Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2018.22707

134 (2018) 99–108
December

Efficiency estimation of water purification with various filtration materials

Iwona Skoczko

Department of Technology and Systems in Environmental Engineering, Faculty of Civil and Environmental Engineering, Bialystok University of Technology, Wiejska 45E, Białystok 15-351, Poland, email: i.skoczko@pb.edu.pl

Received 26 March 2018; Accepted 28 June 2018

ABSTRACT

Iron, manganese, and hardness are main pollutants of groundwater. Water contaminated with these compounds has many negative traits, that is, discoloration and sediments, metallic taste, odor, turbidity, staining of laundry, and sanitary devices. In addition, it promotes the growth of microorganisms that form greasy deposits covering the water pipes. According to the water quality requirements (2000/60/EC, 98/83/EC), Fe and Mn content in water are regulated. Industry-specific requirements are even more stringent. Often, the concentration of both Fe and Mn should be reduced up to 0.0 mg/L. This forces the need for effective methods of water purification. The aim of the present study was to assess the possibility of using the selected filtration deposits for removal of iron and manganese compounds from water. Eight filtration deposits that differed with their composition and properties were chosen for the experiments. In the literature, there is lack of comparison filter masses from point of view of statistics and kinetics. The study showed that tested compounds are difficult to effectively eliminate from the water. The unit processes are insufficient, which requires a multi-stage filtration or preliminary oxidation assistance.

Keywords: Filtration; Porous materials; Iron removal; Manganese removal

1. Introduction

Despite many years of research, the problem of effective groundwater purification is still valid. Micropollutants belong to a group of essential micronutrients for humans, their presence in groundwater above a certain level eliminates their use. Constantly new, effective, and economical methods of removing various impurities from water, including iron and manganese, are searched. And some of the works include those done by Kriš and Dubová [1], Burger et al. [2], Skoczko and Szatylowicz [3] try to find answers. The matter is further complicated by diverse chemical composition of groundwater. Another treatment technology should be used for waters containing lower and higher concentrations of pollutants, the other when the waters are characterized by dissolved gases, ammonium nitrogen, enhanced color and turbidity, increased hardness, and organic compounds [4,5]. Each year, manufacturers bring to the market new filtration materials without necessary repetitive testing of their suitability in wastewater treatment. Often, popular and already tested materials are also subjected to industrial modifications. Despite of the wide choice of filtration materials in the global market, investors still have problem in choosing the best sustainable material to suit their water requirements. In the literature, there is lack of comparison filter masses from statistical point of view and particular factors used to theoretical description of the process of filtration [6–12]. Kinetics calculation is rarely considered in the literature as well [15–22].

Therefore the aim of this work was to carry out the research and to make assessment of suitability of selected filter deposits for the groundwater treatment, mainly for removal of iron and manganese.

Presented at the 13th Conference on Microcontaminants in Human Environment, 4–6 December 2017, Czestochowa, Poland.

2. Materials and methods

The study included conducting the filtration process with eight different filter materials:

- quartz sand – loose sedimentary rock composed of non-bonded mineral grains, in particular, quartz (SiO_2) is a natural and common filtration material; present experiments used 8–1.2 mm particle size sand that was earlier washed out;
- manganese zeolite – commercial name Greensand Plus, is oxidizing and filtering material composed of silica sand coated with manganese dioxide, its chemical composition includes SiO_2, Al_2O_3, K_2O, MgO, and Fe_2O_3; the study used product of 0.3–0.35 mm granulation not requiring pre-oxidation; regeneration was carried out with a solution of potassium permanganate;
- amorphous activated quartz sand MnO_2 – commercial name Birm, it is a specially prepared substance containing insoluble catalyst in the form of MnO_2;
- battery manganese – grainy, natural, high-manganese ore rich in manganese oxides MnO_2, it does not require any chemical regeneration; the study used granules of uneven structure with visible single gray and white grains 0.5–2.0 mm particle diameter.
- anthracite – chemically neutral filtration material comprising broken and screened fragments of natural anthracite coal of 0.6–1.6 mm granulation.
- zeolite – natural mineral from aluminosilicate group; the study used product of 0.8–1.0 mm particle diameter.
- natural crystalline aluminosilicate (Crystal-Right) with properties of a natural cation, which requires rinsing with saturated sodium chloride solution; present study used granulation of 0.3–2.4 mm.
- mixed ionite deposit – mixture of filter deposits, the composition of five high-quality components with ion-exchange and adsorption functionalities; the study used a mixture of trade name Ecomix A rinsed with sodium chloride, the composition of which is proprietary patented.

