Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2015.1043487

57 (2016) 1611–1619
January

Taylor & Francis
Taylor & Francis Group

Efficiency of manganese removal from water in selected filter beds

Iwona Skoczko*, Janina Piekutin, Katarzyna Ignatowicz

Department of Technology in Environmental Protection and Engineering, Technical University of Bialystok, 45A Wiejska Str., 15-351 Bialystok, Poland, Tel. +48 85 746 96 44; email: i.skoczko@pb.edu.pl (I. Skoczko)

Received 23 June 2014; Accepted 23 March 2015

ABSTRACT

Manganese salts in groundwater are among the most troublesome compounds and if these waters are to be used for municipal and industrial purposes, manganese must be removed to meet normative levels in accordance with the regulation of Minister of Health (20 April 2010) and the European Union Council Directive 98/83/EC. The aim of this study was therefore to select the most efficient filter beds to remove manganese from drinking water or water for economic purposes. The research included conducting the filtration process, in which seven different beds were used as the filter material: the Greensand, G-1, the Hydrocarbon, Zeolite, the Crystal Right, Ecomix A, and Ecomix C. All tested beds could be used for elimination of manganese. The authors showed a dependence of the concentrations obtained in the filtrate on the type and the nature of particular beds. It is recommended that the Greensand, the Crystal Right, and Ecomix C should be used in order to purify groundwater, where there is no additional contamination with organic compounds and water has increased hardness. For surface or infiltration water, where there is reduced concentration of manganese, the authors recommend that G-1, the Crystal Right, and Ecomix C should be used, whereas Zeolite, the Hydrocarbon, and Ecomix should not be used as stand-alone filters.

Keywords: Water treatment; Filtration; Removal of manganese

1. Introduction

Groundwater often come from layers located at different depths, as a result, they have varied chemical composition. The occurrence of super-normative manganese content in groundwater and associated with water treatment is a very common problem. According to the Minister of Health dated on 20 April 2010 [1], the concentration of manganese in water should not exceed 0.05 mg/L. That concentration is in accordance with the regulations on the quality of water intended for human consumption in the EU member states, which are set up in European Union Council Directive 98/83/EC which has been in force since 25 December 1998 [2]. Manganese salts in groundwater are the most troublesome compounds and if these waters are to be used for municipal and industrial purposes, manganese must be removed to lower its concentrations to normative levels in accordance with the above regulation.

*Corresponding author.

Presented at the 12th Scientific Conference on Microcontaminants in Human Environment
25–27 September 2014, Czestochowa, Poland

Manganese in groundwater usually occurs with iron, but quantitatively, its level is much lower. Manganese in natural waters can be found in forms of Mn^{1+}, Mn^{3+}, and Mn^{4+}. However, Mn^{4+} is most common and this form migrates [3]. Some authors report its concentration of several to 10 times lower than the iron concentration, and ranging up to a few mg/L [4]. Manganese, like iron, can be bound to humic acids and hence forms complexes or chelates with functional groups of humic acids [5]. In waters, where there is only a small amount of oxygen, the concentration of dissolved manganese may be up to several mg/L. High concentrations of manganese in groundwater are observed in the presence of sulfide deposits up to 50 mg Mn/L and also in some thermal springs [6]. Manganese is present in about 150 minerals, typically as silicates, phosphates, oxides, less frequently as carbonates and sulfates [7]. The concentration of manganese in water is dependent on solubility, which is determined by acidity and redox balance [8]. It was found [9] that the amount of dissolved manganese increases in water-containing organic substances where nitrification processes occur and manganese is released to the water from decayed organisms. Water with an elevated manganese concentration is characterized by an unpleasant odor and taste. An increased concentration of manganese compounds causes darkening of white fabrics, formation of dark deposits in sanitary devices. Besides it also hampers proper functioning of filters and water meters. It is recommended to remove it from waters that are economically utilized by people. Modern technologies indicate oxidative or active beds as most effective in removing the manganese compounds.

The aim of the study was to select the most efficient filter bed to remove manganese from drinking water or water for economic purposes.

