometer in accordance with the Dutch Standard Method NEN 6457. The method used has a detection level of 0.02 mg Mn (II)/ L.

Another series of batch reactor experiments were conducted under anoxic conditions using the protocol outlined by Buamah *et al.* (2008), to develop manganese

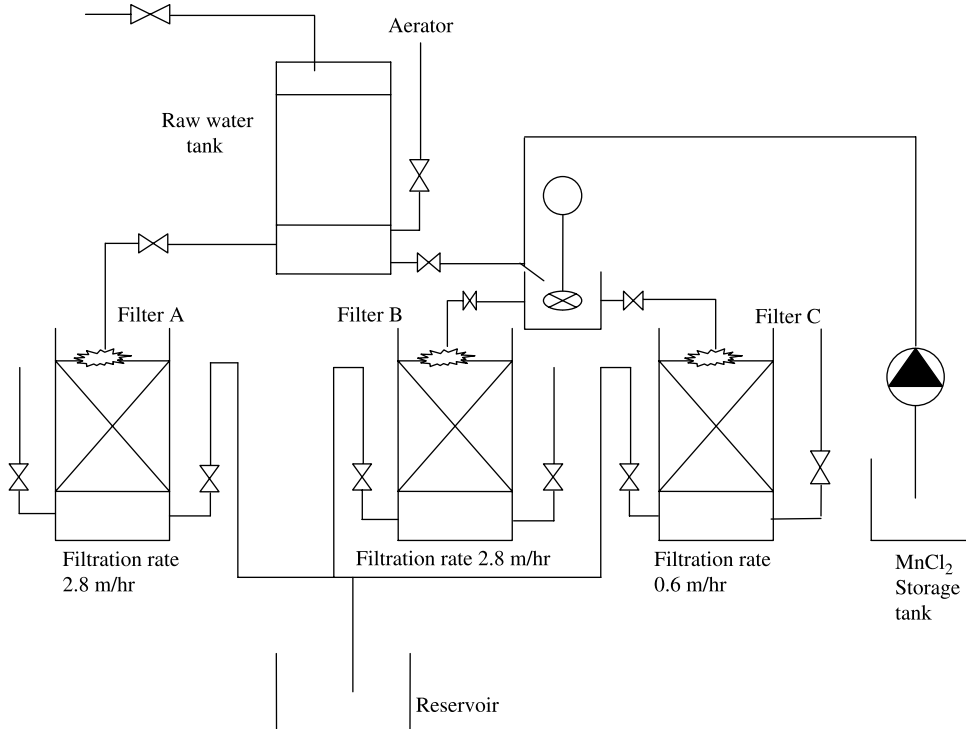


Figure 2 | A schematic diagram of the Haaren pilot set-up.

adsorption isotherms at pH 6 and 8 for six new adsorbents. The adsorbents used included iron oxide coated sand (IOCS), manganese green sand (MGS), Aquamandix (AQM), laterite (LAT), an iron ore and virgin sand. The IOCS comprise sand grains coated with iron oxides and have been obtained from filters used for removing dissolved iron at the Noord Bargeres groundwater treatment plant in the Netherlands. The MGS is formulated from glauconite

and sandstone. The glauconite component is a crystalline iron silicate mineral. Aquamandix is a commercial filter media consisting predominantly of crushed material consisting of manganese dioxide (78%) and generally lower percentages (i.e. < 6% by weight) of ferric oxide, silica and alumina (Aqua-techniek 2007). The laterite used in this study was obtained from Nyinahin (Ghana) and is basically hardened iron-rich mottled clay. The laterite possesses a

