

Iron and manganese removal from groundwater by filtration through a chalcedonite bed

Joanna Jeż-Walkowiak, Zbysław Dymaczewski and Łukasz Weber

ABSTRACT

The aim of this research was to determine the effectiveness of iron and manganese removal from groundwater using chalcedonite sand as a filter bed in rapid filtration. The experiment was conducted at a pilot plant. At the first stage of research, chalcedonite and silica sand were compared. The ripening time for manganese removal of chalcedonite was 27 days while silica sand was ripened within 57 days. At the second stage of research, the filtration process was conducted through chalcedonite sand with the rate of 6.0, 9.0 and 12.0 m/h. There was no significant difference between ripening times for the applied filtration rates. High mass capacity and relatively low head loss growth enabled long filtration runs. To confirm the importance of biological processes in the ripening bed for manganese removal, the third stage of the research was conducted. After the chalcedonite was ripened the bed was disinfected. The manganese concentration in the effluent immediately increased to 0.22–0.28 mgMn/L. To establish the adsorption potential of filtration materials for manganese the Freundlich isotherms were developed for chalcedonite and silica sand. The internal structure parameters (pore surface and volume) of chalcedonite and silica sand were determined using the BET (Brunauer–Emmett–Teller) isotherm method.

Key words | chalcedonite sand, groundwater, filtration, iron, manganese

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INTRODUCTION

In uncontaminated groundwater, iron and manganese generally cause the greatest difficulties for use of that water for municipal and industrial purposes. The iron content in groundwater may range from traces to tens of mg/L, whereas the manganese content ranges from traces to a few mg/L. This matter is of particular concern in Poland, where 56% of the total drinking water produced comes from groundwater sources, and in fact groundwater supplies 87% of Polish drinking water treatment plants (WTPs) (Sozański 2002).

Iron and manganese present in water impart a metallic taste and odour, and stain laundry and household fixtures (Sly *et al.* 1990; MWH 2005). Iron and manganese may discolor industrial products such as textiles and paper. Precipitates can clog pipes and support the growth of iron and manganese bacteria, which can cause taste and odor problems (Knocke *et al.* 2010). Kohl & Medlar (2006)

recommend a 0.02 mgMn/L goal for water utilities to meet an aesthetic standard of water. The deposition of iron and manganese oxides in distribution systems decreases the diameter of pipes causing increased headloss, which in turn increases transport costs (WTPD 1990).

In addition to aesthetic and operational problems, the health aspects of manganese content in drinking water are of concern. Health effects from over-exposure of iron include Kashin–Beck disease and increased risk of heart disease (Sullivan 1981).

The health effects from over-exposure of manganese are dependent on the route of exposure, the chemical form, the age at exposure, and an individual's nutritional status. Irrespective of the exposure route, the nervous system has been determined to be the primary target, with neurological effects generally observed (USEPA 2004). The neurotoxicity of manganese after exposure by inhalation has been well

documented (Ljung & Vahter 2007; Menezes-Filho *et al.* 2011). However, there is increasing evidence of neurotoxicity of manganese by the oral route, especially in infants fed with infant formulae usually containing manganese (Hozyasz & Ruszczyńska 2004). Because infant formula is normally sold in powdered form, the manganese concentration of the water with which the formula is mixed may contribute significantly to the infant's daily manganese exposure (Ljung & Vahter 2007). Recent studies suggest that excess Mn may interfere with developing brain functions. In Bangladeshi children, a negative effect of high Mn level in tube well water on cognitive capacities was observed (Wasserman *et al.* 2006). A significant association between hair manganese levels and hyperactive and oppositional behavior in children exposed to Mn through municipal well water has also been reported (Bouchard *et al.* 2007).

According to Directive 98/83/EC, the maximum permitted level for iron and manganese in drinking water is 0.2 mgFe/L and 0.05 mgMn/L (DWD 1998). Increasing instances of neurotoxicity from manganese exposure warrants a re-evaluation of current guideline values (Ljung & Vahter 2007).

The performance of standard aeration-rapid sand filtration treatment applied for iron and manganese removal can be significantly improved in some situations through better understanding of iron and manganese removal mechanisms, and consequently by identifying and changing the conditions to improve performance. However, in some situations the filtration process has to be modernized. An economically viable solution for improving manganese removal from groundwater can be the replacement of the media in old filters by new media that are capable of removing iron and manganese more effectively.

Groundwater treatment in Poland usually consists of aeration or chemical oxidation and rapid filtration, followed by disinfection. For the filtration step, proper choice of the filtration material and operational parameters are essential for obtaining high efficiency of treatment. The filter bed should be characterized by a high efficiency of iron and manganese removal and an absence of operational difficulties. Economic issues such as capital cost and operational cost (related, for instance, to the duration of filtration cycles, water and air use for backwashing and persistence of the filter material) are also important.

The commonly used filtration materials in Poland are silica sand and dual anthracite-silica sand media. These materials are not chemically active at the beginning of a filtration process to remove iron and manganese. As time passes, the grains become covered with oxides of iron and manganese, formed from iron and manganese removed from the filtered water. The created oxides layer is permanently attached to the grain. This outer layer of the grains plays an important role in further iron and manganese removal. Iron and manganese oxides catalyze the heterogeneous liquid-solid oxidation of iron and manganese to be removed from the treated water (Islam *et al.* 2010; Knocke *et al.* 2010). Start up of effective manganese removal takes quite a long time. Sometimes it takes a few weeks, however in some cases, it takes several months to create an oxide layer capable of catalyzing the oxidation process (Stembal *et al.* 2005). There are some waters which are difficult to treat since the manganese inlet concentration is too low to start up the manganese removal in a reasonable time.

To initiate manganese removal by the filtration material, a minimum manganese concentration in the filter influent is necessary. According to recent research of the authors, the minimum raw water manganese concentration to initiate removal by the filtration material without oxidant dosage is 0.1–0.2 mgMn/L (Jeż-Walkowiak 2013). To start up the filtration material for manganese removal with a lower manganese concentration in raw water, dosing of an oxidant is necessary. Often, potassium permanganate is applied (Sommerfeld 1999). In this case the oxide layer is formed both from manganese coming from the water being treated and manganese from the oxidant dosage. Often, a continuous chlorine dosage to regenerate adsorptive and oxidative properties of the external oxides layer of the grains is also necessary (Knocke *et al.* 1991).

The filtration media investigated in this paper is chalcidonite sand, which is supposed to be quicker to start-up for Mn removal than standard media. Chalcidonite is a natural material extracted at the Inowłódz mine from the 'Teofilów' deposit located in central Poland (51° 31' 37" N, 20° 13' 24" E). The proved reserves of 'Teofilów' deposit is 21,500,000 tons (Bolewski 1991). Chalcidonite sand consists mainly (95%) of amorphous silica (SiO₂) and small amounts of calcium, magnesium, aluminum, iron and manganese. Chalcidonite is characterized by a porous external structure

(Jeż-Walkowiak 2012). A scanning microscopy image of the surface of a chalcodonite grain is presented in Figure 1.