2. Methods

2.1. Material

The research included conducting the filtration process, in which seven different beds available on Polish and European markets were used as the filter material: Greensand, G-1, Hydrocarbon, Zeolite, Crystal Right, Ecomix A, and Ecomix C (Table 1). Descriptions of each of the filter beds are shown in Table 1. The filter beds were placed in laboratory models of gravitational filters of 0.20 m height, 0.07 m diameter, and 0.035 m^3 working capacity. The minimum filtration speed recommended for individual beds, i.e. from 0.7 to 2 m/h was preserved. Laboratory tests of water samples were carried out in the Department of Technology in Engineering and Environmental Protection in Bialystok University of Technology in Poland. The study included determination of the raw water and samples of water filtered after each filter had been selected for the test. Raw water was formulated on the basis of tap water. The model water was prepared in two 100-L tanks, which were combined to pomp system alternately. The tap was left for one day in both tanks. Chlorine residue decreased from the primary level of 0.1 mg/dm^3 to the level of 0.0 mg/L after that time. Such water could be the base for the model of water used in conducted experiments. Next, the solution which was free of chlorine residues was prepared: each 10 L of tap water was mixed with 1.3 g of manganese (III) sulfate, 10 g of enriched broth, 1 g of ammonium sulfate, and 1.2 g of $Ca(OH)_2$, to give the concentration of manganese in raw water of 0.50–0.55 mg/dm^3, ammonium nitrogen of 1.5–2 mg/dm^3, COD-Mn of 8–10 mg/dm^3, and hardness of 200 mg $CaCO_3$/dm^3.

2.2. Research methodology

The scope of water tests included the manganese content, pH of the water, COD-Mn, color, turbidity, and its total hardness. The analysis of manganese concentration met the norm PN-78/C-04545 where the color of studied solution was tested with a spectroscopic method No. 2260 using HACH DR/400 V. The method based on light comparison with the wave length $\lambda = 560$ nm of spectroscopic trace with distilled water. PH of the water was measured with pH-metr "Elmetron" equipped with glass electrode. COD-Mn analysis met the norm PN-85/045578/02 with H_2SO_4, $KMnO_4$, and samples heating within the timespan of 30 min. Water color was analyzed with spectrophotometer HACH DR/40 0 V, the method No. 1670 Color. Water turbidity was analyzed with a spectrophotometer HACH DR/40 0 V, the method No. 3750 turbidity. Total hardness met the norm PN-ISO 6059:1999 with EDTA solution and eriochromic black as an indicator.

The study was conducted in three test cycles. Each cycle lasted until the filtering abilities of beds and filter were used up. It was followed by regeneration and washing up the filters The first series lasted 14 d, the second one 10 d, and the third one also 10 d. The backwash and regeneration followed each series. Regeneration solution and backwash velocity is described in Table 1. The washing was carried out in counter-current and parallel-current flow directions using a medium recommended by the manufacturer and water. Samples for tests were collected daily.