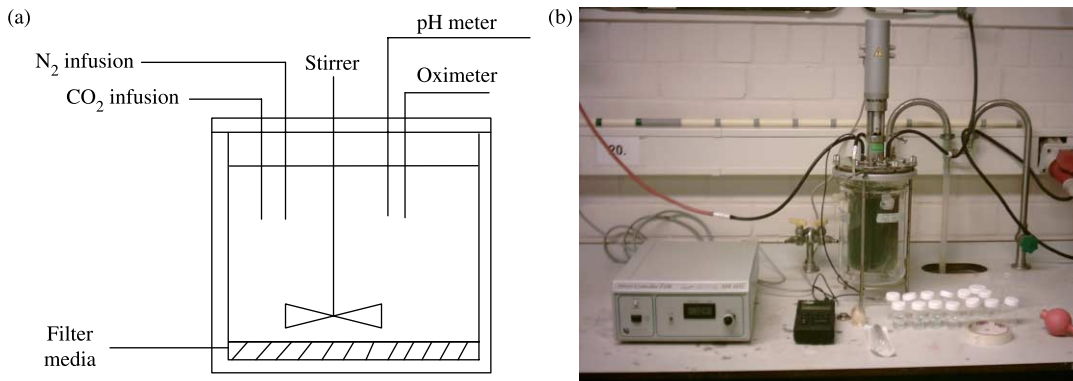


Figure 3 | (a). A schematic diagram and (b) a photograph of the batch experimental set-up.

continuous hard fabric of iron concretions wholly or partly joined together with rounded cavities with secondary aluminium and quartz but low percentage of silica (Raychaudhuri 1980). The iron ore is another natural virgin media obtained from Shiene in Northern Ghana and comprises natural ferruginous tillite with sandstone. The iron mineral present in the ore is mainly haematite (Fe_2O_3) and limonite ($2\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$) with traces of pyrite (Minerals Commission–Ghana 1992).

Experiments on the six new adsorbents under anoxic conditions were done with model water prepared by dosing distilled water with NaHCO_3 and a known concentration of Mn (II). To avoid manganous carbonate precipitation, NaHCO_3 dosage of 1,000 mg/L and 84 mg/L were used for pH 6 and 8 respectively. For each adsorbent various concentrations of the Mn (II) were dosed into the reactor and the manganese adsorption monitored for a known dosage of the adsorbent till the attainment of equilibrium. Periodic sampling was done at regular time intervals to determine the rate of adsorption and equilibrium conditions. Equilibrium was considered to have been reached when the difference in manganese concentration of two consecutive samples taken over a period of 10 hrs was ≤ 0.02 mg/L. All experiments were run in duplicate.

RESULTS AND DISCUSSIONS

Pilot plant experiments

All three filters demonstrated removal of Mn(II). In general it took about 40 days before manganese removal started in all the filters. Filter A (that was run at 2.8 m/hr; with 0.04 mgMn(II)/L and no extra manganese dosage) took 100 days to achieve complete manganese removal while filter B and C (running at 2.8 and 0.6 m/hr and both with a level of about 0.6 mgMn(II)/L) arrived at that stage after 79 and 51 days of operation respectively (Figures 4–6). The potential reasons for these pronounced differences are as follows:

- The built up of adsorptive catalytic manganese oxides is governed mainly by the total amount of manganese entering a filter. This effect may explain why filter B demonstrated a faster achievement of complete manganese removal than filter A (dosed with low Mn(II) but same filtration rate). The manganese influx is more than 10 times higher in filter B. On the basis of this, it should be expected that filter B would perform better than filters A and C. However the results showed filter C doing better.

