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Original Research

Removal of Iron and Manganese from Water Using Filtration by Natural Materials

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Abstract

In many cases, water intended for drinking purposes must be treated in order to meet the requirements of Regulation of the Government of the Slovak Republic No. 354/2006 on drinking water. There is a tendency to find more efficient and cost-effective materials and technologies used in water treatment. The goal of this study is to compare activated natural zeolite-clinoptilolite with activated filtration sand and the imported material Birm (from the Clack Corporation, USA) in removal of iron and manganese from water. Obtained results carried out in the water treatment plant in Holíč prove that Klinopur-Mn is suitable for removal of iron and manganese from water and is comparable with other imported materials.

Keywords: removal of iron and manganese from water, contact filtration, natural materials, clinoptilolite, modified clinoptilolite, drinking water

Introduction

Groundwater is the most common resource of drinking water in Slovakia (83.9 percent of the population is supplied with drinking water from ground resources). In localities without a quality drinking water resource (groundwater), the surface water is used for this purpose or water from an other locality is supplied through long-distance distribution systems [1]. In 2006 there were 5,507 groundwater resources registered in Slovakia. On average, the amount of 11.665 $l \cdot s^{-1}$ was used (8.836 $l \cdot s^{-1}$ for water supply), including 2.63 $l \cdot s^{-1}$ that is required to be treated. The treatment is mostly related to undesirable concentrations of iron and manganese. According to the 2006 Report on the Environment in Slovakia, the concentration of iron exceeded the limit 0.2 $mg \cdot l^{-1}$ in more than 36.5 % of samples, and the concentration of manganese exceeded the limit 0.05 $mg \cdot l^{-1}$ in more than 40.1% of groundwater samples. The limit values are defined under the Regulation of the Government of Slovak Republic No. 354/2006 specifying the requirements on water intended for human consumption and quality of water intended for human consumption [2].

Forms of Occurrence of Iron and Manganese in Water

Iron and manganese occur in dissolved forms as single ions (Fe^{2+}, Mn^{2+}) or in undissolved higher forms mainly as $Fe(OH)_3$ or $Mn(OH)_4$, respectively. They can also be present in colloid form (bound to humic substances). The form of their occurrence depends on oxygen concentration, solubility of Fe and Mn compounds in water, pH value, redox potential, hydrolysis, the presence of complex-forming inorganic and organic substances, water temperature, and water composition (e.g. CO_2 content).

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Effect on Water Quality

Adverse effects of higher Fe and Mn concentrations in drinking water can be summarized as follows:

1. iron (II) and manganese (II) ions are oxidized to higher forms in a water distribution system and this results in the formation of hydroxide suspensions causing undesirable turbidity and colour of water,
2. the presence of iron and manganese bacteria in water supply system causes change in water quality (smell) and bacterial growth in pipes,
3. in the case of the occurrence of iron (II) and manganese (II) ions at the consumer's point, iron and manganese are oxidized and precipitated under suitable conditions (e.g. in washing machines, boilers).

Following the above-mentioned facts, higher concentrations of iron and manganese in water cause technological problems, failure of water supply systems operation, water quality deterioration and, in water with slightly higher concentrations of oxygen, they form undesirable incrustations that result in the reduction of pipe flow cross-section.

Methods of Iron and Manganese Removal

The principle of most methods used for iron and manganese removal is that originally dissolved iron and manganese are transformed into undissolved compounds that can be removed through single-stage or two-stage separation. Oxidation and hydrolysis of these compounds is done under strict conditions with respect to water properties and type of equipment for iron and manganese removal.

Single-stage water treatment (filtration) is designed for iron and manganese concentrations to 5 mg·l^{-1}, and the two-stage treatment (settling tanks or clarifiers and filters) is used for water with iron and manganese concentrations higher than 5 mg·l^{-1}. In case water contains higher concentrations of Ca, Mg, and CO_2 (eventually H_2S), aeration is done before settling or filtration.