Table 1
Studied filter beds' properties

Properties	Ecomix A	Ecomix C	G-1	Zeolite	Greensand	Cristal Right	Hydrocarbon
Temp.	0–40°C	0–40°C	5–40	5–40	5–35	5–40	0–40
pH	5–10	5–10	5–9	5–9	6.2–8.0	5.5–40	3–12
Flow: normal	20–25 m/h	20–25 m/h	10–20 m/h	36–48 m/h	12–24 m/h	8–12 m/h	3–50 m/h
backwash regeneration	10–15 m/h 3–5 m/h	10–15 m/h 3–5 m/h	30–60 m/h –	50–65 m/h –	20–30 m/h 7–12 m/h	15–20 m/h 3–5 m/h	35–95 m/h –
Regeneration	NaCl 8–10%	NaCl 8–10%	Water	Water	$KMnO_4$ 0.2–0.5%	NaCl 5–10%	Water
Ion exchange capacity	0.7–0.8 eq/dm^3	0.6–0.7 eq/dm^3	–	–	–	0.5–0.6 eq/ dm^3	–
Granulation	0.3–1.2 mm 80–90% 2.0–4.0 mm 10–20%	0.3–1.2 mm 80–90% 2.0–4.0 mm 10–20%	0.5–4 mm	0.75–1.0 mm	0.3–0.35 mm	1.2–1.6 mm	0.8–4.0 mm
Appearance	Mix of white, gray, beige, brown, and dark brown granules	Mix of white, gray, beige, brown, and dark brown granules	Brown granules with single white and gray grains	White and gray porous grains	Black granules	White, Gray and rose granules	Flat black grains
Density	0.8 t/m^3	0.8 t/m^3	4.0 t/m^3	0.8–1.3 t/m^3	2.4 t/m^3	1.29 t/m^3	1.45 t/m^3
MnO_2 cover	–	–	75%	–	1.2%	–	–
Provenance	Chemical industry	Chemical Industry	Natural material	Natural material	Natural activated material	Natural material	Natural material
Other	Does not depend on pH, organic pollution, chlorine, and sulfate	Does not depend on pH, organic pollution, chlorine, and sulfate	Contaminated water up to 30 mg Fe/dm^3 and 2 mg Mn/dm^3	Easily dissolved in HCl and change into gel silicate	Remove up to 15 mg Fe /dm^3 and 5 Mn mg/dm^3	–	–

3. Results and discussion

Despite years of research, the problem of an effective groundwater treatment referring to excessive contents of manganese is still valid. New, effective, and economical methods of its removal from water have been searched for. The issue is even further complicated by diverse chemical composition of groundwater. Another treatment technology should be used for waters containing lower and higher concentrations of pollutants, when manganese is present in water together with carbon dioxide, dissolved gases, ammonium ion, increased color and turbidity, increased hardness, and organic compounds. A particular problem is the presence of organic impurities at the concentration higher than 5 mg O_2/dm^3. Most of the catalyst and oxidation deposits are sensitive to their

Table 2
Average pH values during three experimental series

Test No.	I	II	III	IV	V
Raw water	5.86	5.2	5.77	5.6	4.25
Ecomix A	8.04	6.8	6.65	6.5	5.95
Ecomix C	7.03	7.3	7.01	6.9	6.5
G-1	6.48	5.5	6.15	5.8	5
Zeolite	6.55	5.5	6.17	6.13	4.85
Greensand	7.35	5.47	6.02	5.9	4.8
Crystal Right	6.91	6.43	6.53	6.5	6
Hydrocarbon	7.07	5.6	6.37	6.11	4.68

Table 3
Average COD-Mn values during three experimental series (mgO_2/L)

Test No.	I	II	III	IV	V
Raw water	10.1	9.6	9.9	9.5	10.4
Ecomix A	10	8.9	9.8	9.3	9.4
Ecomix C	9.9	9.4	9	8.7	9.1
G-1	10	9.6	9.4	9	9.6
Zeolite	10	9.4	9.2	9	9.5
Greensand	10	9.4	9.6	9.4	10.3
Crystal Right	10	8.8	9.7	9.3	9.8
Hydrocarbon	10.1	9.4	9.6	9.3	9.7

Table 4
Average color values during three experimental series (mg Pt/L)

Test No.	I	II	III	IV	V
Raw water	79	79	71	77	72
Ecomix A	38	15	21	13	43
Ecomix C	42	1	27	28	39
G-1	53	23	25	41	34
Zeolite	31	15	10	30	17
Greensand	24	1	2	22	13
Crystal Right	30	10	10	29	24
Hydrocarbon	49	14	18	40	27

Table 5
Average turbidity values during three experimental series (NTU)

Test No.	I	II	III	IV	V
Raw water	9	1	5	6	6
Ecomix A	8	2	0	2	8
Ecomix C	8	0	1	4	9
G-1	8	0	0	7	6
Zeolite	2	0	0	7	2
Greensand	2	0	0	6	1
Crystal Right	4	0	0	7	3
Hydrocarbon	4	0	0	7	3

Table 6
Average total hardness values during three experimental series (mval/L)