Chemical activation for manganese removal is integrated with biological processes and leads to transformation of chemically inactive to chemically active filtration material. During the activation process grains of chalcodonite become covered with iron and manganese oxide coatings. The developed contact layer is permanent and capable of autocatalytic oxidation of iron and manganese. In contrast with silica sand, the porous structure of chalcodonite enables adsorption and microbial colonization.

The aim of the research reported herein was to establish technological parameters for filtration through chalcodonite sand as well as to determine whether chalcodonite sand can be used as an effective filtration material for iron and manganese removal from groundwater, with a short activation time for manganese removal in comparison with the standard filtration material, for example silica sand.

MATERIALS AND METHODS

To meet the goal of the research, the authors conducted comparative investigations, using silica sand media and chalcodonite sand under the same process conditions. Silica sand is the traditionally applied media for iron and manganese removal in a filtration process and in this experiment is used as a reference material for comparison.

The next step of the research was filtration through chalcodonite sand at different rates to determine process

parameters and operational conditions of the tested material, and to establish the influence of filtration rate on the efficiency of iron and manganese removal from treated water.

The research was conducted according to the methodology of a pilot plant experiment (Sozański & Huck 2007). Filtration rate and the bed depth are the key parameters of filtration. Tested beds were 1.6 m high. The applied filtration rates (6, 9, 12 m/h) are typical values used for groundwater treatment. Higher filtration rates, up to 15 m/h, may be applied after determining their applicability in a pilot plant experiment. Such experiments are expected to determine filtration parameters, duration of filter run as well as backwash parameters.

The third stage of the research was conducted to prove the importance of biological processes in ripening the filtration material – chalcodonite – to manganese removal. The clean chalcodonite sand was placed into a filtration column. The material filtrated water from the same WTP. After ripening, the bed was exposed to disinfectant. The influence of disinfection on manganese removal effectiveness was observed.

The experiment was conducted using a pilot plant installation consisting of three filtration columns, each 3 m high with a diameter of 8.2 cm. The installation was supplied with aerated groundwater from the Września WTP intake in central Poland. Natural draft tower aerators are implemented in the WTP for water aeration.

To determine the internal structure, parameters of grains, pore volume and surface adsorption method was used. The principle of this method is based on the determination and interpretation of sorption isotherms from which the distribution of pore volume and surface can be calculated. In order to measure sorption isotherms, high-vacuum sorption equipment was used. The extent of adsorption was measured on the basis of the lengthening of quartz spirals whose length has been previously determined. From isotherms of carbon dioxide and benzene sorption, the volumes of ultramicropores, micropores and mezopores of chalcodonite and silica sand were calculated. From CO₂ sorption, the ultramicropore surface was calculated and from benzene sorption surface of micropores was calculated. The surface of mezopores was calculated from benzene desorption. For each sample the specific surface area of the internal structure was defined, measured with the BET (Brunauer–Emmett–Teller) isotherm method (Perry & Green 1997).

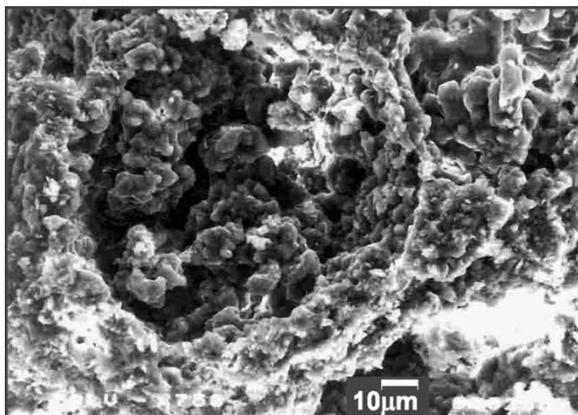


Figure 1 | Scanning microscopy image of chalcodonite sand.

The adsorption parameters were determined according to Freundlich isotherms. The chalcedonite and silica sand samples of 1 g and grain size of 1.0–1.4 mm, were exposed to the manganese solutions with concentrations of 0.15, 0.2, 0.5, 1.0, 2.0, 3.0 mgMn/L. To every bottle, the sample of 100 ml of manganese solution was added. The pH of the solution was equal to 6.4. The oxygen concentration was equal to 2–3 mg/L.

The bottles were then placed in rotating tumbler for 180 minutes, the time needed to reach the equilibrium. After this period the residual manganese concentration was determined in the solution. The contact time was determined according to preliminary research on the time needed to establish the equilibrium. The initial experiment was conducted for 36 h and within the conditions of the experiment (initial concentration and mass of adsorbent) the equilibrium was achieved after 2–2.5 h.

The granulometric parameters of chalcedonite sand and silica sand used as filtration materials were the same and are presented in Table 1. The granulometry of the tested media were chosen according to design guidelines (Sozański 2002; MWH 2005).

The characteristics of water supplying the installation are shown in Table 2.

During the first stage of the research, with a filtration rate of 6 m/h, 10 filter runs through chalcedonite were conducted and nine through the silica sand column. During the next step of the investigation filter runs through three filtration columns filled with chalcedonite were conducted. The first column filtered water at a rate of 6 m/h for nine cycles, second column at 9 m/h for 10 cycles, and the third at 12 m/h for 10 cycles.

Table 1 | Granulometric parameters of filtration beds

Parameter	Unit	Silica sand	Chalcedonite sand
		SERIE I	SERIE I, II, III
d_{\min}	[mm]	0.5	0.5
d_{10}	[mm]	1.0	1.0
d_{60}	[mm]	1.4	1.4
d_{90}	[mm]	1.8	1.8
d_{\max}	[mm]	2.0	2.0
Uniformity coefficient	[-]	1.4	1.4

Table 2 | Aerated groundwater quality

Water quality parameter	Unit	Range of values
Colour	[mgPt/L]	20.4–56.0
Turbidity	[NTU]	0.4–3.2
pH	[-]	7.0–7.3
COD-KMnO ₄	[mgO ₂ /L]	3.5–5.1
Chloride	[mgCl/L]	11.0–14.0
Total hardness	[mgCaCO ₃ /L]	240–370
Ammonia	[mgNH ₄ ⁺ /L]	0.1–0.56
Nitrite	[mgNO ₂ ⁻ /L]	0.01–0.03
Nitrate	[mgNO ₃ ⁻ /L]	0.31–0.5
Iron	[mgFe/L]	0.6–1.6
Manganese	[mgMn/L]	0.21–0.40
COD-Cr	[mgO ₂ /L]	20.9–31.5
Temperature	[°C]	9–10

COD: chemical oxygen demand.

Table 3 presents the length measured in hours of the filter runs for chalcedonite and silica sand. The end of the filtration run occurred when the head loss increased by 2 mH₂O.

The total filtration time presented in Figures 2 and 3 is summarized from the first to last filter run for each filtration column.

During the pilot plant experiments, the following parameters of the filtration process were determined: iron and manganese concentrations in samples taken at the inlet, outlet and at various filter bed depths 1–2 times a day; ammonium concentration in samples taken at the inlet and outlet; and head losses across filter bed depth, every 8 hours.

The filtration rate was kept constant using a stabilizing device. At the end of every filtration cycle the bed was back-washed with water (5 minutes), air (2 minutes) and water (5 minutes). Air intensity was 54 m³/m² · h. The water intensity was 65 m³/m² · h, giving the expansion of 25% for chalcedonite and silica sand.