Removal of Fe and Mn from groundwater and surface water can be done by several methods:

- oxidation by aeration,
- removal of Fe and Mn by oxidizing agents (O_2, Cl_2, O_3, $KMnO_4$),
- removal of Fe and Mn by alkalinization (by adding the lime),
- contact filtration for removal of Fe and Mn,
- removal of Fe and Mn by ion exchange,
- removal of Fe and Mn using membrane processes,
- removal of Fe and Mn using biological filtration,
- removal of Fe and Mn using in situ method.

Fe^{2+} and Mn^{2+} oxidation rate as well as hydrolysis of emerging oxides of higher iron and manganese oxidation forms in groundwater depends on the pH value. Various graphic dependencies of these relationships with respect to oxidation time are listed in literature. The pH value should be equal or greater than 7 in removal of iron from groundwater. For removal of manganese without catalyst, the pH value should be equal to or greater than 8 [3].

Removal by using the oxidized film on grains of filter medium is one method for elimination of dissolved manganese. The film is formed on the surface of filter medium by adding permanganate potassium (not only $KMnO_4$ but also other strong oxidizing agents). The film serves as a catalyst for the oxidation process. Grains of filter medium are covered by higher oxides of metals. In such a case, it is related to special filtration so-called "contact filtration" – filtration by using manganese filters. The oxidation state of the film of MnO_x(s) filter medium is important in removal of dissolved manganese. Manganese removal efficiency is a direct function of MnO_x(s) concentration and its oxidation state. The films with different ability to remove dissolved manganese from water are formed on the surface of various filter media [4-8].

Natural or synthetic zeolite can be used as a filtration material for removal of iron and manganese from water. Birm, Greensand, Pyrolox, and MTM are the most frequently used materials in filtration.

Birm is a granulated filter medium (imported from the USA) used for iron and manganese removal from water. It is a specially developed material containing MnO_2 film on the surface (catalyst). It is recommended to use Birm for lower iron concentrations (to Fe^{2+} concentration of 6.0 mg·l^{-1} and Mn^{2+} about 3.0 mg·l^{-1}) and for household water treatment. It can also be used in gravity or pressure filters.

Contact with filter material results in oxidation of dissolved iron and manganese. Subsequently, precipitated Fe and Mn hydroxides (pH of 8 to 9 is required for Mn removal) are easily removed by filtration. Filter medium is cleaned by backwashing. There is no need of chemical regeneration. In cleaning process the time of backwashing and wash water velocity are important factors. Long service life is also one of the advantages of this medium.

Klinopur-Mn is produced in Slovakia from natural zeolites. It is an activated zeolite-clinoptilolite (rich deposits of clinoptilolite are in the East Slovakia Region). Mineralogical and chemical analysis of zeolite from the Nižný Hrabovec deposit are listed in Tables 1 and 2.

On the surface of clinoptilolite grains there is a factory-made film consisting of manganese oxides (MnO_x) which enable this material to be used in the contact filtration. The filter material is produced by Zeocem Bystré and it is much cheaper compared to materials imported from the USA.

Table 1. Mineralogical analysis of zeolite from the Nižný Hrabovec deposit.

Mineral	Content [%]
Clinoptilolite	84
Cristobalite	8
Feldspar	3-4
Illite	4
Crystal	traces
Carbonate minerals	traces (<0.5 %)

Table 2. Chemical analysis of clinoptilolite from the Nižný Hrabovec deposit.

Compound	Content %	Compound	Content %
SiO_2	66.4	MgO	0.56
Al_2O_3	12.2	Na_2O	0.29
K_2O	3.33	MnO	0.02
CaO	3.04	TiO_2	0.15
Fe_2O_3	1.45	P_2O_5	0.02

Table 3. Filtration materials and some selected parameters.

Material	Clinoptilolite	Birm	Greensand	Filtration sand
Grain size [mm]	0.3-2.5	0.48-2.0	0.25-0.8	0.7-2.0
Specific gravity [$g\cdot cm^{-3}$]	2.39	2.0	2.4-2.9	2.66
Apparent density [$g\cdot cm^{-3}$]	0.84	0.7-0.8	1.36	1.55
Porosity [%]	64.8	-	-	41.7
Abrasion [%]	8.2	-	-	0.57

Based on experiments (pilot tests) performed by experts of the Department of Sanitary and Environmental Engineering at the Faculty of Civil Engineering of the University of Technology in Bratislava, as well as experts of the Water Research Institute Bratislava, it can be stated that the surface of clinoptilolite activated by manganese oxides is comparable with imported Birm, and it is possible to use it for removal of Fe and Mn from water.