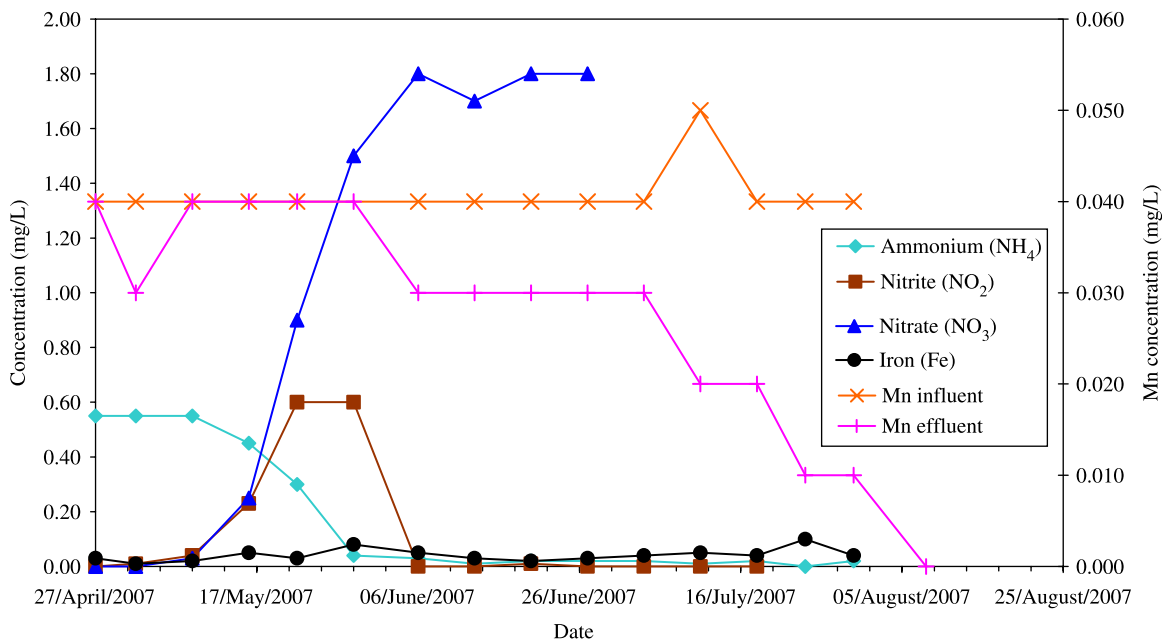


Figure 4 | Development in water quality parameters monitored for filter A running at 2.8 m/hr with 0.04 mg Mn(II)/L and 0.4 mg Fe(II)/L.

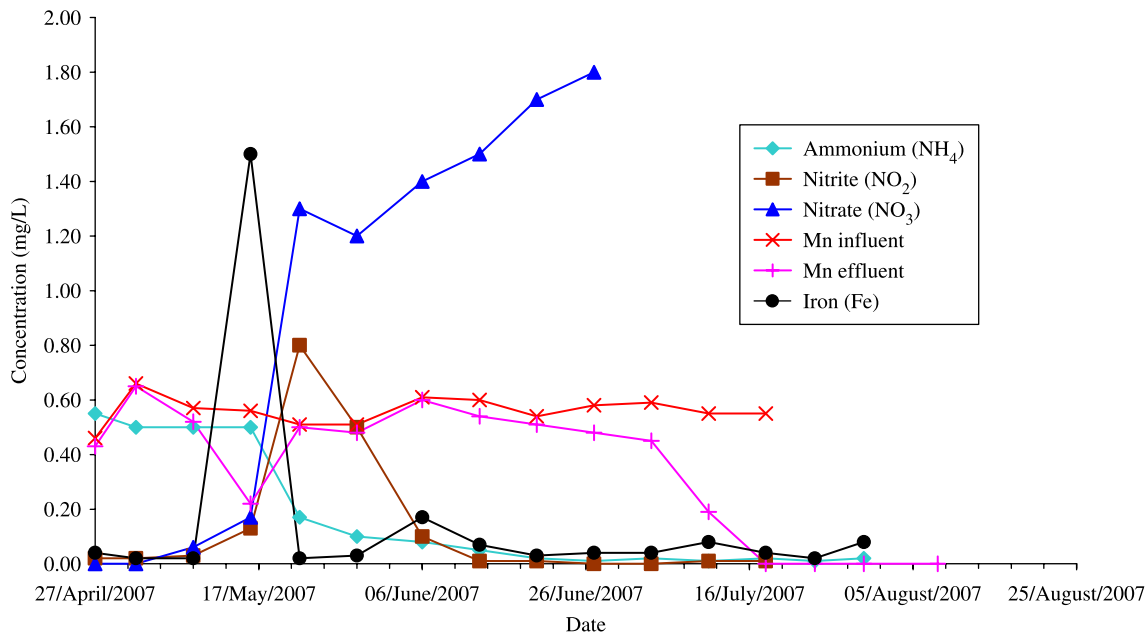


Figure 5 | Development in water quality parameters monitored for filter B running at 2.8 m/hr with 0.6 mgMn(II)/L and 0.4 mgFe(II)/L.

