Effectiveness of oxidative filter materials for manganese removal from groundwater

Joanna Jeż-Walkowiak and Zbysław Dymaczewski

ABSTRACT

The experiments reported in this paper were conducted at a pilot plant consisting of filtration columns filled with oxidative filter materials. The installation was supplied with water containing manganese in concentrations ranging from 0.2 to 1.4 mg/L. The aim of the experiments was to determine the effectiveness of manganese removal on the three filter media as a function of their internal structure parameters (volume and pore surface area) and MnO_2 content. To interpret the results, the authors introduce a new parameter: catalytic activity coefficient, the product of the parameters mentioned above. This coefficient predicts the extent of manganese removal in a filtration process using an oxidative filter material. The coefficient may be the basis for a general classification suitable for all kinds of oxidative filter materials.

Key words | filtration, groundwater, manganese removal, oxidative filtration materials

Joanna Jeż-Walkowiak
Zbysław Dymaczewski (corresponding author)
Poznan University of Technology,
Institute of Environmental Engineering,
ul. Piotrowo 5,
60-965 Poznan,
Poland
E-mail: zbyslaw.dymaczewski@put.poznan.pl

INTRODUCTION

In uncontaminated groundwaters, iron and manganese cause the greatest difficulties for use of these waters 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. Present in water, iron and manganese ions impart a metallic taste and odor, and stain laundry and household fixtures (Knocke et al. 2010). 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 (Sly et al. 1990; MWH 2005). Deposits decrease the diameter of pipes, causing head losses growth, which increases transport costs. According to the European Community Directive 98/83/EC (DWD 1998), the maximum levels for iron and manganese in drinking water are equal to 0.2 mgFe/L and 0.05 mgMn/L, respectively. Other researchers propose even lower values, e.g. Kohl & Medlar (2006) recommend a 0.02 mgMn/L goal for water utilities to meet esthetic standards of water.

The new Directive (2007) in Poland lowered the maximum allowed iron and manganese concentrations in

drinking water from 0.5 to 0.2 mgFe/L and from 0.1 to 0.05 mg Mn/L, respectively. It is expected that in the next few years, many groundwater-based drinking water plants in Poland will be forced to enhance their effectiveness of iron and manganese removal.

An economically reasonable solution for technological problems of manganese removal efficiency can be replacement of the old filter bed by oxidative filter materials capable of removing iron and manganese more effectively. Such media have already been introduced in water treatment processes, but their exploitation principles have not yet been fully developed. The term 'oxidative media' describes filtration materials in which catalytic and heterogenic oxidation reactions of iron and manganese take place on the surface of grains. Iron and manganese oxides present on the surface of grains catalyze the heterogenic liquid–solid oxidation of iron and manganese to be removed from the treated water (Islam et al. 2010; Knocke et al. 2010). During the filtration, Mn(II) present in water can be adsorbed onto MnO_2 (constituent of surface of grains) and then oxidized by oxygen.

The reaction sequence for oxygenation of Mn(II) with oxygen present in water is suggested to be (Faust & Aly 1998):

$$Mn^{+2} + O_{2(g)} \Leftrightarrow MnO_{2(s)} \qquad (1)$$

$$Mn^{+2} + MnO_{2(s)} \Leftrightarrow Mn^{+2} \cdot MnO_{2(s)} \qquad (2)$$

$$Mn^{+2} \cdot MnO_{2(s)} + O_2 \Leftrightarrow 2MnO_{2(s)} \qquad (3)$$

Reaction 1 is very slow at pH below 9. The rate of conversion of Mn(II) to MnO_2 involves an autocatalytic process where the formation of MnO_2 solid provides adsorption of Mn(II) and accelerates conversion of Mn(II) to MnO_2. Because of this catalytic effect, not all Mn(II) that is removed from the process is converted to MnO_2 and may simply be adsorbed onto MnO_2. The products of manganese oxygenation appear to be nonstechiometric and show various degrees of oxidation ranging from about $MnO_{1.3}$ to $MnO_{1.9}$, depending upon the pH (Stumm & Morgan 1996; MWH 2005).