Test No.	I	II	III	IV	V
Raw water	4.48	4.8	4.64	4.4	4.24
Ecomix A	0	0	0	0	0
Ecomix C	0	0	0	0	0
G-1	4.4	4.56	4.8	4.56	4
Zeolite	4.8	4.88	4.48	4.08	4.24
Greensand	5.04	5.2	4.64	4.4	4.08
Crystal Right	3.44	0.16	0.32	1.12	1.84
Hydrocarbon	5.2	4.8	4.64	4.64	4.56

presence. The efficiency of manganese removal is considerably decreased then. Color remains in the water, which is a parameter that disqualifies such water for consumer and economic purposes. Chemical oxidation applying chlorine, chlorine dioxide, ozone, or potassium permanganate can be performed. However, only strong chemical oxidants are capable of breaking down the organic chains and then oxidize manganese. Nevertheless, they require some additional equipment in the form of complex dosage devices and appropriate permits for the storage and the use of corrosive and environmentally hazardous substances.

As a part of this study, the effectiveness of manganese removal by means of filtration beds of various application, which are available on the European market, was verified. The obtained results are shown in Figs. 1–3. The side pollutants average values are shown in Tables 2–6. Each table includes average values from three experimental series.

The Greensand-type beds produced from glauconitic sand are a common material used for removing manganese from water. The sand is coated with a thin layer of manganese dioxide, which in the presence of reducing agents is converted into a reduced form of manganese (III). The content of MnO_2 in a commercial product is 0.6–1.5%. It requires flushing with potassium permanganate after using up the oxidizing properties, which is also a frequent defect disqualifying this bed when used by less experienced engineers. Many researchers have confirmed its high effectiveness in removing the manganese and iron forms from water [10,11]. According to available literature, under technical operating conditions and when using preferred operating speed, the initial manganese concentration in the range of 0.03–0.05 mg/dm^3 can be obtained. In the present study, even lower manganese concentrations at the outlet of the filter, ranging between 0.002 and 0.005 mg/dm^3 were achieved. This made it possible to achieve 95–99% of removal as compared to the raw water. It should be noted that low filtration speed adapted to the laboratory conditions was applied, which contributed to achievement of good results. Only at the end of each cycle, the concentrations of manganese rose to the value of 0.1–0.3 mg/dm^3, which was caused by filters clogging due to precipitated sediments. The bed showed some sensitivity to the presence of organic substances (about 8–10 mg/dm^3) and ammonium nitrogen (about 1.5–2.5 mg/dm^3). It remarkably shortened the timespan between backwash to about 10 d. The second and third series of tests were characterized by similar results. In both series, water at the outlet from the Greensand bed contained significantly elevated levels of manganese, i.e. from 0.05 to 0.03 mg/dm^3 and 0.5 mg/dm^3 immediately before backwashing, which gives the effect of the removal of manganese in the range of 96.3–62.8%. These values exceed the limits for drinking water [1]. The bed clogging was observed, as it was the case in the first series, after about 10 d. The accumulation of organic material deposits in the bed, precipitation of hardness, and the excess of precipitated MnO_2 influenced on reduced bed purification and time between backwash. This also confirms the need to regenerate the bed using potassium