Individual filter media were placed in laboratory models of gravity filters 0.20 m high, 0.07 m in diameter, and 0.035 m^3 of working volume. A minimum filtration rate recommended for particular materials was maintained, that is, from 0.7 to 2 m/h. Laboratory tests of water samples were carried out in the Department of Technology in Engineering and Environmental Protection at the Bialystok University of Technology. The study included examination of the raw water and filtered water samples after each filter selected for the study. Raw water was formulated on the basis of dechlorinated tap water. Per 10 L of tap water, 1.3 g manganese (III) sulfate, 10 g enriched broth, 1 g ammonia sulfate, and 1.2 g $Ca(OH)_2$ were used, which gave the manganese concentration in raw water 0.50–0.55 mg/L, total iron 1.0–1.4 mg/L, ammonia nitrogen 1.5–2 mg/L, COD-Mn 8-10 mg/L, and total hardness 196–240 mg $CaCO_3$/L.

The study was conducted in two test cycles. Each cycle lasted until the exhaustion of filtration ability of the filter and filter breakthrough. It was followed by regeneration and filters rinsing. Washing was carried out upstream and downstream using the agent recommended for individual deposits and with water. Samples were collected daily.

The scope of water determinations included: manganese and iron concentrations, water pH, COD-Mn, color, turbidity, and total hardness. Concentrations of Mn and Fe were determined using a Thermo Scientific iCE3300 atomic absorption spectrometer applying flame atomization and graphite cuvette. Standard specimens were prepared in 50 cm^3 flasks to enable a calibration curve consisting of 4–5 measurement levels. Measurement of pH were made using a pH meter CX-315's ELMETRON, and the measured turbidity as well as ammonia nitrogen probe YSI Professional Plus. Determination of COD-Mn was made by using manganate (VII) solution in accordance with PN/C-04578.02. Color was tested with IR spectroscopy and total hardness in accordance with PN-EN ISO 9308-3:2002.

3. Results and discussion

3.1. *Effectiveness of water treatment by manganese zeolite*

The manganese zeolite Greensand Plus appeared to be the most effective iron-removing agent (Table 1). Throughout the period of filtration, the levels decreased to values required for water intended for human consumption, that is, less than 0.2 mg/L. Iron removal efficiency ranged from 82.59% to 97.61%. The total iron concentration in water after filtration in the 1st test cycle was in the range of 0.033 to 0.168 mg/L. After filter regeneration, an improvement in the iron removal occurred, and the efficiency increased from 82.59% to 97.05%. A high removal effect from 94.03% to 97.05% was observed during the entire second test cycle, when the concentration of iron in the filtered water occurred in the range 0.032 to 0.062 mg/L. Manganese was not so effectively removed on analyzed filter as iron. Its concentration in the 1st test cycle grew from 0.003 to 0.264 mg/L (at the efficiency from 51.64% to 99.12%). After regeneration in the second test cycle, a similar trend was observed. The normative value below 0.05 mg/L was achieved only in the first half of the first cycle. Many researchers have confirmed its high efficiency in removing the iron and manganese from water [5,6]. According to Chatuverdi and Pragnesh [7], the Greensand deposit is able to remove up to 99% of iron, manganese, and hydrogen sulfide, and the actual removal capacity will vary depending on the characteristics of each compound. The effectiveness of Greensand deposits in removing the iron from water was also proved by Barloková and Ilavský [4]. Granops [5] confirmed that Greensand agent very well removes iron and manganese compounds from water. However, at higher concentrations of these indicators, a single-stage filtration should be avoided. In studies carried out in the frames of present work, deposition of excessive, well-precipitated iron compounds that cause the loss of water flow was observed on the surface of the filter, which as a consequence is associated with the need for frequent cleaning of the deposit. This thesis was attempted to confirm by authors by observing other indicators of water pollution having a direct impact on its quality, that is, pH, color, turbidity, hardness, ammonia nitrogen, and COD-Mn.