Oxidative materials applied in water treatment technologies may be classified as follows (Jeż-Walkowiak 2000):

- Silica sand coated with iron and manganese oxides – the catalytic layer is created during the start-up process of the technical filters. The coatings are made from iron and manganese compounds removed from water and captured onto the surface of grains.
- Natural oxidative materials – manganese ores consisting mostly of MnO_2 (often more than 90%).
- Artificially activated filter materials prepared according to patented technologies.

To start up the clean silica sand for manganese removal, it takes several months to create an oxide layer capable of catalyzing the iron and manganese oxidation process. According to recent research, the minimum raw water manganese concentration to start up the filtration material in the time of 3–6 months is equal to 0.1–0.2 mgMn/L without oxidant dosage (Weber 2011). This research was conducted for aerated groundwater (without chemical dosage): pH 6.9–8.3, alk. 100–310 mgCaCO₃/L, Mn 0.11–0.85 mgMn/L, filtration rates 6–9 m/h.

To eliminate the start-up period, the natural or artificially activated oxidative materials may be applied (Sommerfeld 1999; Sozański & Huck 2007). These media are able to catalyze the process of oxidation from the start of operation. Properly selected oxidative material gives an expected efficiency when the bed depth is calculated using the kinetics of adsorption. Good results of filtration through manganese ores have been achieved at several water treatment plants (WTPs) in Poland.

On the market, there are many kinds of filtration materials capable of catalyzing the process according to manufacturer information. It is crucial to detect whether these media have a real capability for catalyzing the iron and manganese oxidation, ensuring the process proceeds with proper efficiency and good kinetic parameters. The purpose of the research was to define the important technical parameters of filter materials with oxidative properties, as well as to set criteria for their use in groundwater treatment. In the literature, oxidative filter materials are described by their name/type or method of start up and efficiency of iron and manganese removal (AWWA 1999, 2005a). The authors propose the method for evaluation if a given filtration material is suitable for manganese removal from groundwater. The described method is a physical–chemical criterion for prediction of expected effectiveness of manganese removal in filtration based on catalytic oxidation. This criterion is helpful in interpretation of the effects of manganese removal achieved in the pilot plant experiment. This interpretation may also be used for validation of accuracy of the proposed criterion. The proposed criterion may be the base for classification of oxidative filtration materials in aspects of its effectiveness for manganese removal from groundwater. The criterion is a supplement of known and used methods for evaluation of pilot experiments for manganese removal from groundwater.

The following physical and chemical properties of the filter materials were determined: the MnO_2 content and the specific surface and volume of the pores of external catalytic layer of grains. These parameters were chosen because of the role of adsorption and heterogenic oxidation on the surface of grains during the manganese removal from groundwater.

MATERIALS AND METHODS

The examined filter materials were as follows:

- Three natural oxidative beds of manganese ores: one from Gabon (Gabon) and two ores called Pyrolox (Pyrolox I obtained in Poland and Pyrolox II obtained in Canada).
- One artificially activated filter material: Hydrolit.
- An oxide-coated filter media (ZP) obtained from the operating filters at Poznan WTP (Poland).
- Silica sand, not oxidative material as reference.

Table 1 | The quality of raw water used in the experiment

	Range of values	
Water quality parameter	**Series I (university lab.)**	**Series II (Poznan WTP)**
Manganese (mg/L)	0.2–1.4	0.2–1.0
Iron (mg/L)	0.05–0.2	0.15–1.0
Alkalinity (mgCaCO$_3$/L)	180–210	180–200
Bicarbonate (mgCaCO$_3$/L)	180–210	180–200
Total hardness (mgCaCO$_3$/L)	195–345	275–370
Ammonia (mgN/L)	0.0–0.11	0.6–1.0
Nitrate (mgN/L)	0.1–3.5	0.1–4.0
COD KMnO$_4$ (mgO$_2$/L)[a]	<4.0	3.2–4.0
Dissolved O$_2$ (mgO$_2$/L)	6.0–10.0	10.2–10.4
pH	7.0–7.6	7.1–7.4
Temperature (°C)	10–12	9–10

[a]COD, chemical oxygen demand – KMnO$_4$ method (permanganate value).