- The unexpected difference in behaviour of filter B and C might be caused by a difference in the backwash regime e.g. due to the higher filtration rate, filter B has been backwashed more frequently than filter C. As a result more newly formed adsorptive catalyst might have been removed.
- Difference in bacterial growth due to ammonium removal might be another potential reason for the observed differences. However, there is no pronounced difference in the trends of the start-up and complete ammonium removal. The formation and disappearance of nitrite might

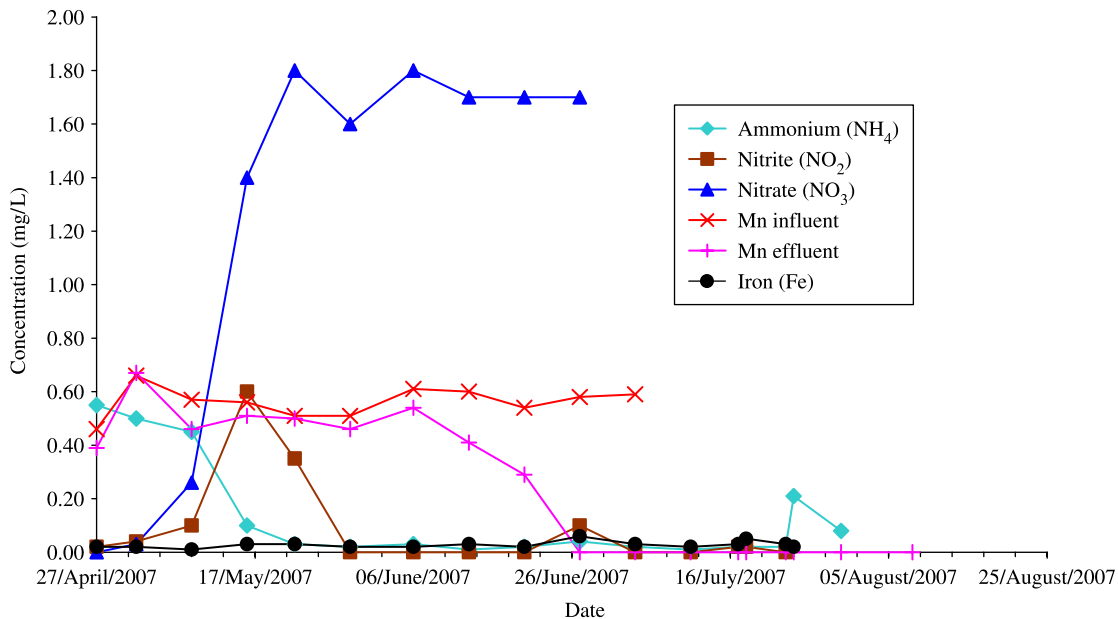


Figure 6 | Development in water quality parameters monitored for filter C running at 0.6 m/hr with 0.6 mgMn(II)/L and 0.4 mgFe(II)/L.