The pH of the water in the first test cycle was in the range from 4.80 to 7.35, while in the second from 5.53 to 6.69. The color of water after filtration through Greensand Plus in the 1st test cycle comprised within the range from 15 to 86 mg Pt/L and in the second from 1 to 24 mg Pt/L, while required

Table 1
Contaminants concentration in the raw water and water filtrated with Greensand Plus bed during both series

	Time (d)	Iron (mg Fe/L)		Manganese (mg Mn/L)		pH		Color (mg Pt/L)		Turbidity (NTU)		Total hardness (mval/L)		Ammonia nitrogen (mg NH_4/L)		COD-Mn (mg O_2/L)	
		Raw water	Filtrated water	Raw water	Filtrated water	Raw water	Filtrated water	Raw water	Filtrated water	Raw water	Filtrated water	Raw water	Filtrated water	Raw water	Filtrated water	Raw water	Filtrated water
I cycle	2	1.14	0.109	0.503	0.004	5.86	7.35	78	86	3	4	3.7	4.2	2.43	1.63	10	9.2
	4	1.378	0.033	0.52	0.003	5.2	5.47	84	27	3	1	3.4	4.4	2.575	0.955	10.2	9.7
	6	0.973	0.138	0.512	0.004	5.77	6.02	83	37	6	5	3.6	3.44	2.04	1.776	9.4	9.5
	8	1	0.093	0.52	0.005	5.6	5.9	76	15	2	0	2.64	2.48	2.026	1.29	10.1	9
	10	1.012	0.093	0.501	0.003	4.25	4.8	76	39	6	7	3.04	3.44	2.552	1.906	10.3	6.3
	12	0.968	0.121	0.546	0.131	4.45	4.81	79	25	2	2	3.52	3.76	2.448	1.653	9.6	9.7
	14	0.965	0.168	0.546	0.264	4.47	4.86	86	24	1	1	3.52	4	2.72	1.684	10.2	9
II cycle	1	1.085	0.032	0.54	0.058	5.67	6.11	79	24	9	2	4.48	5.04	2.156	1.216	10.1	10
	2	1.021	0.041	0.55	0.187	6.49	6.13	79	1	1	0	4.8	5.2	2.9	1.375	9.6	9.4
	3	1.039	0.062	0.568	0.187	6.72	6.13	71	2	5	0	4.64	4.64	2.393	1.603	9.9	9.6
	4	1.13	0.052	0.525	0.198	6.35	6.69	77	22	6	6	4.4	4.4	2.9	1.874	9.5	9.4
	5	1.117	0.046	0.529	0.303	6.32	5.53	72	13	6	1	4.24	4.08	3.1	2.174	10.4	10.3

color of the water is 15 mg Pt/L. A similar trend was observed for turbidity. In the first cycle, the turbidity ranged within 0–7 NTU, and in the second from 0 to 6 NTU. Total hardness values developed in the range from 2.48 to 4.40 meq/L in the first cycle of filtration and from 4.08 to 5.20 meq/L in the second one. Ammonia nitrogen content after filtration through Greensand Plus medium ranged from 0.955 to 1.906 mg/L (from 12.94% to 62.91% of purification efficiency) in the 1st cycle, and from 1.216 to 2.174 mg/L in the second one. After filter regeneration, a slight improvement in the ammonia nitrogen removal occurred in the second test cycle, and the efficiency increased from 29.87% to 52.59%.