The research was conducted at pilot scale. The experiment evaluated manganese removal during the filtration process by each tested bed. There were two research series.

Series I

The installation was located in the laboratory of the Institute of Environmental Engineering at Poznan University of Technology. The filter columns filled with Gabon ore, Pyrolox I, Pyrolox II and Hydrolit were supplied with feed water based on tap water, with the addition of manganese sulfate to achieve a manganese concentration of 0.2–1.4 mg/L (Table 1).

Series II

The installation was located at Poznan WTP. The filter columns filled with oxide-coated filter media and clean silica sand were supplied with natural, aerated groundwater from the Poznan WTP. This water had a natural manganese content in the range 0.2–1.0 mg/L. The experiment schedule is given in Table 2. Poznan WTP, where Series II was conducted, supplies water to this part of the city, where the university laboratory is situated. Because of this fact, the parameters of water used for research in both series are similar.

The experiments were conducted using a pilot plant consisting of filtration columns, operated at a filtration rate (v_f) of 5.0 and 10.0 m/h. These values of filtration rate give a range of recommended values applied in drinking water treatment. The columns were 3 m high, with a diameter of 6 cm. A schematic diagram of the installation is presented in Figure 1. The
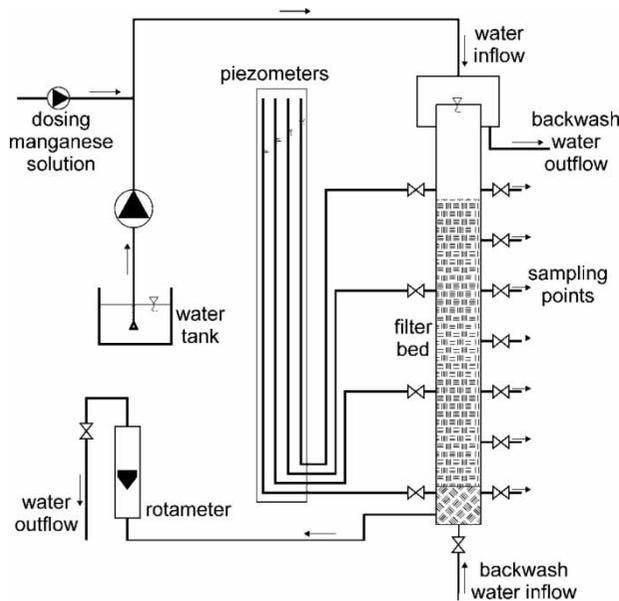
Table 2 | Schedule of the experiments

	Number of runs	Length of run 1 ($v_f = 5$ m/h) (h)	Length of run 1 ($v_f = 10$ m/h) (h)	Length of run 2 ($v_f = 5$ m/h) (h)	Length of run 2 ($v_f = 10$ m/h) (h)	Sampling frequency
University lab. Series I						
Gabon	2	12	12	12	12	Every 3 h
Pyrolox I	2	12	12	12	12	Every 3 h
Pyrolox II	2	12	12	12	12	Every 3 h
Hydrolit	2	12	12	12	12	Every 3 h
Poznan WTP Series II						
ZP	2	40	31	126	49.5	Every 4–5 h
Sand	2	86.5	35	164	48.5	Every 4–5 h

Figure 1 | Schematic diagram of the pilot filter.

experiments were conducted according to research methods used in water treatment technology (Sommerfeld 1999; Sozański & Huck 2007). In Table 1, the raw water quality for both experimental series is presented.

Table 3 presents granulometry parameters: d_{10} and uniformity coefficient d_{60}/d_{10}, filter bed depth H (m), specific density (g/cm^3) and bed porosity. In addition, a unit price of each filtration material (range of gross price in Poland, converted from Polish Zloty to Euro/kg) is given.