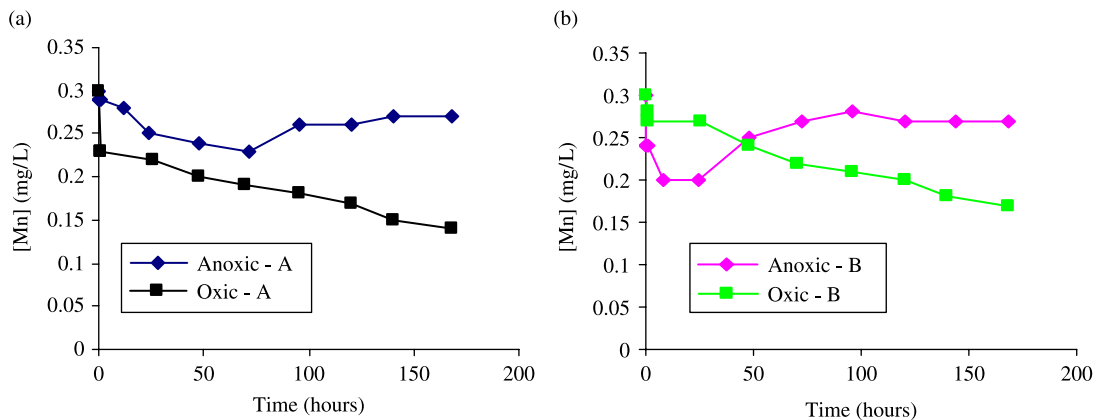


Figure 7 | Manganese removal at pH 8 under oxic and anoxic conditions with grains from (a). filter A and (b). filter B.

indicate an effect on the development of Mn (II) removal. Figures 4–6 demonstrate that Mn (II) removal starts immediately after the disappearance of nitrite.

Laboratory and bench scale investigations

The bench scale batch experiments showed that, for the various filter media (i.e. filters A, B and C) the adsorption capacities of the grains do not differ much within the first 100 hours under both the oxic and anoxic conditions (Figures 7–9). However, it was observed that, under the anoxic conditions after an initial relatively fast manganese removal (occurring within the first hour), the dissolved manganese concentration in the reactor stabilized indicating an equilibrium position (Figure 9(a)). Under the oxic

conditions after the initial fast drop in the first hour, the dissolved manganese concentration decreases continuously indicating that new adsorption sites are created (Figure 9(b)).

The creation of the new adsorption area is possibly due to the oxidation of the adsorbed manganese. This trend of manganese removal under oxic conditions was common to all the filter media and the manganese removal rate per gramme of the media were found to be about 5.2×10^{-4} mg per gramme media per hour for all the filters A, B and C after the first hour (Figure 9(b)).

Translating the measured removal rate to a real filter, assuming the same rate and a 0.6 mg Mn(II)/L in the influent, the following results. The amount of manganese removed in a filter bed with a surface area of 1 m² and filter height 0.75 m (bulk density 1,600 kg/m³), and operation at a filtration rate of 2.8 m³/m²hr is able to remove 0.63 g Mn(II) per hour. The inflow of manganese per hour is 1.68 g Mn(II). So this calculation indicates that the removal rate capacities measured in the lab and bench scale tests are too low to explain the complete manganese removal (Figures 4–6). Possible reasons are:

- the adsorptive catalyst on the top layer has been partially covered with ferric hydroxide and so have been made inactive or inaccessible;
- the mass transfer in a real filter is much higher than in the laboratory and bench scale test;

Under the anoxic conditions, after the initial drop, the dissolved manganese concentration was found to have increased before levelling off (media of filter B, Figure 9(a));

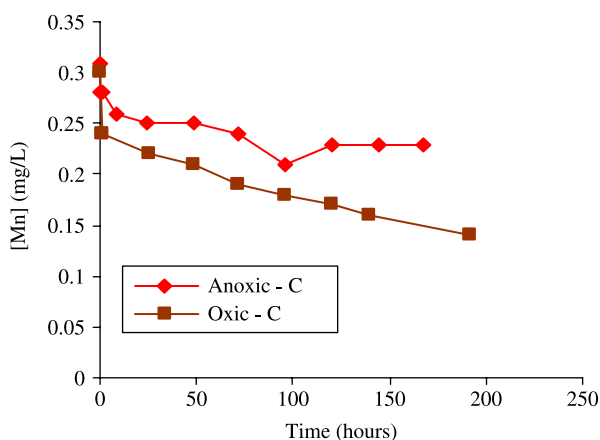


Figure 8 | Manganese removal at pH 8 under oxic and anoxic conditions for filter C grains.