COD ranged within 6.3–9.7 mg O_2/L in the 1st test cycle, while in the 2nd cycle, it did not fall below 9.4 mg O_2/L, giving the effect of a reduction at 4.90%–38.83% in the first cycle and 0.96%–3.03% in the second. On the basis of experiments, it was found that Greensand Plus showed sensitivity to the presence of organic substances (approximately 8–10 mg/L) and ammonium nitrogen (approximately 1.5–2.5 mg/L). This significantly reduced the time between rinsing operations to about 10 d and decreased the efficiency of iron and manganese removal. It was noted that accumulation of organic substances in a deposit, precipitation of hardness, and excess precipitated MnO_2, affected the reduction in the treatment effects, and time of the proper filter operation between washes.

3.2. *Effectiveness of water treatment by crystalline aluminosilicate*

The iron compounds were also effectively removed on a natural crystalline aluminosilicate Crystal-Right (Table 2). Its concentration ranged from 0.069 to 0.373 mg Fe/L in the 1st test cycle at the removal efficiency from 61.35% to 94.99%. Water purified on a filter Crystal-Right met acceptable standards for the first 10 d of operation. Continuously deteriorating effect of iron removal forced to make a decision to clean the bed. During the second filtration cycle, the iron levels in water ranged between 0.068 mg Fe/L on the 1st day to 0.122 mg Fe/L on the 5th day of deposit operation. A high degree of iron removal from 89.08% to 93.73% still maintained. Regeneration improved the efficiency of iron removal from water and throughout the second cycle, its concentration did not exceed the standard values. Water filtering through a crystalline aluminosilicate made it possible to obtain a very high effect of manganese removal. Its concentrations in the filtrate were within the range 0.001–0.009 mg/L in the first cycle of test and 0.001–0.037 mg/L in the second cycle. Manganese was a parameter that was best retained on a crystalline aluminosilicate. During the first test cycle, its concentration starting just from the first day was recorded far below acceptable standards in the filtered water, that is, 0.001–0.009 mg/L, which allowed to obtain a very high purification effect from 98.61% to 99.82%. Beginning of the second filtering cycle brought even better results in the manganese removal from water. The effect of treatment decreased from almost 100% to 93%. High efficiency and decrease in the concentrations of both iron and manganese is explained by Kaleta et al. [8] that the Crystal-Right deposit removes iron (II) and manganese (II) during the process of ion exchange, while insoluble compounds of iron (III) and manganese (IV) are retained in the process of filtration and removed during the filter washing. Anielak and Arendacz [9] also noted low

Table 2
Contaminants concentration in the raw water and water filtrated with crystalline aluminosilicate Crystal-Right bed during both series

	Time [d]	Iron (mg Fe/L)		Manganese (mg Mn/L)		pH		Color (mg Pt/L)		Turbidity (NTU)		Total hardness (mval/L)		Ammonia nitrogen (mg NH_4/L)		COD-Mn (mg O_2/L)	
		Raw water	Filtrated water	Raw water	Filtrated water	Raw water	Filtrated water	Raw water	Filtrated water	Raw water	Filtrated water	Raw water	Filtrated water	Raw water	Filtrated water	Raw water	Filtrated water
I	2	1.14	0.137	0.503	0.009	5.86	6.91	78	86	3	3	3.7	2.5	2.43	0.42	10	8
cycle	4	1.378	0.069	0.52	0.007	5.2	6.53	84	29	3	3	3.4	2.6	2.575	0.469	10.2	10.2
	6	0.973	0.138	0.512	0.004	5.77	6.53	83	69	6	1	3.6	1.52	2.04	0.171	9.4	8.8
	8	1	0.185	0.52	0.009	5.6	6.5	76	35	2	6	2.64	0.72	2.026	0.181	10.1	9.5
	10	1.012	0.115	0.501	0.004	4.25	6	76	50	6	3	3.04	0.72	2.552	0.022	10.3	8.5
	12	0.968	0.259	0.546	0.001	4.45	5.73	79	30	2	3	3.52	1.76	2.448	0.2	9.6	9.4
	14	0.965	0.373	0.546	0.004	4.47	5.63	86	15	1	2	3.52	2.16	2.72	0.215	10.2	7.3
II	1	1.085	0.068	0.54	0.001	5.67	7.22	79	30	9	4	4.48	3.44	2.156	0.304	10.1	10
cycle	2	1.021	0.083	0.55	0.001	6.49	6.65	79	10	1	0	4.8	0.16	2.9	0.298	9.6	8.8
	3	1.039	0.118	0.568	0.001	6.72	7.06	71	10	5	0	4.64	0.32	2.393	0.456	9.9	9.7
	4	1.13	0.117	0.525	0.018	6.35	6.9	77	29	6	7	4.4	1.12	2.9	0.208	9.5	9.3
	5	1.117	0.122	0.529	0.037	6.32	6.61	72	24	6	3	4.24	1.84	3.1	0.464	10.4	9.8