All materials tested in the experiment were allowed to be used for drinking water treatment technology as filtration materials and fulfilled all the requirements for strength and

composition. Proper selection and good exploitation guarantee a period of not less than 20–30 years of operation of filtration material. The additional condition for a long lifetime of filtration materials is a relatively stable raw water quality.

The following methods were used to determine the physical and chemical parameters of the filter media tested.

- Sieve analysis – granulometry.
- Adsorption method – internal structure parameters – pore volume and surface. The principle of the 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 is measured on the basis of the lengthening of quartz spirals whose length has been previously determined. For each sample the specific surface area of the internal structure was defined, measured with the Brunauer–Emmett–Teller (BET) isotherm method (Sozanski et al. 1987; Perry & Green 1997).
- Chemical analysis – MnO_2 percentage content in filtration material, water quality parameters obtained by standard methods (AWWA 2005b).

RESULTS

The average efficiency of manganese removal, E(Mn), for a filtration cycle was calculated according to:

$$E(\text{Mn}) = \frac{1}{n} \cdot \sum_{i=1}^{n} E_i(\text{Mn}), \tag{4}$$

Table 3 | Parameters of filter bed

	d_{10} (mm)	d_{60}/d_{10}	H (m)	Specific density (g/cm³)	Porosity	Unit price (Euro/kg)
Gabon	0.7	2.40	1.6	4.03	0.30	3.3–3.8
Pyrolox I	0.6	1.75	1.8	3.53	0.40	3.6–4.2
Pyrolox II	0.6	1.50	1.8	3.53	0.41	3.6–4.2
ZP	1.6	1.22	1.6	2.64	0.42	[a]
Hydrolit	1.1	1.50	1.6	2.92	0.45	1.0–1.2
Sand	1.3	1.25	1.6	2.63	0.36	0.2–0.4

[a]Oxide-coated silica sand.

where

$$E_i(\text{Mn}) = \frac{(c_\text{d})_i - (c_\text{o})_i}{(c_\text{d})_i} \times 100, \tag{5}$$

c_d and c_o are the concentrations of manganese at the inlet and outlet of the filter measured n times during the filtration cycle (mg/L) and n is the number of samples taken during a filtration run.

The results of the research and the corresponding operating parameters are presented in Table 4. The table contains values of the following parameters.

- Specific surface of the internal structure – S-BET (m^2/g).
- Pore volume – PV (cm^3/g).
- Percentage content of manganese dioxide in the filter media – [MnO_2] (%). (The percentage content of MnO_2 for homogenous material (Gabon and Pyrolox) was determined for the whole mass of the grains. The oxide coating of silica sand and Hydrolit was first removed out of the grains and then the catalytic layer was analyzed and the percentage content of MnO_2 was calculated with respect to the catalytic layer mass.)
- Efficiency of manganese removal $E(\text{Mn})$ (%) in the filtration process with filtration rate of 5 and 10 m/h.

The standard deviation for efficiencies is calculated. The values of S-BET, PV and [MnO_2] are the averages from two results. The difference between both results was less than 3%.

DISCUSSION

The characteristic parameters describing catalytic activity of oxidative media are:

- the percentage content of manganese dioxide in the filter media – [MnO_2] (%);
- the specific surface of the internal structure – S-BET (m^2/g);
- the pore volume – PV (cm^3/g).

The authors propose a method of evaluation of oxidative filter materials based on the physical and chemical parameters listed above. This method can be applied for all types of oxidative beds, i.e. manganese ores, oxide-coated filter beds and artificially activated materials. Values of these parameters allow a preliminary classification of media tested, according to their potential catalytic properties. The parameters mentioned above describe the physical and chemical properties of the external catalytic layer; therefore, they can be used for setting general criteria for all kinds of oxidative filter materials.