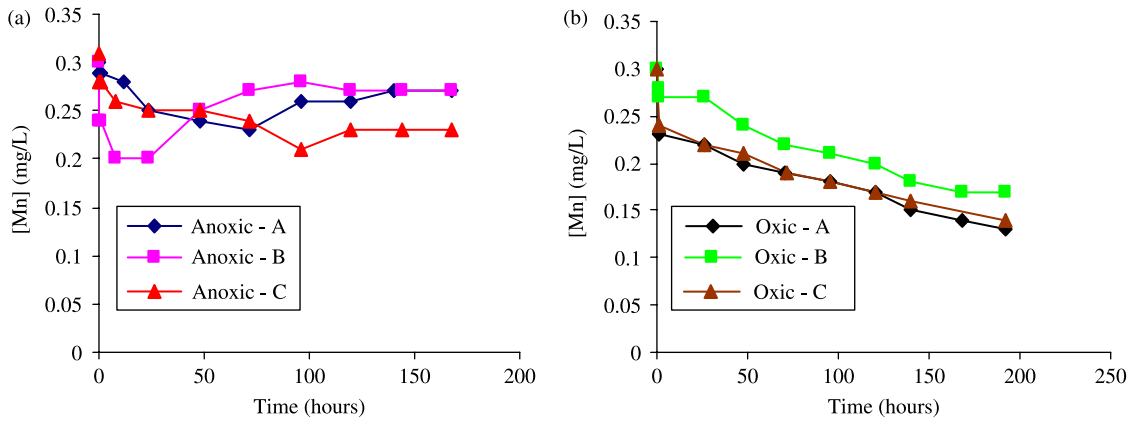


Figure 9 | The combined manganese removal graphs at pH 8 for the various filter grains under (a). anoxic and (b). oxic conditions.

this manganese release may probably be the dissolution of manganous carbonate that might have precipitated locally and gotten embedded within the mineral coating formed during the pilot experimentation. This might have been induced by a higher pH due to unintended additional aeration. Using solubility product equations and Phreeq c software programme, for pH 8 and an alkalinity value of 3 mmol/L, manganous carbonate precipitation commences when dissolved manganese concentration is > 0.3 mg/L (Buamah et al. 2008); so a slight increase in pH might result in manganous carbonate precipitation.

From the second series of bench scale experiments, Freundlich's isotherms were developed for the 6 different filter media at pHs 6 and 8 under anoxic conditions (Figure 10). All the media demonstrated adsorption

capacity for Mn(II) at pH 6 and 8 except Manganese green sand and virgin sand that showed manganese adsorption at pH 8 only. Manganese adsorption capacity is substantially higher at pH 8. At pH 6 MGS showed release of manganese instead of adsorption.

The manganese adsorption capacities of the various media are in the order (Figure 10):

- At pH 6; AQM > IOCS > Iron-ore > Laterite > Virgin sand.
- At pH 8; AQM > IOCS > MGS > LAT > Iron-ore > Virgin sand.

Aquamandix shows the highest manganese adsorption capacity, so it is a potential candidate to replace sand as filter media in situations of slow start-up of manganese