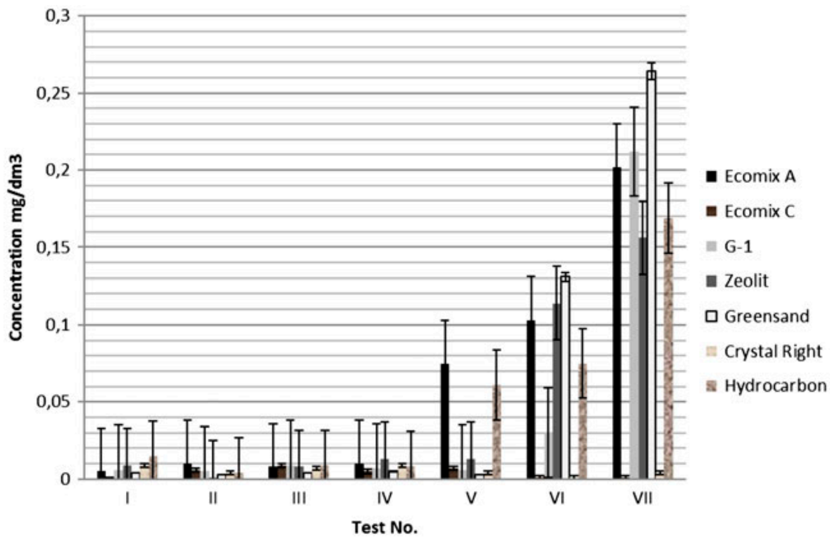

Fig. 1. Manganese concentrations achieved in filtered water after passing through beds: Ecomix A, Ecomix C, G-1, Zeolite, Greensand, Crystal Right, and Hydrocarbon in the first test series.
Note: Vertical lines linked to each presented bar described standard error.

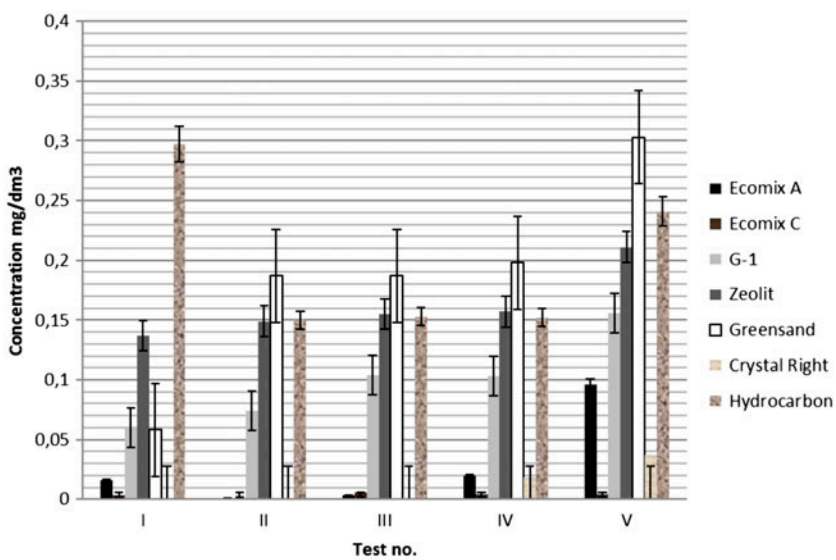

Fig. 2. Manganese concentrations achieved in filtered water after passing through beds: Ecomix A, Ecomix C, G-1, Zeolite, Greensand, Crystal Right, and Hydrocarbon in the second test series.
Note: Vertical lines linked to each presented bar described standard error.

permanganate solution, which is recommended by the manufacturer and other researchers [5,10,11].

Another analyzed bed was G-1. It is a naturally occurring mineral in the form of brownish-black dust-free granulate. It is an abrasion-resistant mineral. It is used to filter water containing excessive amounts of iron and manganese, particularly in the case of their occurrence in organic forms. The bed is rinsed with water. On G-1 bed, the speed of filtration was 1.17 m/h and studies were conducted identically to the first analyzed bed. Manganese removal effectiveness during the first series on the active G-1 during the first six test samples was approximately 99%, which gave the concentration of 0.005–0.03 mg/dm^3, whereas at the end of the first series, it was reduced to about 0.2 mg/dm^3, i.e. 57%. In the second and third cycles of the test after backwashing with water, the manganese concentration in purified water was higher