The oxide-coated filter media obtained from Poznan WTP (ZP) have the most complex internal structure, which is indicated by high values of specific surface and PV. The manganese ore from Gabon has the highest manganese dioxide content. Figures 2–4 show the results of the research presented as a relationship between manganese removal efficiency ($E(\text{Mn})$) and either the internal structure parameters or the MnO_2 content:

$$E(\text{Mn}) = f(\text{PV}) \tag{6}$$

$$E(\text{Mn}) = f(\text{S-BET}) \tag{7}$$

$$E(\text{Mn}) = f([\text{MnO}_2]) \tag{8}$$

Very good results for manganese removal were achieved in filtration through Gabon, Pyrolox I, Pyrolox II and the

Table 4 | Experimental results, standard deviation given for $E(\text{Mn})$

	S-BET (m^2/g)	PV (cm^3/g)	[MnO_2] (%)	$E(\text{Mn})$ v_f = 5 m/h (%)	$E(\text{Mn})$ v_f = 10 m/h (%)
Gabon	33.1	0.079	81.0	100 (0)	100 (0)
Pyrolox I	9.4	0.033	55.0	100 (0)	100 (0)
Pyrolox II	10.5	0.032	51.3	100 (0)	100 (0)
ZP	110.5	0.030	63.7	100 (0)	100 (0)
Hydrolit	5.5	0.012	31.4	80 (8)	68 (10)
Sand	0.0	0.008	0.0	26 (5)	20 (5)
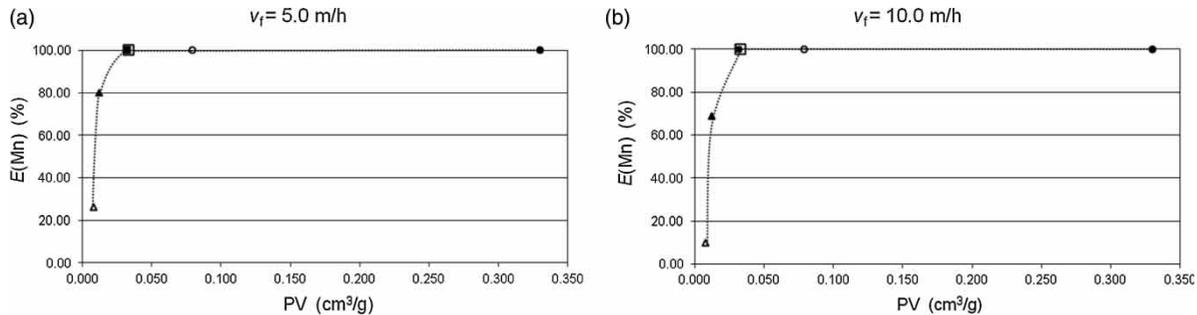
Figure 2 │ Relationship between manganese removal efficiency and PV of the filter media. (a) $v_f = 5$ m/h and (b) $v_f = 10$ m/h. Pyrolox I □; Pyrolox II ■; Gabon ○; oxide-coated sand (ZP) ● ; Hydrolit ▲; clean sand △.
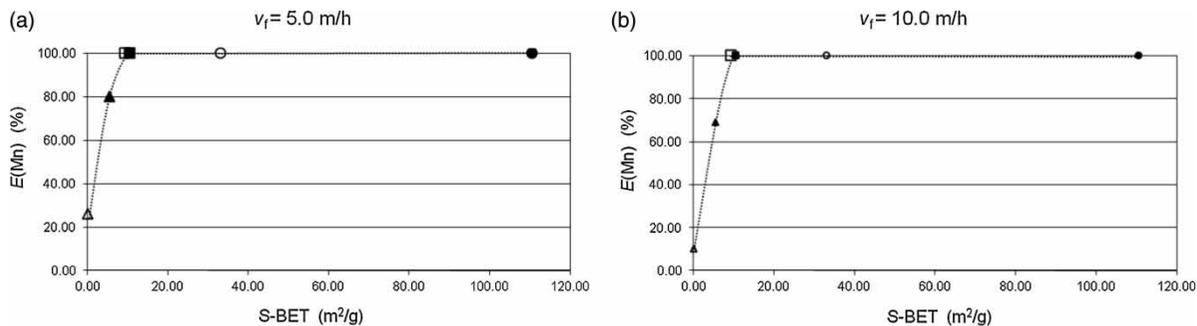
Figure 3 │ Relationship between manganese removal efficiency and specific surface (S-BET) of pores of the filter media. (a) $v_f = 5$ m/h and (b) $v_f = 10$ m/h. Pyrolox I □; Pyrolox II ■; Gabon ○; oxide-coated sand (ZP) ●; Hydrolit ▲; clean sand △.
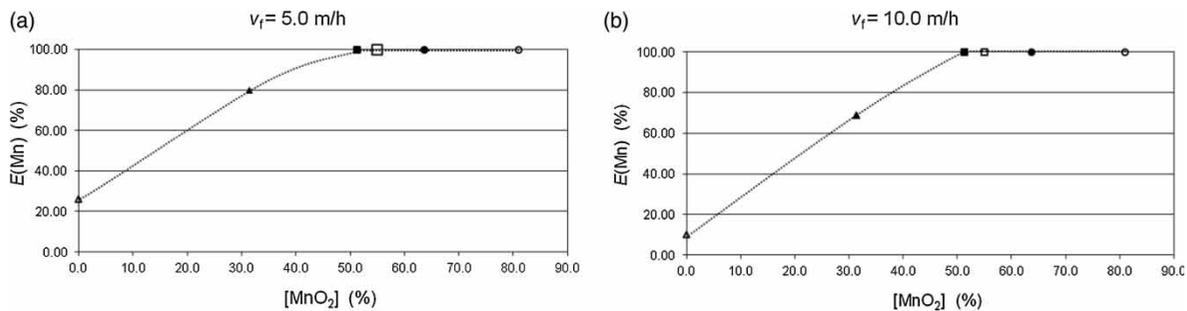
Figure 4 │ Relationship between manganese removal efficiency and percentage MnO₂ content in the filter media (mass basis). (a) $v_f = 5$ m/h and (b) $v_f = 10$ m/h. Pyrolox I □; Pyrolox II ■; Gabon ○; oxide-coated sand (ZP) ●; Hydrolit ▲; clean sand △.