Clinoptilolite $(NaK)_6(Al_6Si_{30}O_{72})\cdot 20H_2O$ is one of the most frequently used natural zeolites. At present it is also applied to the water treatment process. Sufficient mechanical resistance, chemical stability, and abrasion values (even if they categorize it among soft materials) enable clinoptilolite to be used as a filtration material.

The specific weight of clinoptilolite is lower than the weight of silica sand. Moreover, its porosity and sludge capacity are 1.5 times greater compared to filtration sand. Using the zeolite in slow sand filtration allows filtration rate to be increased by four times. Furthermore, it also reduces the amount of wash water and time needed for filter backwashing [9].

Properties of some filtration materials used for removal of manganese and iron are listed in Table 3.

Experimental Procedures

The objective of the study conducted at the Holíč Water Treatment Plant was to compare the efficiency of iron and manganese removal in the water treatment process using filter material on the basis of chemically activated natural zeolite (Klinopur-Mn) produced in Slovakia with imported Birm that is commonly used abroad to remove dissolved iron and manganese from water, mainly for small water resources or with modified filtration sand used directly in the water treatment plant. It was important also to monitor the time of single filtration cycles, regeneration of filter materials by using potassium permanganate, and the amount of water used for filter backwashing.

Water Treatment Model

To verify the efficiency of iron and manganese removal from water resource in the town of Holíč, three filtration columns containing Birm, Klinopur-Mn, and filtration sand were used. The adsorption column was made of glass.

Table 4. Results of raw water chemical analysis.

Parameter	Unit	Raw water	Parameter	Unit	Raw water
pH		8.30	NH_4^+	$mg\cdot l^{-1}$	0.81
conductivity	$mS\cdot m^{-1}$	65	Fe total	$mg\cdot l^{-1}$	0.48
colour	$mg\cdot l^{-1}Pt$	38	Mn	$mg\cdot l^{-1}$	0.42
turbidity	FTU	7	Na^+	$mg\cdot l^{-1}$	25.77
Alkalinity (ANC)	$mmol\cdot l^{-1}$	4.34	Ca^{2+}	$mg\cdot l^{-1}$	103.1
Acidity (BNC)	$mmol\cdot l^{-1}$	1.32	Mg^{2+}	$mg\cdot l^{-1}$	24.74
Ca+Mg	$mmol\cdot l^{-1}$	3.59	Cl^-	$mg\cdot l^{-1}$	59.68
$CHSK_{Mn}$	$mg\cdot l^{-1}$	1.68	NO_3^-	$mg\cdot l^{-1}$	1.21
TOC	$mg\cdot l^{-1}$	3.0	SO_4^{2-}	$mg\cdot l^{-1}$	165.4
Insoluble substances	$mg\cdot l^{-1}$	24	HCO_3^-	$mg\cdot l^{-1}$	264.7
Soluble substances	$mg\cdot l^{-1}$	470	CO_2	$mg\cdot l^{-1}$	27.28

Table 5. Filtration conditions.

Parameter	Klinopur-Mn	Birm	Filtration sand
Grain size [mm]	1.0-2.0	1.0-2.0	1.0-2.0
Height of filtration medium [cm]	120	120	120
Volume of filtration medium [cm^3]	2356	2356	2356
Average discharge through column [ml·min^{-1}]	172.6	173.6	174.6
Average filtration rate [m·hour^{-1}]	5.27	5.30	5.33
Total filtration time [hour]	1194	1194	1194
Total volume of water flown through [m^3]	12.300	12.374	12.447
Average active bed volume [BV·hour^{-1}]	4.395	4.421	4.445
Average residence time in column [min]	13.65	13.57	13.50

The parameters of adsorption column are as follows: diameter = 5.0 cm; height = 2 m; surface = 19.635 cm^2; filtration medium height = 120.0 cm.