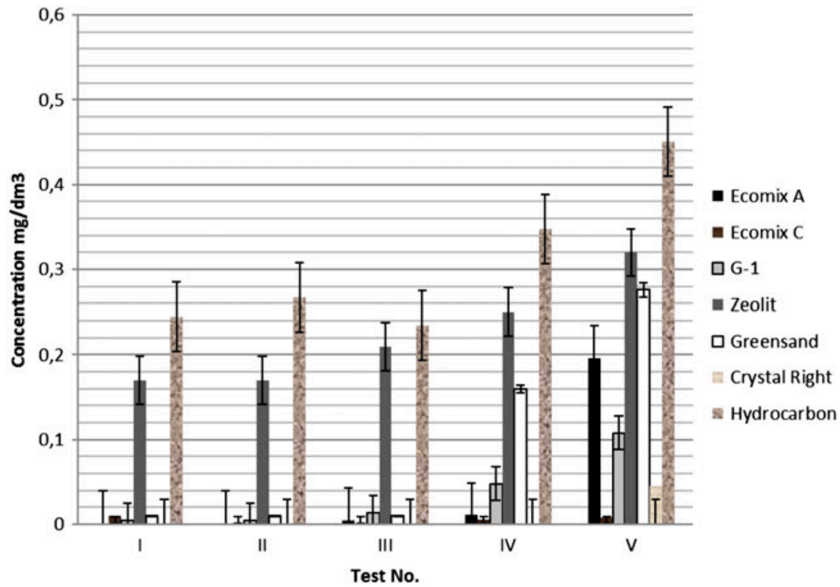

Fig. 3. Manganese concentrations achieved in filtered water after passing through beds: Ecomix A, Ecomix C, G-1, Zeolite, Greensand, Crystal Right, and Hydrocarbon in the third test series.
Note: Vertical lines linked to each presented bar described standard error.

and amounted to 0.05–0.1 mg/dm^3 giving the efficiency of removal of about 72.8–85%. At the end of this series, the concentration of manganese in the filtrate was about 0.15 mg/ dm^3, which was converted onto about 68% of removal. However, G-1 is a natural porous rock resistant to clogging due to organic contaminants and ammonium nitrate. Compared to the Greensand, the particles are much larger and, as a result, are the spaces between them, too. This makes it possible to accumulate a larger amount of suspensions from purified water. It is characterized by high specific gravity of about 4t/m^3. Effective rinsing must therefore be carried out quite intensively; otherwise, low purification effects are obtained. Mohammad et al. [12] verified the possibility of manganese and other metals removal from water in pyrolusite bed having similar properties as G-1. The best results were obtained by the sorption of lead. The efficiency of manganese removal remained at the level of 70–80%. The high efficiency of the process was noted by Means and Rose [13]. He reported that hardness of the water was a disturbing factor after several cycles of filtration. However, in surface water contaminated with manganese and characterized by low hardness, the manganese removal efficiency ranged about 97–99.6% at the concentrations in the filtrate of 0.002–0.01 mg/dm^3.

The third analyzed bed was Hydrocarbon. It is a natural charcoal, which is mainly used to improve the filtering effect and to lengthen the filtration cycle. It is widely applied in the multilayer filtration for the protection of filters filled with activated carbon, ionites, the reverse osmosis system, and for fine filtration after softening and rapid de-carbonization. The charcoal beds were popular in the 1990s of the twentieth century. One of the researchers praising their versatility was Khoe and Waite [14], who studied their use in the purification of water contaminated with iron and manganese. He evidenced a significant loss of both elements in the purified water, i.e. 95% iron and 75% manganese, up to concentrations required for drinking water. The authors of this study did not appreciate charcoal beds as recommended for the treatment of manganese. Tested Hydrocarbon had the shape of planar carbon flaps of approximately 2 × 4 mm dimensions. In the first series of research, manganese concentrations required by the EU Directive were achieved within 7 d, after which the filtration purification effect rapidly deteriorated. The second and third series of tests confirmed its low efficiency. The efficiency of purification was rated on average 50% and the concentrations of tested compound in the filtrate were in the range of 0.15–0.3 mg/dm^3 regardless of the time of filtration. Munter et al. [15] claims that charcoal may be used to remove iron from water, and due to its inert nature, it is not suitable for manganese. Jeż-Walkowiak et al. [16] noted that the effectiveness of manganese removal by charcoal bed depends on the degree of "working-out." The more "worked-out" the bed, the more visible manganese concentration decrease in the test water occurs. On the other hand, this type of filtration is useful for removal of organic compounds [17,18].