oxide-coated filter bed (ZP). In all of these cases, the efficiency of manganese removal was 100%. These beds are characterized by high values of pore surface and volume. The Hydrolit bed did not give such good results and the efficiency of manganese removal was 80% for $v_f = 5$ m/h and 68% for $v_f = 10$ m/h. The worst results for manganese removal were obtained in filtration through a clean sand bed, as was expected. The efficiency of manganese removal during filtration through this bed was 26% for $v_f = 5$ m/h

and 20% for $v_f = 10$ m/h. The sand bed is characterized by the lowest values of pore surface and volume. Therefore, the results of the experiment allow us to conclude that the surface and PV of the filtration material influence the results of manganese removal. The higher the values of pore surface and volume, the better the effectiveness of the manganese removal.

The second part of the interpretation consists of the estimation of the correlation between the percentage of MnO₂

in the media (on a mass basis) and the efficiency of manganese removal. This criterion, based on MnO_2 content, describes the redox potential of oxidative filter media (Faust & Aly 1998; Jeż-Walkowiak 2000). The results of the experiments show that the effectiveness of manganese removal is directly proportional to the percentage of MnO_2 content in the filter materials (Figure 4).

To provide further interpretation, a parameter termed catalytic activity coefficient (CAC) was introduced. The value of the coefficient is the product of the following characteristic parameters: PV and surface and MnO_2 percentage content:

$$CAC = (PV) \cdot (S\text{-}BET) \cdot ([MnO_2]). \qquad (9)$$

The practical significance of this parameter is demonstrated by presenting the relationship between CAC values calculated for all materials tested and the corresponding manganese removal:

$$E(Mn) = f(CAC) \qquad (10)$$

Figure 5 presents values of CAC calculated for the tested materials and Figure 6 presents the relationship shown in Equation (10).

The presented results were obtained at filtration rates of 5 and 10 m/h. Interpretations based on CAC values assume the same importance of PV and surface and manganese dioxide content (the three factors of the CAC) for the catalytic activity of oxidative beds.