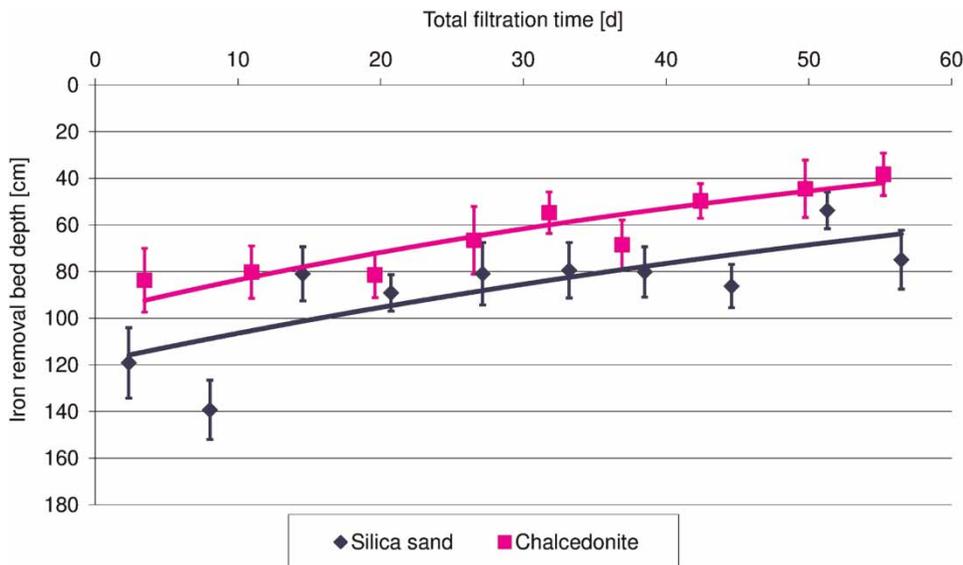
RESULTS AND DISCUSSION

The results of this research allowed us to establish the following: the bed depth necessary for iron removal (so

Table 3 | Length (in hours) of filter runs for chalcedonite and silica sand in three series of research

Number of filter run	Filtration column					
	I series		II series			III series
	Silica sand 6 m/h	Chalcedonite 6 m/h	Chalcedonite 6 m/h	Chalcedonite 9 m/h	Chalcedonite 12 m/h	Chalcedonite 6 m/h
1	113	166	171	171	27*	120
2	160	194	189	148	135	96
3	152	221	198	235	159	168
4	145	112	27*	113	134	168
5	163	141	74*	157	50*	168
6	128	104	204	150	165	96
7	126	160	163	151	174	144
8	166	192	47*	124	128	168
9	156	71*	187	98	167	96
10	93			105	157	

*Filtration runs were finished early due to organizing issues at working WTP.

**Figure 2** | Relationship between 'iron removal depth zone' and total filtration time for chalcedonite sand and silica sand.

called 'iron removal depth zone') to reach a treated water concentration of 0.2 mgFe/L; the time of start-up of chalcedonite sand for manganese removal from groundwater; the mass capacity and head loss of the filter bed; the influence of ripened bed disinfection on further manganese removal; internal structure parameters, pores volume and surface; and adsorption parameters according to

Freundlich isotherms. Each of these is discussed in detail in the following sub-sections.

Iron removal

The study evaluated iron removal efficiency of the tested materials for all applied filtration rates. The average

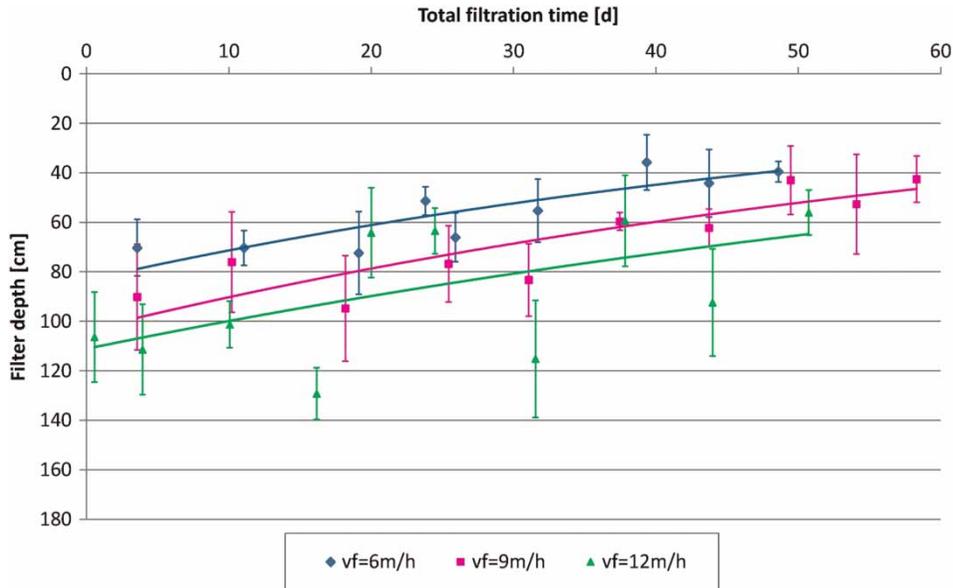


Figure 3 | Relationship between 'iron removal depth zone' and total filtration time for the chalcedonite bed operated with filtration rates of 6, 9 and 12 m/h.

efficiency of iron removal – E , for a filtration cycle, was calculated according to Equation (1)

$$E = \frac{1}{n} \times \sum_{i=1}^n E_i \quad (1)$$

where

$$E_i = \frac{(c_{in})_i - (c_{out})_i}{(c_{in})_i} \times 100 \quad (2)$$

c_{in} , c_{out} – concentrations of iron at the inlet and outlet of the filter, respectively, measured n times during the filtration cycle (mg/L), n – number of samples taken during a filtration run, the samples were taken every 12 hours.

The average efficiency of iron removal during the whole experiment was very high for silica sand and chalcedonite, varying from 90 to 100%. Right from the beginning of an experiment iron was removed to a concentration below the effluent requirement of 0.2 mgFe/L.

The measurement of iron concentration at various depths in the filter bed allowed establishment of an 'iron removal depth zone', necessary to obtain treated water of good quality. The calculation of the 'iron removal depth zone' was done for silica sand and chalcedonite for given

filtration rates for every filtration run. In Figures 2 and 3, the relationships between iron removal depth zone and total filtration time are presented for the tested media and for both the first and second stages of the research, with standard deviations for the calculated values.

The results presented in Figure 2 clearly show that for both materials (silica sand and chalcedonite) the depth of the iron zone necessary to achieve the effluent standards tends to decrease during the total filtration time. In the end of first series a depth of only 40 cm was required for iron removal in chalcedonite bed and 60 cm in silica sand. Reduction in the depth of the iron zone occurred due to activation of the filtration media as a result of covering the grains with iron oxides. Iron and manganese oxide coatings promote the autocatalytic and heterogenic oxidation of iron and manganese, accelerating the iron and manganese removal process. Due to iron removal in the top layer, good conditions for manganese removal activation are created in the lower part of the bed, that is, without iron–manganese competition.