Another tested bed was Zeolite that is a natural mineral classified as a group of aluminosilicates. Its core design provides a unique molecular-sieve, adsorption, and ion exchange properties. Zeolites are used for mechanical purifying of water, they effectively remove ammonium ions and soften the water at the same time improving its pH. They also absorb manganese ions. Adamczyk et al. [19] studied the possibility of eliminating high manganese concentrations from aqueous solutions. Its concentration in solution before sorption was 5.09 mg/dm^3, which was one hundred times higher than the normative values. Determinations of manganese concentrations in the solutions after sorption were carried out in 0.5–24 h. According to the authors of this study, the lowest concentration of the metal in solution was obtained after sorption carried out for 1 h. The concentration amounted to 0.047 mg Mn/dm^3 giving a 99.08% reduction of the metal concentration in water. Along with the sorption time, the concentration of manganese in solution increased, which may be due to the reaction of giving away the metal ions by Zeolite to the solution. Sorption studies revealed that the equilibrium of the process was achieved in a very short period of time—about 2 h. The percentage of reduction the Mn concentration in solution using Zeolite was very high and typically amounted to 97%. After washing in the second and third cycles, the efficiency slightly decreased to about 74% with a subsequent decrease along with the tests. Zeolites are not widely used for manganese removal from water. The authors of this study confirm their high efficiency in the removal of ammonium nitrogen (up to 0.2 mg/dm^3) and organic compounds (up to 3 mg/dm^3). They also retain organic manganese complexes. However, Zeolites should not be used for the removal of mineral forms. They can therefore be applied in the purification of surface or infiltration water with low concentrations of manganese and elevated COD.

Another tested bed: The Crystal Right is also from a group of Zeolites. It is a Zeolite produced especially for the treatment of utility and technological water for the purpose mainly of softening and pH adjustment. Zeolite resin is made of hydrated sodium aluminosilicate and regenerated with sodium chloride like ion exchange resins. The Crystal Right bed used in the study allowed for effective removal of manganese from water. The resulting concentrations in the first series were between 0.001 and 0.008 mg/dm^3, while in the second and third series, the removal amounted to 0.01–0.03 mg/dm^3 90–99.7%. The filtered water also increased pH to about 8.8–9.2. Refs. [3,4,6,8] emphasize that the process of manganese removal is more effective at pH above 9. Thus, it can be concluded that the Crystal Right has an enhanced ability to eliminate manganese. As a derivative of Zeolites with high sorption capacity, it can retain organic manganese bindings. As a natural ion exchanger, it allows for the precipitation of MnO_2 at elevated acidity due to atmospheric oxygen dissolved in water. The agent also showed very high affinity for neutralization of water hardness within the range of 95–100%. It also enabled the effective removal of ammonium ions up to the concentration of 0.1–0.3 mg/dm^3. The results of these studies were worse in samples, where elevated COD values were recorded. Nevertheless, rinsing the deposits eliminated the problem. Research on the Crystal Right bed was also done by Kaleta et al. [20]. She examined water with a significant hardness 290–365 mg $CaCO_3$/dm^3, which also contained excessive manganese contents ranging between 2.04 and 3 mg/dm^3, and ammonium nitrogen in the range of 1.25–3 mg/dm^3. The first cycle was carried out to the point of depletion, which was defined due to the concentration of manganese. Next, the bed was regenerated while the second cycle was carried out. Manganese concentrations remained below the permissible norm, i.e. 0.05 mg/dm^3 in the first test cycle. The break point in the second test cycle was reached after filtration of the half volume of water permeated through the filter in the first cycle. This may indicate a dependence of manganese removal on the concentration of organic compounds in water which was noticed in the present study. According to tested bed's producer, the Crystal Right is sensitive for elevated concentration of COD and ammonia. It causes worse efficiency of removal of other compounds present in water. That is why the time of effective filtration could be shortened and elevated concentration of manganese appeared in the filtrated water. Bigger organic parts block small pores in grains, and without proper intensive backwash, they cannot be removed.