output levels of manganese and iron at concentrations in the raw water below 2.5 mg Fe/L and less than 1 mg Mn/L.

The attention was also paid to the significant increase in the pH of the filtered water above pH 9. During the study conducted in the framework of this research, such high pH values were not achieved. The pH of water in the first test cycle was included in the range from 5.63 to 6.91, while in the second cycle from 6.61 to 7.22. According to Funes et al. [21], the crystalline aluminosilicate has a capacity of increasing the pH of slightly acidic water above pH 5.5 by absorption of acidic hydrogen (H^+), that is further released and rinsed into the saline.

Ammonia nitrogen concentration values over the research remained at a similar level. In the first filtering cycle, these contents ranged from 0.022 to 0.469 mg/L. In the second cycle, the concentration of ammonium nitrogen in water ranged from 0.298 to 0.464 mg/L. After washing the deposit, a slight deterioration in removal efficiency was observed, which ranged from 80.94% to 92.83%. At the same time with the exchange of ammonium ions, the exchange of calcium (Ca^{2+}) and magnesium (Mg^{2+}) cations was found, which was a reduction of water hardness. Mainly in the second filter cycle, a significant reduction in hardness below the lower limit of the standard range for drinking water occurred (1.2–10 meq/L). This parameter was shaped in the range from 0.72 to 2.60 meq/L. Skoczko and Szatylowicz [3] and Kaleta et al. [8] also noted the success in reducing the concentration of ammonia nitrogen in the water to be treated. At the same time, reducing in the concentrations of iron, manganese, ammonium, and hardness in the study occurred only till a specific time, then these values increased and need regeneration. Parameters that exceeded the legal limits were color, turbidity, and COD-Mn. In the first test cycle, water color after filtration was within the range of 15 to 86 mg Pt/L, while in the second cycle, this parameter ranged from 10 to 30 mg Pt/L. For the first 2 d, the increased water color was observed but then it decreased. The second test cycle demonstrated to achieve better results also due to the turbidity of water which ranged from 1 to 6 NTU.

The effect of COD-Mn reduction was low at the time of the experiments and remained at the level of 0%–28.43%. In the first test cycle, its concentration fell to the limits of 7.3–10.2 mg O_2/L, while in the second cycle, it was maintained at a level of 8.8 to 10.0 mg O_2/L. After 4 d of filtration, the COD-Mn value was at the level of raw water. In the second test cycle, the effect of COD-Mn lowering ranged from 0.99% to 8.33%. During water filtration on the Crystal-Right deposit, reduction in the indicator to the limit value was not reached.