The results presented in Figure 3 shows the influence of the filtration rate on the required depth of the iron removal zone. The higher the rate, the greater the depth of the active iron removal zone. Similar to the results in Figure 2, the depth of the iron removal zone tends to decrease as a function of time during the experiment.

Manganese removal

Natural activation (without chemical dosage) of chemically inactive filtration material (for example silica sand, chalcedonite or anthracite) for manganese removal from groundwater is a slow process, usually lasting several months. The acceptable start-up time is 3 months but in many cases it takes much longer.

At the start of the experiment filter columns were filled with clean chalcedonite and silica sand and therefore the bed initially had no ability to remove manganese. As time passed, the filtration material was continuously undergoing the process of natural start-up for manganese removal. At the beginning of the first stage of research the effectiveness of manganese removal in the chalcedonite bed was about 25% and in silica sand was about 20% at a filtration rate of 6 m/h. After the second filtration cycle, the effectiveness of manganese removal of the chalcedonite started to increase and during the next two cycles the outlet manganese concentration stabilized below the desired limit of 0.05 mg/L. In Figure 4 the relationship between manganese outlet concentration and total filtration time is presented. From the

results presented it is possible to establish the time necessary for the activation of chalcedonite sand for manganese removal, 27 days, while the silica sand was ripened in 57 days.

The second stage started after completion of the first stage. All filter columns in the second stage of research were filled with new, clean chalcedonite sand, with granulometry presented in Table 1. The installation was also supplied with aerated water from Września WTP.

Figure 5 presents the relationship between filtration time and the outlet manganese concentration for columns operated with filtration rates of 6, 9, 12 m/h, in the second stage of the research. This figure also shows the start-up process of the chalcedonite bed for manganese removal and indicates that there is no measurable influence of filtration rate on start-up time. For the filtration rates tested, the start-up time was 42–48 days.

The differences in the bed-ripening period for manganese removal with a filtration rate of 6 m/h in all series of research was a result of some differences in raw water quality. The water quality is presented in Table 2. The ripening time to some extent depends on Mn, Fe and NH_3 concentrations in raw water. Ammonia and iron

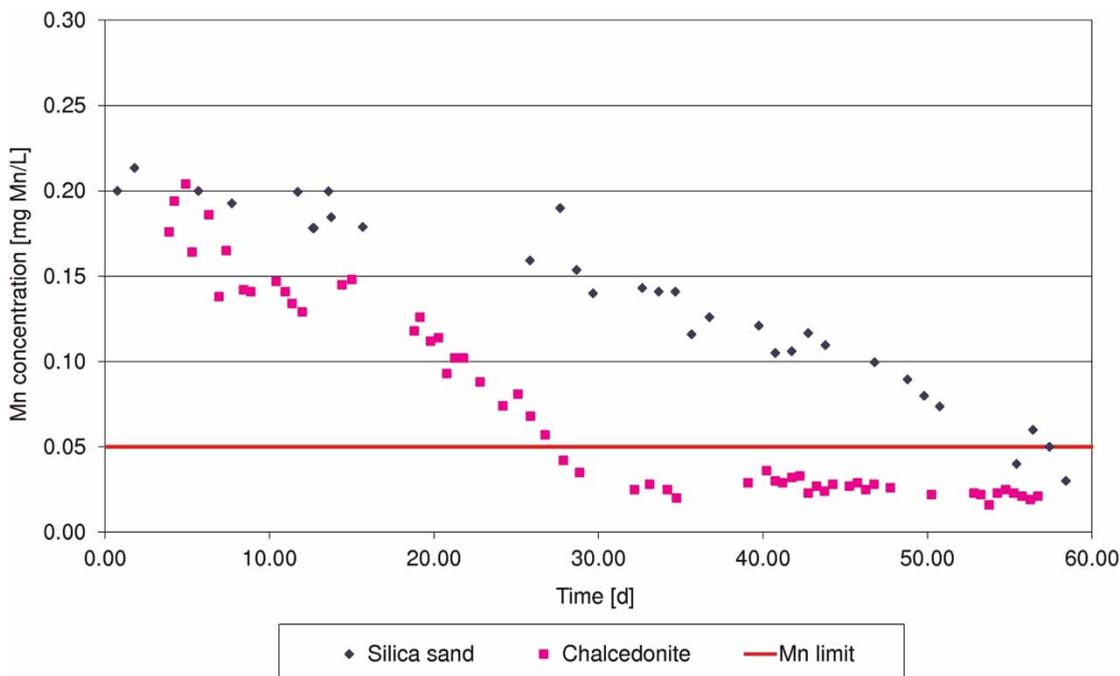


Figure 4 | Relationship between filtration time and the outlet manganese concentration for chalcedonite sand and silica sand media.

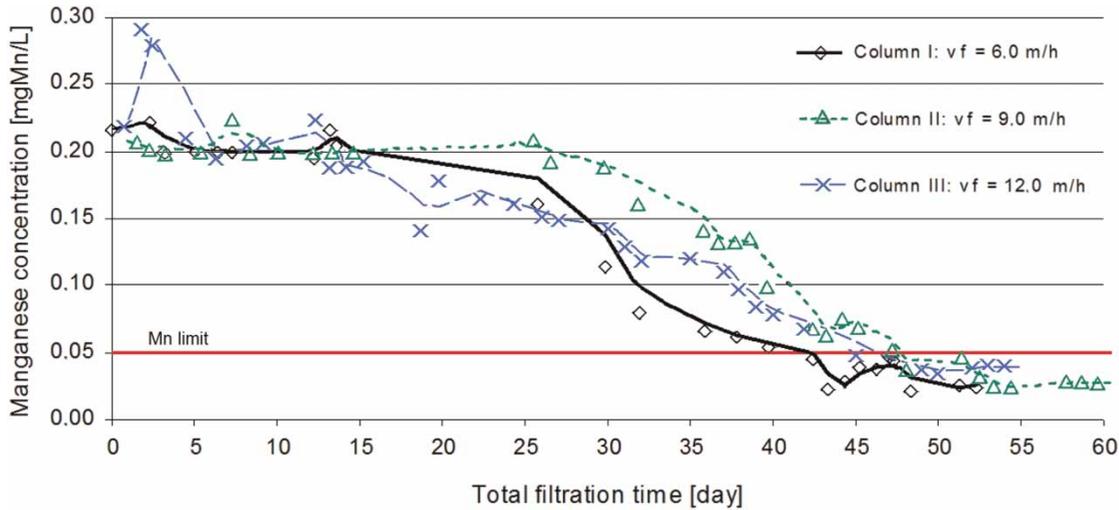


Figure 5 | Relationship between filtration time and outlet manganese concentration for the chalcedonite bed operated with filtration rates of 6, 9, 12 m/h.

are water constituents competing with manganese in the oxidation process. Higher ammonia and iron concentrations usually result in longer ripening time for manganese removal. On the other hand, the higher Mn concentration in raw water, the shorter ripening time is observed. The interaction between these factors affecting ripening filtration materials accounts for the difference in the time of start-up for manganese removal during the experiment.

Mass capacity and bed head loss

The mass of iron and manganese oxides retained in the filter increases the head loss.