The results presented in Figure 6 allow the determination of the minimum value of CAC above which the
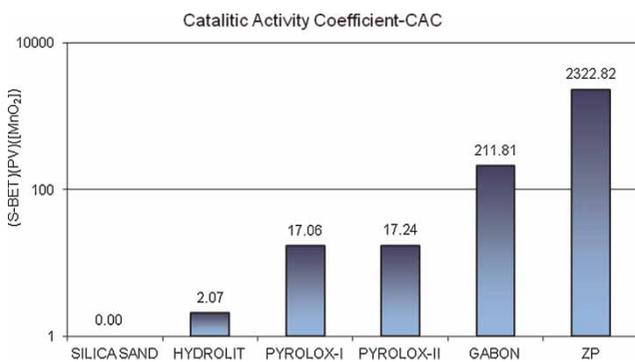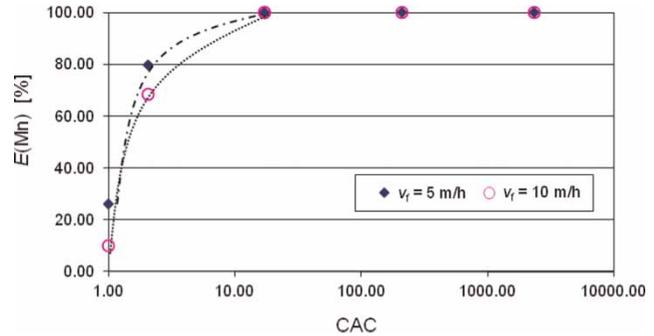

Figure 6 │ Relationship between CAC values and manganese removal efficiency of tested materials.

high performance of oxidative filter materials is assured. The efficiency of almost 100% corresponds with the minimum values of internal structure parameters and MnO_2 content. These critical values are $PV_{min} = 0.03 \text{ cm}^3/\text{g}$, $S\text{-}BET_{min} = 9.0 \text{ m}^2/\text{g}$ and $[MnO_2]_{min} = 45\%$.

The efficiency of media characterized with parameters below the critical values is highly dependent on CAC value. The critical values mentioned above are only valid for minerals tested in this study.

CONCLUSIONS

1. The results of the research clearly show the influence of internal structure parameters (specific surface and PV) and MnO_2 percentage content in oxidative filter media on the effectiveness of manganese removal.
2. The significance of these three parameters for evaluation of oxidative filter materials is confirmed by the relationship between manganese removal efficiency $E(Mn)$, and values of these parameters (Figures 2–4).
3. An increase of the above-mentioned parameters caused improvement of effectiveness of manganese removal up to a point of complete removal ($E(Mn) = 100\%$).
4. There are critical values of the parameters, ensuring high efficiency of manganese removal ($PV_{min} = 0.03 \text{ cm}^3/\text{g}$, $S\text{-}BET_{min} = 9.0 \text{ m}^2/\text{g}$, $[MnO_2]_{min} = 45\%$). These critical values are determined according to the relationships presented in Figures 2–4.
5. The authors propose to introduce a new parameter: CAC a product of specific surface, PV and MnO_2 percentage content in the oxidative filter media. The significance of

Figure 5 │ Values of CAC calculated for tested materials.

this parameter for evaluation of oxidative filter materials is confirmed by the relationship between CAC and manganese removal efficiency E(Mn). The media characterized with high CAC values represent high effectiveness of manganese removal.

The goal of the application of the described method is preliminary evaluation of the suitability of the filtration materials for manganese removal from groundwater. The evaluation based on this method may be carried out before the research on adsorption capacity (isotherm parameters) and adsorption kinetics. Research on adsorption is usually conducted for specific water and tested filtration materials. The proposed criterion is related specifically to the properties of the filtration materials, regardless of the water. Thus, the method may be considered as a preliminary (introduction) stage, allowing the selection *a priori* of oxidative materials for the schedule of specific research. The presented method allows the prediction of manganese removal efficiency in all types of oxidative filtration beds: natural ores, commercial oxidative materials and oxide-coated silica sand.

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