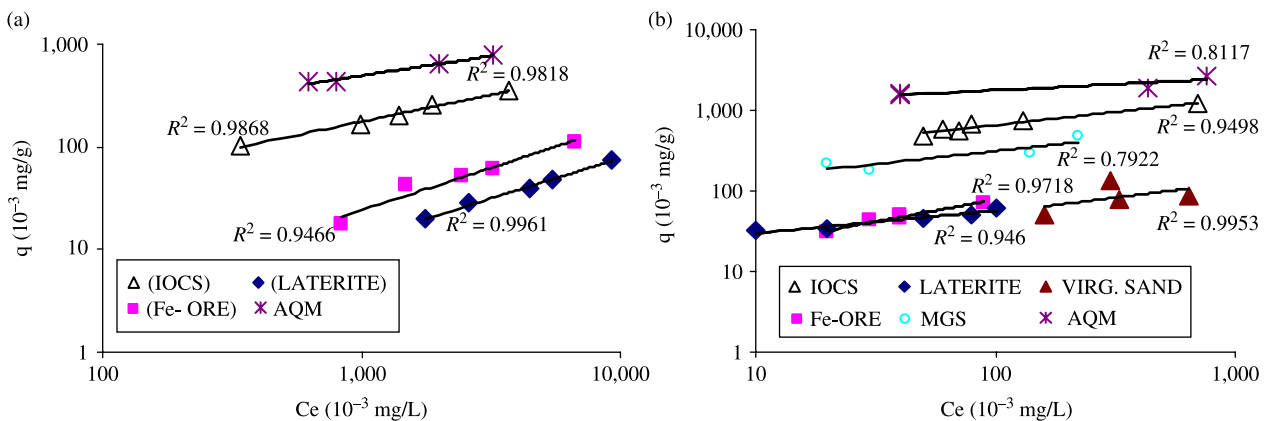


Figure 10 | Manganese adsorption isotherms for the various media at (a) pH 6 and (b) pH 8.

Table 1 | The Freundlich's isotherm constants obtained at pH 6 and 8

Filter media	pH 6		pH 8	
	K	n	K	n
AQM	34.69	2.60	875.21	6.55
IOCS	4.73	1.91	147.27	3.08
MGS	0.00	0.00	63.73	2.81
Laterite	0.06	0.79	15.85	3.60
Iron-ore	0.08	1.21	6.17	1.81
Virgin sand	0.00	0.00	0.01	0.61

Unit of K: $((10^{-3} \text{ mg/g})/(10^{-3} \text{ mg/L})^{1/n})$

removal. Iron oxide coated sand might be a cheaper second candidate (Table 1).

CONCLUSIONS

In conclusion the following could be deduced:

- The three filters filled with sand developed full manganese removal after several weeks. The filters fed with water containing 0.6 mg Mn(II)/L and operating at filtration rates of 2.8 and 0.6 m/hr developed complete manganese removal in 79 and 51 days of operation respectively. The filter fed with 0.04 mg Mn(II)/L and running at 2.8 m/hr achieved full manganese removal after 100 days of operation.
- The positive effect of a low rate of filtration is attributed to the more favourable backwashing regime for the filter running at lower filtration rate.
- The long period that the filter fed with low manganese needed to arrive at full manganese removal is attributed to the low influx of manganese required to develop sufficient adsorptive catalyst surface area.
- Nitrite might have a negative effect on the development of the adsorptive catalyst, therefore the disappearance of nitrite, as more nitrate get formed may have a positive effect on manganese removal, however this has to be verified.
- Adsorption capacity measurements, measured under oxidic conditions on the media of the three filters, taken after 15 weeks, demonstrated a continuous removal of manganese. The removal rates were in the same order of magnitude, which is in concert with the observation

that total removal of manganese had developed in all the filters. This test might be a powerful tool in judging the removal capacity of filtering materials.

- Out of the six filtration media, the Aquamandix demonstrated the highest adsorptive capacity measured under anoxic conditions. As its capacity is much higher than sand, the Aquamandix is a potential candidate to substitute sand in situations of a slow start-up of manganese removal.
- The removal rate capacity of the top layer of the media after 15 weeks of operation, determined in lab and bench scale tests, was 0.52 mg Mn(II) per kg media per hour. This value results in a removal rate of 0.8 g Mn(II) /hr, which is lower than the inflow of 1.4 g Mn(II)/hr filter operating at 2.8 m/hr and a Mn(II) concentration of 0.5 mg/l. Most likely the manganese adsorptive catalyst on media of the top layers has been partly covered with ferric hydroxide.
- Iron oxide coated sand, containing sufficient manganese is the second best option with a reasonably high adsorption capacity and being a by-product of the water treatment plants could be the cheapest substitute. Virgin sand has by far the lowest adsorption capacity.

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