Mass capacity (MC; g/m^2) was calculated according to Equation (3)

$$MC = t \times (c_{\text{in}} - c_{\text{out}}) \times v_f \quad (3)$$

where t – time of filtration (h), v_f – filtration rate (m/h), and c_{in} , c_{out} – concentrations of iron at the inlet and outlet of the filter, respectively (g/m^3).

The mass capacity was calculated for every filtration run, taking into account the mass of iron and manganese removed in a particular cycle. Thus, at the beginning of every new cycle the MC was zero ($t=0$), increasing with the time of filtration during the cycle.

The head loss was established according to the values of piezometric pressure read at the beginning of, and during, the filtration cycle.

In Figure 6, the relationship of head loss versus mass capacity for chalcedonite and silica sand is presented. Values of head loss presented in the graph do not include the initial head loss, so for mass capacity equal to zero, the head loss is also zero.

There is a big difference in head loss for a given mass capacity, determined for chalcedonite and silica sand media, and this is presented in Figure 6. The significantly better performance of chalcedonite is the result of the internal structure parameter, that is, the porosity of grains. The porous media create better conditions for adhesion. The porous structure of filter material grains has an influence on lower head loss formation compared with materials with no internal structure (Gimbel 1982).

As indicated previously, the second stage of the research consisted of three series of filtration runs conducted through three filtration columns with rates of 6.0, 9.0 and 12.0 m/h.

Figure 7 presents the relationship between mass capacity of the chalcedonite filter bed and corresponding head loss growth for all three series (filtration rates 6, 9, 12 m/h). The data presented in Figure 7 come from numerous filtration cycles. The research was conducted at the WTP. The installation was supplied with natural aerated water with quality parameters within a certain range of values.

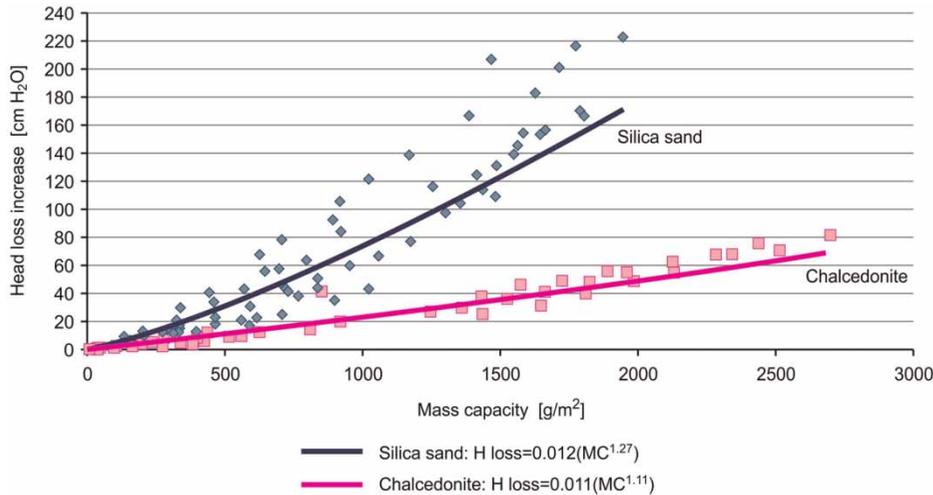


Figure 6 | Relationship between head loss growth and mass capacity for silica sand and chalcedonite.

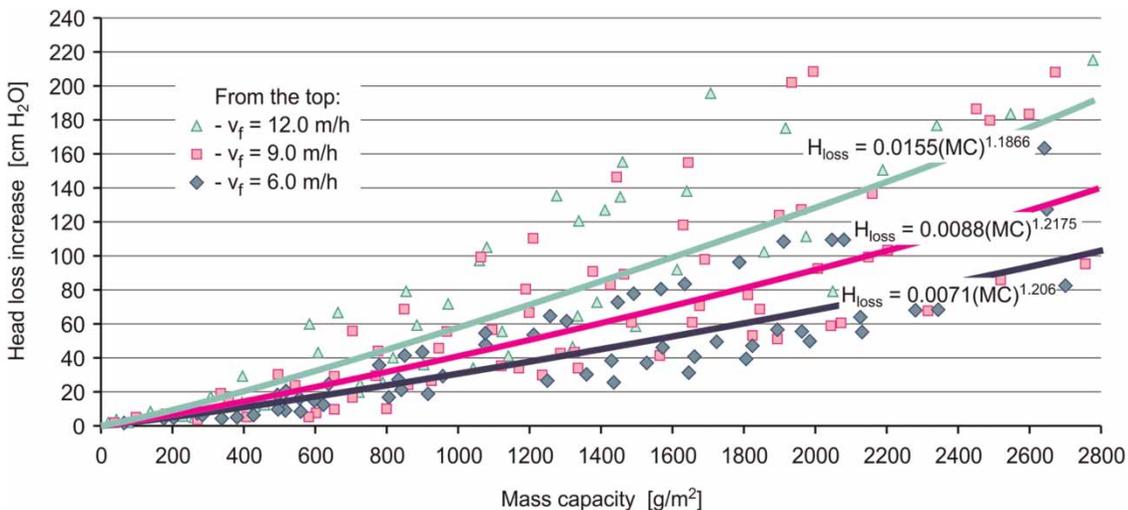


Figure 7 | Relationship between mass capacity and head loss growth for chalcedonite bed operated with filtration rate of 6, 9, 12 m/h.

The results obtained in different filtration runs (Figures 6 and 7) gave the values in a certain range because of the raw water quality variation. Especially the ratio of $\text{Fe}^{2+}/\text{Fe}_{\text{total}}$ influences the value of the head loss. Removal of fully oxidized Fe(III) will produce higher head loss than the removal of Fe(II), kept in filtration material due to catalytic, heterogenic oxidation.

The results presented in Figures 6 and 7 are relevant only for the given combination of water treatment system and groundwater composition.

The relationship between mass capacity and head loss (H_{loss} ; cm) may be described by the empirical equation

$$H_{\text{loss}} = \left(0.0031 e^{0.13 v_f}\right) MC^{1.2} \quad (4)$$

Equation (4), representing the relationship of head loss, mass capacity and filtration rate, is established for the conditions of the experiment (i.e. flow rate and raw water quality parameters). For this stage of the research, the

filtration columns were filled with chalcedonite sand with the same granulometry (Table 1). Although there is scatter in the data, the relationship does reflect the general trend observed for a given flow rate.

The head losses of the chalcedonite bed can be calculated according to Equation (4), in relation to mass capacity and filtration rate. According to Equation (4), a mass capacity equal to 2250 g/m² (the value characterizing a well-performing filter; Sozański 2002) would lead to a head loss of

- $H_{\text{loss}} = 71.2 \text{ cm H}_2\text{O}$ for $v_f = 6.0 \text{ m/h}$
- $H_{\text{loss}} = 105.2 \text{ cm H}_2\text{O}$ for $v_f = 9.0 \text{ m/h}$
- $H_{\text{loss}} = 155.4 \text{ cm H}_2\text{O}$ for $v_f = 12.0 \text{ m/h}$.

The fact that the calculated values are low (less than 2 mH₂O) shows the possibility of having long filtration runs and high mass capacity of chalcedonite filters.

Ammonia removal

One of the factors having significant impact on filter bed start-up for iron and manganese removal is the ammonia concentration in raw water (Bray & Olańczuk-Neyman 2001; MWH 2005; Gimbel et al. 2008).