3.3. Effectiveness of water treatment by battery manganese

Another deposit subjected to the study was a natural deposit battery manganese G-1 (Table 3). It is that material which join such treatment mechanisms as: chemical (transformation Mn^{+2} to Mn^{+4}), physical (suspension separation) and biological (manganese bacteria have a part in Mn degradation) [2,10,11]. The iron content in the water after filtration in the first cycle ranged from 0.080 to 0.490 mg/L and in the second it ranged from 0.101 to 0.392 mg/L. Iron removal efficiency ranged from 94.19% to 49.22%. However, the high degree of iron elimination occurred only during the first 2 d of deposit operation. Rinsing the G-1 deposit resulted only

Table 3
Contaminants concentration in the raw water and water filtrated with battery manganese G-1 bed during both series

	Time [d]	Iron (mg Fe/L)		Manganese (mg Mn/L)		pH		Color (mg Pt/L)		Turbidity (NTU)		Total hardness (mval/L)		Ammonia nitrogen (mg NH_4/L)		COD-Mn (mg O_2/L)	
		Raw water	Filtrated water	Raw water	Filtrated water	Raw water	Filtrated water	Raw water	Filtrated water	Raw water	Filtrated water	Raw water	Filtrated water	Raw water	Filtrated water	Raw water	Filtrated water
I	2	1.14	0.167	0.503	0.006	5.86	5.86	78	93	3	5	3.7	3.6	2.43	1.18	10	7.7
cycle	4	1.378	0.08	0.52	0.005	5.2	5.2	84	41	3	5	3.4	3.6	2.575	0.876	10.2	9.5
	6	0.973	0.172	0.512	0.009	5.77	5.77	83	70	6	3	3.6	3.6	2.04	1.776	9.4	8.8
	8	1	0.198	0.52	0.007	5.6	5.6	76	24	2	3	2.64	2.48	2.026	1.285	10.1	9.7
	10	1.012	0.185	0.501	0.006	4.25	4.25	76	52	6	5	3.04	3.6	2.552	2.152	10.3	9.2
	12	0.968	0.252	0.546	0.003	4.45	4.45	79	47	2	8	3.52	3.36	2.448	2.408	9.6	8.2
	14	0.965	0.49	0.546	0.212	4.47	4.47	86	25	1	8	3.52	4	2.72	2.33	10.2	9.4
II	1	1.085	0.101	0.54	0.06	5.67	5.67	79	53	9	8	4.48	4.4	2.156	2.055	10.1	10
cycle	2	1.021	0.172	0.55	0.074	6.49	6.49	79	23	1	0	4.8	4.56	2.9	2.657	9.6	9.6
	3	1.039	0.392	0.568	0.104	6.72	6.72	71	25	5	0	4.64	4.8	2.393	2.193	9.9	9.4
	4	1.13	0.385	0.525	0.103	6.35	6.35	77	41	6	7	4.4	4.6	2.9	2.9	9.5	9
	5	1.117	0375	0.529	0.156	6.32	6.32	72	34	6	6	4.24	4	3.1	2.967	10.4	9.6

in a temporary improvement of iron removal efficiency. The reason for worse iron removal effect can be a quick deposit breakdown and clogging with iron compounds, which in consequence results in the need for frequent washing of the filter. The increase in water pH was observed during filtration.

The highest effect of ammonia nitrogen removal was observed at the beginning of the filtration process (51.44%–65.98%); however, the reduction in this parameter value to the normative value was not achieved. In the initial period of filtration, the water color was elevated, then it was removed to a greater extent along with the cycle duration. The removal effect ranged from 15.66% to 70.93%. In the case of the water turbidity, for the most of filtration period it was higher than before filtration.

The deposit is characterized by low ability to remove the oxygen consumption as well as total and calcium hardness. Several studies revealed an increase in the total hardness of water, although both in the raw and filtrated water, standards for drinking water were met. Laboratory studies upon the effectiveness of iron and manganese removal during the filtration on the catalyst deposit G-1 were conducted by Duranceau and Trupiano [12]. A very high degree of iron removal at the level of 90%–100% was reported. Iron values in these studies did not exceed 0.3 mg/L.