Raw Water Chemical Analysis

Based on water analyses carried out during these tests, the iron and manganese concentrations in raw water after aeration and sedimentation ranged from 0.36 to 0.68 mg·l^{-1} of Fe (average value 0.46 mg·l^{-1} 1 of Fe) and 0.39 to 0.56 mg·l^{-1} of Mn (average value 0.41 mg·l^{-1} of Mn). pH value ranged from 8.26 to 8.38 (average value 8.3). The results of analysis of raw water are listed in Table 4 (it is an analysis of some selected parameters).

Filtration Conditions

Raw water passed through the filtration columns in downward direction and the average filtration rate was in the range from 5.27 m·hour^{-1} to 5.33 m·hour^{-1}. The total time of filtration of raw water was 1,194 hours, total volume of water filtered during this period was in the range 12.3 m^3 to 12.447 m^3. Filtration conditions are shown in Table 5.

The quality of raw water (Fe and Mn content) and treated water at outlets from separate filtration columns was monitored during the experiments. At the same time, the amount of water at inlets to filtration columns and water discharge at outlets from the columns were measured by water meter.

Results and Discussion

The results of experiments are best described by Figs. 1 and 2 showing iron and manganese concentrations in raw water (RW), and values measured after water passed filtration materials. The figures also show the limit value for manganese (0.05 mg·l^{-1}) and iron (0.2 mg·l^{-1}) in drinking water pursuant to Government Regulation No. 354/2006 Coll. Regeneration time of filtration media is indicated by the arrow.

In the first cycle (time between regeneration) the concentration of manganese exceeded the limit value in treated water after 148 hours of operation, in the second cycle after 281 hours and in the third cycle after 462 hours during filtration by Klinopur-Mn and Birm (Table 6).

Filtration media were backwashed approximately once every three days (according to the amount of precipitated ferric hydroxide trapped in a filter). After some time, as can be seen in Fig. 1, the concentration of manganese in treated water increased to 0.05 mg·l^{-1} after filtration by Klinopur-Mn (Birm), then the filtration medium was regenerated by potassium permanganate solution (0.5% solution). After regeneration, the values of dissolved manganese were in compliance with the Regulation of the Government of the Slovak Republic No. 354/2006.

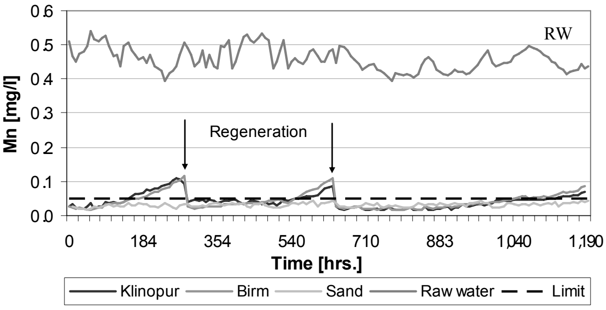

Fig. 1. Manganese removal process during water filtration in Holíč.

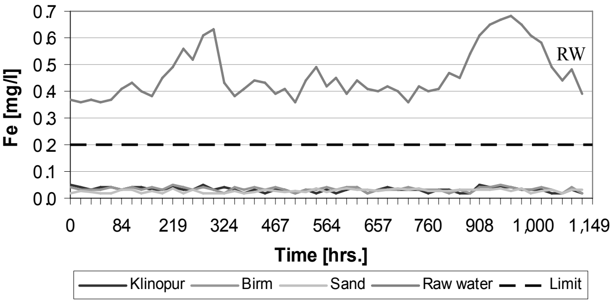

Fig. 2. Iron removal process during water filtration in Holíč.

Table 6. Filtration time during filtration with material Klinopur-Mn or Birm.

Filtration cycle	Filtration total time [hour]	Filtration time until exceeding the limit 0.05 mg·l^{-1} [hour]	
		Klinopur-Mn	Birm
1st cycle	283	148	160
2nd cycle	371	281	281
3rd cycle	540	462	397

Table 7. Amount of filtered water during filtration with material Klinopur-Mn or Birm.