The ion exchange resins having the trade name Ecomix A and Ecomix C were the last tested agents. Ecomix A is a versatile bed for water treatment in the form of a mixture of filter beds. According to the manufacturer, it removes organic compounds, ammonia, hardness, calcium carbonate, and iron, however, the manufacturer does not guarantee the effective removal of manganese. Regeneration can be done by means of sodium chloride. Ecomix C is the perfect bed for the removal of hardness, iron, ammonium ion, and organic contaminants in potable water and water used for industrial processes. It is regenerated with sodium chloride like Ecomix A. Beds Ecomix A and Ecomix C are new to the Polish market and registered by a patent. According to the analyses made by the authors, both deposits are a mixture of ion exchange resins, Zeolites, and neutral particles. In the available literature, there is no information on the research conducted with the use of these beds. Ecomix C turned out to be a better bed in the process of manganese removal. In the first cycle of the test, the efficiency of the first attempt amounted to 100%. Much worse results were recorded for Ecomix A—about 96% at a concentration of 0.005 mg/dm^3. In further observations, Ecomix C was characterized by consistently high ability to remove the test parameter from water since its efficiency in further tests was about 99% at manganese concentration in purified water within the range of 0.005–0.01 mg/dm^3, while in Ecomix A bed—about 50%, i.e. about 0.5 mg/dm^3. In a subsequent test cycle after bed regeneration using brine, i.e. 5% NaCl solution, the Ecomix C manganese removal efficiency was maintained at a constantly high level—about 99% or 0.005 mg/L. In the case of Ecomix A—about 95%, i.e. 0.05 mg/dm^3, followed by a sharp decline in the effectiveness of treatment. As a result, both beds required another regeneration. In the next cycle, in a short time Ecomix A again was broken, while Ecomix C still maintained good efficiency of manganese removal. As mentioned earlier, the manufacturer did not recommend that Ecomix C should be used to remove mineral impurities and metal ions from water. He emphasized the high removal efficiency of organic pollutants and ammonia nitrogen. This was confirmed by carried out research. The COD concentration in the filtrate was obtained at the level of 1–5 mg/dm^3, ammonia nitrogen 0.0–0.5 mg/dm^3. Purified water was characterized by a color of 0.0 mg/dm^3, turbidity of 0.5 NTU, and about pH 7.5. The only parameter whose efficiency was lower than 50% was hardness. Similar results were obtained by Skoczko [21] who examined the quality of water flowing out of the range of several columns filled with different homogeneous ion exchange resins. Ecomix A, as opposed to the manufacturer's recommendations, did not allow for the removal of manganese ions from water to the level of 0.05 mg/dm^3. The bed showed some ability to remove hardness (up to 100%). Cations (NH_4^+) and organic substances were not eliminated from water.

According to the manufacturers, all tested beds can be used for the elimination of manganese. The authors showed the dependence of obtained concentrations in the filtrate on the type and the nature of different beds. For the purification of groundwater, where there is no additional contamination with organic compounds and there is increased hardness, it is recommended that the Greensand, the Crystal Right, and Ecomix C (group 1) should be used. For surface or infiltration water, beds that eliminate the above-mentioned impurities are needed. Moreover, in these waters, there is a decreased concentration of manganese. On the basis of performed analyzes, the authors recommend that in these cases, G-1, the Crystal Right, and Ecomix C beds (group 2) should be used. Despite being tested in the present study, Zeolite, Hydrocarbon, and Ecomix A are not listed in both groups of beds. According to the authors, they should not be used as a stand-alone filters; instead, they can be used in combined systems or to the water pre-treatment in order to extend durability of beds from groups 1 and 2.

4. Conclusions

(1) Among all tested beds, Ecomix C, the Greensand, and the Crystal Right appeared to be the best in reducing the manganese concentration in raw water. Filter backwashing every 5–7 d is a precondition for treatment efficiency.
(2) Natural porous beds retain organic substances and ammonia nitrogen contained in water. They are less effective in manganese removal.
(3) Beds with neutral acidity and not having the catalyst properties pass higher manganese concentrations in the filtrate rather than those increasing the acidity or having an active MnO_2 coating.
(4) The quality of beds' activity should not be assessed on a base of the first test cycles since the results are diminished. At least 3 test series should be performed to evaluate the abilities of beds to remove selected parameters.

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