During this research, the inlet concentration of ammonium was relatively low, equal to 0.1–0.56 mgNH₄⁺/L, the limit according to European law is 0.5 mgNH₄⁺/L. The initial effectiveness of ammonium removal in the first stage of this research on chalcedonite was in the range from 2–18% giving an effluent ammonium concentration lower than the limit of 0.5 mg/L. From Day 10 to Day 30 of the total filtration time through chalcedonite (counted from the beginning of series I) the effectiveness linearly increased to 95–100% and stayed at this value until the end of experiment.

The initial effectiveness of ammonium removal in silica sand was 0–13%. The effluent ammonium concentration was lower than 0.5 mg/L. The effectiveness of ammonium removal linearly increased up to 100% until the end of experiment. It appeared that chalcedonite achieved higher efficiency in ammonium removal faster than silica sand.

The results presented in Figure 8 show that the biological activation of chalcedonite occurred before the biological activation of silica sand. It shows a better ability of chalcedonite for bacteria settlement and growth on the grains of media. The time needed for biological activation of chalcedonite and silica sand was very similar to the ripening time for manganese removal for each of the tested materials (see

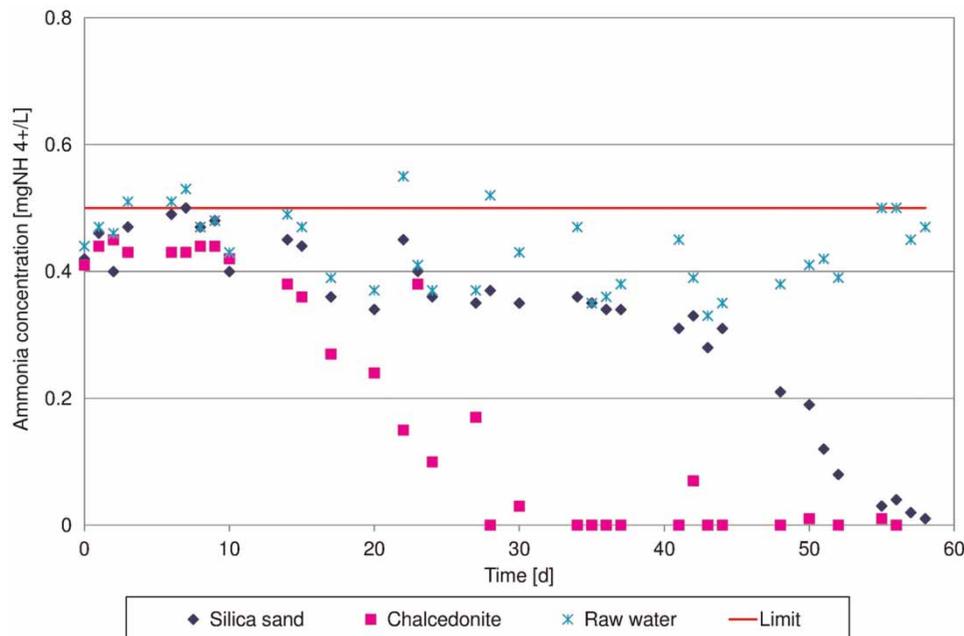


Figure 8 | Ammonia removal.

Figures 4 and 8). To check the correlation of ripening of tested media for manganese and ammonia removal, two graphs were constructed and presented in Figures 9 and 10.

The relationship of NH_4^+ and Mn concentrations in the effluent from filtration columns are shown as a function of total filtration time for the chalcedonite bed (Figure 9) and

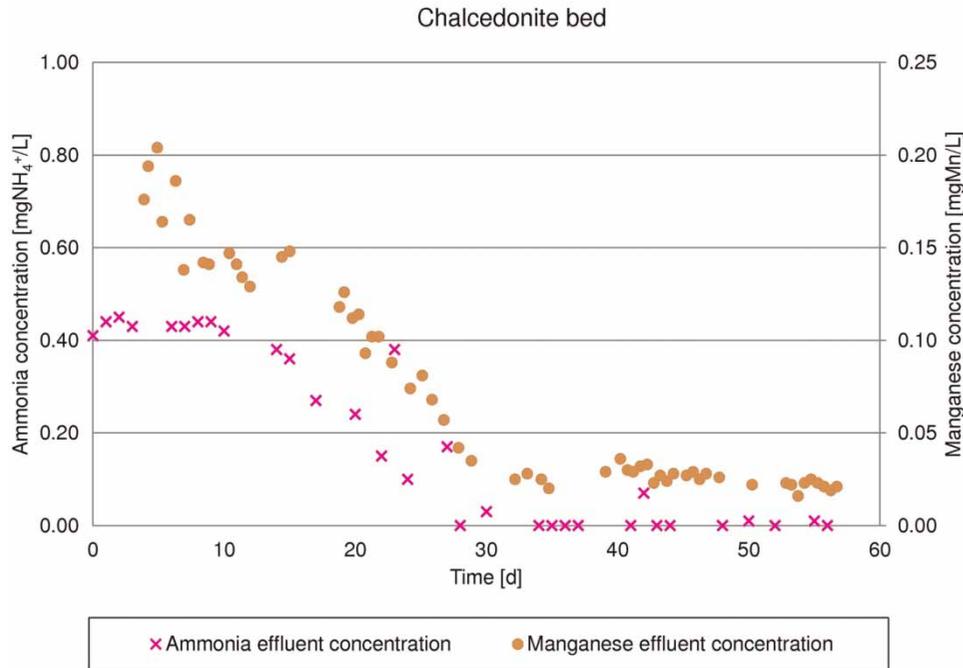


Figure 9 | Comparison of ammonia and manganese removal on chalcedonite bed.

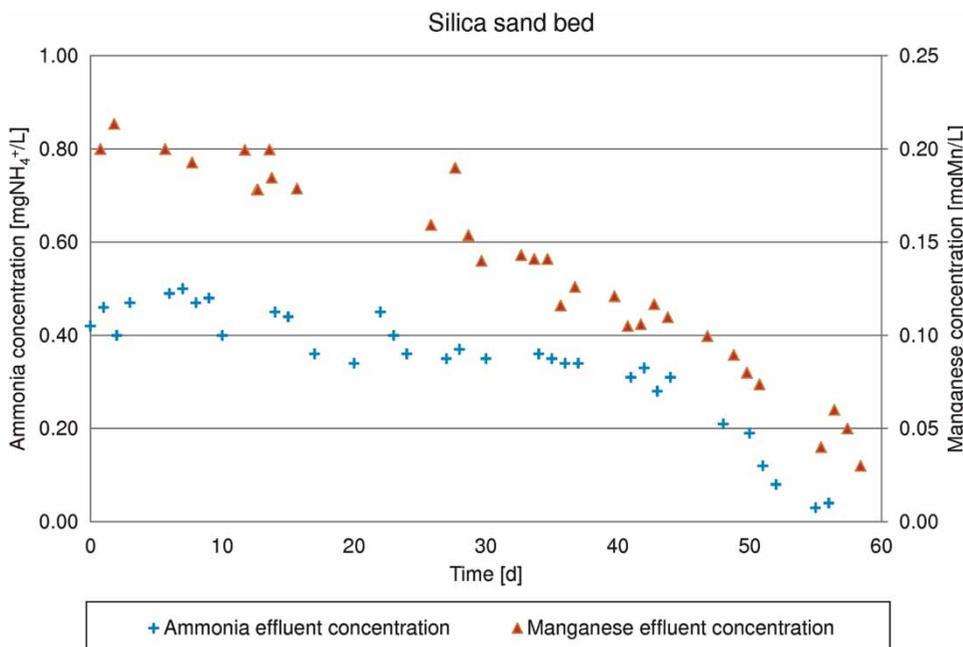


Figure 10 | Comparison of ammonia and manganese removal on silica sand bed.

the silica sand bed (Figure 10). There is a strong correlation between the process of ripening beds for manganese and ammonia removal. The graphs in Figures 9 and 10 clearly show that the ripening process for both beds runs parallel for Mn and NH_4^+ removal.