Filtration cycle	Total amount of filtered water [m^3]		Amount of filtered water until exceeding the limit 0.05 mg·l^{-1} [m^3]	
	Klinopur-Mn	Birm	Klinopur-Mn	Birm
1st cycle	2.844	2.858	1.487	1.615
2nd cycle	3.896	3.925	2.937	2.959
3rd cycle	5.560	5.591	4.734	4.068

Filtration time period without regeneration was gradually extended. It means that industrially activated clinoptilolite (Klinopur-Mn) is necessary to be used several times directly on site, which will result in prolonged filtration cycles. After some time no regeneration will be required (analogous to modified filtration sand).

Measured values of water filtered through the filtration column with Klinopur-Mn and Birm, calculated bed volumes – volume of the water passed through filtration column (V) to volume of the adsorption column (V_0) and efficiency of manganese removal (considering limit value 0.05 mg·l^{-1} Mn) in individual cycles are shown in Tables 7 and 8.

Klinopur-Mn can also be used for removal of iron from water. Our results show that during the whole period of measurements (1,194 hours), iron concentration did not exceed the limit value 0.2 mg·l^{-1} specified pursuant to Government Regulation No. 354/2006 (Fig. 2). The efficiency of iron elimination raw water in Holíč is comparable to Birm or modified filtration sand.

In addition to Mn concentrations, the amount of water needed for backwashing both materials for the time period (10 minutes) and the height (elevation) of filter medium during the backwashing were monitored at the outlet from filtration columns. The amount of water required for washing the Klinopur was lower by 1/3 compared to filtration sand – Table 9.

For filtration, a bed of Klinopur-Mn was observed expanding during backwashing. Backwash bed expansion is presented in Fig. 3.

Conclusions

Obtained results prove the possibility of using Klinopur-Mn for removal of iron and manganese in the water treatment process. Klinopur-Mn is comparable with imported filtration material Birm. The results also show that the repeated use of Klinopur-Mn leads to extended filtration cycles and based on this fact it is comparable with prepared filtration sand. In comparison with filtration sand, the advantage of Klinopur-Mn is that it requires a lower amount of water for backwashing, which results in a more cost-effective operation.

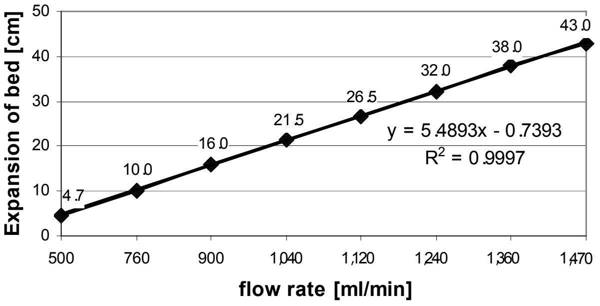

Fig. 3. Backwash bed expansion of Klinopur-Mn.

Table 8. Efficiency of Mn removal in individual cycles considering bed volumes.

Filtration cycle	Total bed volume BV = V/V$_0$		BV until exceeding the limit 0.05 mg·l^{-1}		Filtration efficiency [%]	
	Klinopur	Birm	Klinopur	Birm	Klinopur	Birm
1st cycle	1,207	1,213	631	686	52.28	56.55
2nd cycle	1,653	1,666	1,264	1,256	76.46	75.39
3rd cycle	2,360	2,373	2,009	1,727	85.13	72.78

Table 9. Amount of water required for washing filtration materials.

Parameter	Klinopur-Mn	Filtration sand
Average volume of wash water [m^3] for one backwashing of filter column	0.228	0.328

The content and form of occurrence of iron and manganese in water, as well as water pH and dissolved oxygen concentration (min. 15% of Fe+Mn content), are among the important criteria for Fe and Mn removal efficiency (lower efficiency in removal of iron bound to humic acids). The efficiency of Mn removal is influenced by the contact time between water and filter material (height of filtration layer, filtration time), properties of preparation active layer, i.e. layer thickness and its chemical composition, regeneration method, $KMnO_4$ concentration, plus times for backwashing and regeneration.

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