Internal structure parameters

The porous structure of the external contact layer creates very good conditions for the fast and effective activation of chalcedonite for iron and manganese removal compared with other chemically inactive filtration materials with no or lower internal porosity. The porous structure of chalcedonite promotes adsorption of Mn on the material; the higher the value of the pore surface, the higher the manganese adsorption potential of the filtration material (Jeż-Walkowiak & Dymaczeński 2012).

The pore surfaces as determined by the authors using the BET method, are presented in Table 4. The sorption isotherms for carbon dioxide and benzene determined by gravimetry, using high-vacuum apparatus, led to the following findings: there is a developed internal surface area of chalcedonite and there were no ultramicropores, micropores and mezopores in the grains of tested silica sand.

A porous structure creates good conditions for bacterial growth, thus enhancing biochemical processes, e.g. nitrification and manganese and iron removal. According to the determined internal structure parameters presented in Table 4, it can be expected that the porous structure of chalcedonite promotes the faster ripening for manganese removal.

Adsorption parameters

The affinity of the adsorbate for an adsorbent is quantified using adsorption isotherms, which are used to describe the amount of adsorbate that can be adsorbed onto an

adsorbent at equilibrium and at a constant temperature. For most applications in water treatment, the amount of adsorbate adsorbed is usually a function of the aqueous-phase concentration and this relationship is commonly called an isotherm.

The Freundlich adsorption isotherm is used to describe the data for heterogeneous adsorbents. The Freundlich equation has the form:

$$q_A = K_A(C_e)^{1/n} \quad (5)$$

where C_e – equilibrium concentration of manganese in solution (mg/L), q_A – equilibrium adsorbent-phase concentration of manganese (mg/g), K_A – Freundlich adsorption capacity parameter [(mg/g)(L/mg) $^{1/n}$], and $1/n$ – Freundlich adsorption intensity parameter.

The terms K_A and n are constants and the units of K_A are determined by the units of q_A and C_e . The linear form of the Freundlich equation is:

$$\log(q_A) = \log(K_A) + (1/n)\log(C_e) \quad (6)$$

Figure 11 presents isotherms using the linear form of the Freundlich equation for both tested media. A $\log(q_A)$ versus $\log(C_e)$ plot results in a straight line and allows determination of the Freundlich parameters. Table 5 contains calculated Freundlich adsorption capacity parameter, K_A [(mg/g)(L/mg) $^{1/n}$], and the Freundlich adsorption intensity parameter, $1/n$.

The constant K_A in the Freundlich equation is related primarily to the capacity of the adsorbent for the adsorbate and $1/n$ is a function of the strength of adsorption. The lowest values of C_e (equilibrium concentration of manganese in solution) within a given contact time were obtained for chalcedonite. Also the highest values of q_A (equilibrium adsorbent-phase concentration of manganese) was obtained for this material for a given C_e . Good manganese adsorption capacity was observed for chalcedonite compared with silica sand.

The established adsorption parameters according to the Freundlich isotherm show the higher adsorption capacity of chalcedonite in comparison to silica sand. The ability of chalcedonite to adsorb Mn from water solution is crucial in shortening the ripening of the filtration material.

Table 4 | Specific surface of internal structure of chalcedonite and silica sand

	Specific surface S-BET, (m ² /g)
Chalcedonite sand	3.9–6.1
Silica sand	0

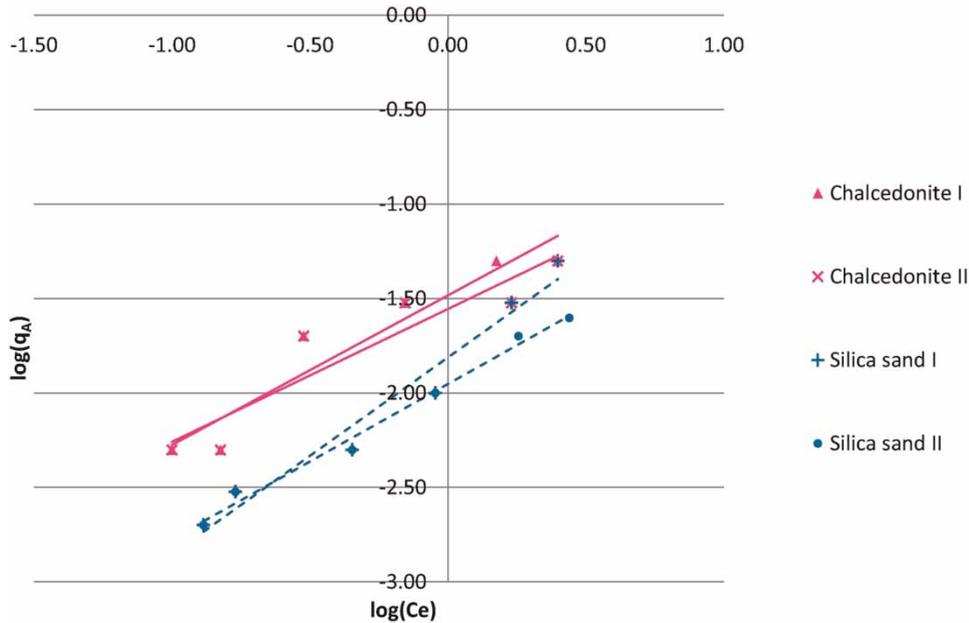


Figure 11 | The Freundlich isotherm plot using linear regression.

Table 5 | Values of Freundlich adsorption capacity parameter, K_A and Freundlich adsorption intensity parameter, $1/n$

Media	Chalcedonite		Silica sand	
	Sample 1	Sample 2	Sample 1	Sample 2
$\log(K_A)$	-1.483	-1.555	-1.811	-1.952
K_A [(mg/g)(L/mg) ^{1/n}]	0.0329	0.0279	0.0155	0.0112
$1/n$ [-]	0.792	0.704	1.041	0.821
R^2	0.9119	0.8715	0.9630	0.9895

It allows the creation of so called active places for further autocatalytic Mn oxidation and faster formation of oxide layers to catalyze the process.

Impact of biological processes

Activation of chemically inactive filtration materials (for example silica sand, anthracite, chalcedonite) usually occurs through chemical and biological means (Olańczuk-Neyman & Bray 2000; Buamah *et al.* 2009). Biological treatment is fundamentally a filtration process that takes advantage of the ability of certain bacteria to oxidize iron and manganese, and to assimilate ions (Mouchet 1992;

Tekerlekopoulou & Vayenas 2008; Chen *et al.* 2011). Biological activation of chalcedonite is also promoted by the porous structure of chalcedonite grains, which facilitates deposition by iron and manganese bacteria, starting the process of activation. Biological processes are important for Mn removal during the ripening process (Bray 2005). After the start-up, when the grains are covered with oxide coatings the catalytic oxidation of manganese plays the main role in manganese removal (Olańczuk-Neyman & Bray 2000). According to previous research, especially in the early stage of filter start-up, biological oxidation of manganese by manganese-oxidizing bacteria enhances filter performance (Mouchet 1992; Bray 2005).

Due to the porosity of the chalcedonite grains, it can be supposed that the bacteria could easily settle on the material, allowing a biological support for manganese removal. The importance of bacterial interaction in the ripening process was also checked by the authors. In the III series of the research, filtration through new, clean chalcedonite sand with a filtration rate of 6.0 m/h was conducted. The experiment was performed at the same WTP. Granulometry of chalcedonite was the same as in series I and II. Chalcedonite was ripened for manganese

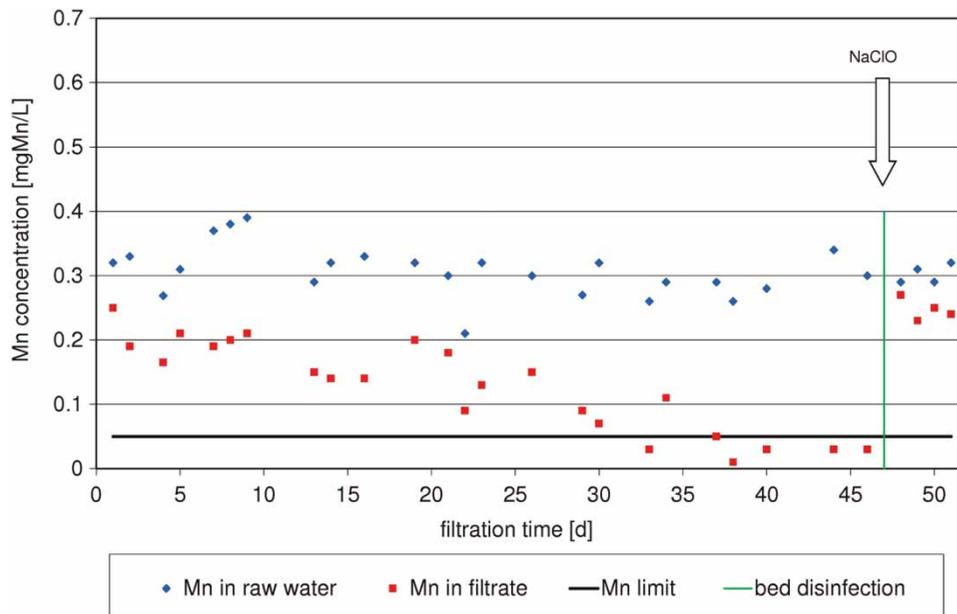


Figure 12 | Influence of bed disinfection on Mn removal results.

removal in 37 days. After reaching an effluent manganese concentration lower than the 0.05 mg/L limit value, the media were exposed to a 3.4 mg/L sodium hypochlorite solution for 12 hours. After disinfection, the lowering of manganese removal of the chalcedonite bed was observed. After the disinfection, the effectiveness of manganese removal decreased and the outlet manganese concentration was equal to 0.22–0.28 mgMn/L. Due to the disinfection of the filtration material, the population of bacteria was diminished and the bacterial contribution for manganese removal was significantly reduced. The result of this experiment allows us to conclude that a biological contribution in ripening materials for manganese removal occurred.

The results of series III are presented in Figure 12. On this graph the relationship of manganese effluent concentration versus total filtration time is presented. The moment of disinfection is marked and the increase in effluent manganese concentration is shown. It is also possible that the change of oxides structure could influence Mn removal. This change in outer oxides structure could occur through the transformation of the active catalytic layer, based on active partially oxidized manganese compounds, to the inert end product of manganese oxidation (e.g.

manganese dioxide) which is less active in the autocatalytic reaction (Anschutz *et al.* 2005).

Results and discussion from the literature, and the author's experience leads us to conclude that it is difficult to separate these two mechanisms of Mn removal: adsorption and biological oxidation. It seems that adsorption plays a more important role, but the role of biology in ripening the bed for Mn removal can not be excluded.

Economic aspect

The cost of chalcedonite is similar to anthracite and only 2–3 times higher than silica sand. The approximate gross prices in Poland (2012/2013) of different filter materials were: chalcedonite 0.6–0.8 euros/kg, anthracite ca. 0.7 euros/kg and silica sand 0.2–0.4 euros/kg. Prices of some oxidative filter materials were: Pyrolox 3.6–4.2 euros/kg, Gabon manganese ore 3.3–3.8 euros/kg (Jeż-Walkowiak & Dymaczewski 2012). Considering the prices presented, chalcedonite is a favorable proposal, especially where manganese concentration is relatively low and so it is difficult to ripen the bed without oxidant dosage. By applying the chalcedonite it is possible to avoid costs related to continuous or periodical chemical dosing.

CONCLUSIONS

The results of the research show the high efficiency of chalcedonite sand when applied as a filtration material for iron and manganese removal from groundwater.

Chalcedonite removed iron with an efficiency of 100% from the beginning of the experiment. No time was needed for the startup of the chalcedonite bed for iron removal. The silica sand bed also was 100% effective for iron removal. The 'iron removal depth zone' was established to be about 40 cm for chalcedonite and 60 cm for silica sand at the end of the experiment conducted with a filtration rate of 6 m/h (I series of research).

The 'iron removal depth zone' in chalcedonite was dependent on the filtration rate. An increase in filtration rate resulted in an increase of the 'iron removal zone'. For given filtration rates, the iron removal zones of the following values were obtained: 6 m/h–40 cm; 9 m/h–50 cm; 12 m/h–60 cm (II series of research).

In every series of research, the iron removal zone decreased with total filtration time, due to covering the grains with iron oxides. The established shallow 'iron removal depth zone' in the chalcedonite bed allowed manganese removal to occur in the lower part of the bed without iron competition.

According to the experimental data, the chalcedonite bed reached a high mass capacity with moderate head loss values thus allowing long filtration runs.

For manganese removal, chalcedonite sand is characterized by a short startup time. In this research it was 27–48 days. In comparison, for silica sand the ripening period was 57 days. It was found that the time needed for the start up of chalcedonite for Mn removal does not depend on the filtration rate.

The two mechanisms of Mn removal in a filtration material are discussed: Mn adsorption and biological oxidation. We can conclude from this work that the adsorption mechanism plays the main role in fast chalcedonite ripening, although the impact of biological processes may be of some importance.

Considering actual filtration material prices, chalcedonite is an interesting choice, especially in a situation of relatively low manganese concentration when it is difficult to ripen the bed without oxidant dosage.

In summary, chalcedonite sand is a promising natural filtration material which can be used for effective removal of iron and manganese from groundwater.

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