3.4. Effectiveness of water treatment by quartz sand activated with MnO_2

The next studied deposit was amorphous quartz sand activated with MnO_2 with a trade name Birm (Table 4). In the first filtration cycle during the first 6 d of the experiment, the total iron concentration in the filtered water exceeded acceptable levels. The highest value, that is, 0.6 mg/L, was observed at the very beginning of the research on the treatment efficiency of 47.37%. A high removal effect from 88.15% to 85.12% was shaped for the entire second test cycle, when the concentration of iron in the filtered water occurred in the range from 0.122 to 0.156 mg/L. The Birm is a relatively new product, hence there is a small number of publications on the subject. Kaleta et al. [8] determined the usefulness of Birm for the simultaneous removal of iron and manganese at the parameters of raw water pH 7.0, the iron content of 5.0 mg/L, and manganese 0.5 mg/L. They obtained quite good results of iron removal, which fluctuated within the range of trace levels in the filtered water, while the content of manganese compounds after filtration was not satisfactory. In studies carried out within the framework of this paper, lower initial concentration of iron was applied, that ranged about 1.0 mg/L, while manganese 0.5 mg/L. Obtained research evidenced the high degree of manganese removal.

Furthermore, the filtered water was characterized by elevated pH value relative to the raw water. First the pH increased to 9.69, then reached a value of 7.67. During the entire second series of tests, it remained at this level, that is, within the limits of pH 7.95–7.59. The indicated pH range belongs to slightly alkaline group. With the introduction of additional aeration [13,14], the pH can increase up to approximately 9.0, which additionally supports the removal of manganese compounds.

The Birm was characterized by high porosity at low bulk density. This feature was reflected in an effective removal of

Table 4
Contaminants concentration in the raw water and water filtrated with catalytic Birm bed during both series

	Time (d)	Iron (mg Fe/L)		Manganese (mg Mn/L)		pH		Color (mg Pt/L)		Turbidity (NTU)		Total hardness (mval/L)		Ammonia nitrogen (mg NH_4/L)		COD-Mn (mg O_2/L)	
		Raw water	Filtrated water	Raw water	Filtrated water	Raw water	Filtrated water	Raw water	Filtrated water	Raw water	Filtrated water	Raw water	Filtrated water	Raw water	Filtrated water	Raw water	Filtrated water
I	2	1.14	0.600	0.503	0.027	5.86	9.69	78	32	3	8	3.7	1.64	2.43	0.91	10	7.0
cycle	4	1.378	0.442	0.52	0.008	5.2	8.22	84	12	3	5	3.4	2.12	2.575	1.01	10.2	6.4
	6	0.973	0.211	0.512	0.009	5.77	8.15	83	18	6	2	3.6	1.55	2.04	0.89	9.4	7.1
	8	1	0.154	0.52	0.008	5.6	7.96	76	22	2	1	2.64	1.89	2.026	0.78	10.1	5.2
	10	1.012	0.142	0.501	0.007	4.25	7.25	76	9	6	1	3.04	1.65	2.552	0.92	10.3	6.1
	12	0.968	0.152	0.546	0.007	4.45	7.56	79	8	2	1	3.52	1.47	2.448	0.99	9.6	5.5
	14	0.965	0.174	0.546	0.009	4.47	7.67	86	9	1	1	3.52	1.77	2.72	0.95	10.2	4.8
II	1	1.085	0.156	0.54	0.004	5.67	7.85	79	7	9	1	4.48	1.25	2.156	0.85	10.1	3.2
cycle	2	1.021	0.122	0.55	0.002	6.49	7.59	79	5	1	2	4.8	1.32	2.9	0.89	9.6	4.3
	3	1.039	0.141	0.568	0.004	6.72	7.89	71	5	5	1	4.64	1.54	2.393	0.97	9.9	4.5
	4	1.13	0.134	0.525	0.004	6.35	7.95	77	5	6	1	4.4	1.62	2.9	0.99	9.5	5.7
	5	1.117	0.155	0.529	0.009	6.32	7.94	72	5	6	2	4.24	1.51	3.1	1.12	10.4	4.6

color, turbidity, and organic contaminants from water. The highest color of filtered water, that is, 32 mg Pt/L finally decreases to 8 mg Pt/L on the 12th day. In the second test cycle, the filtered water color was stabilized within 5–7 mg Pt/L. Equally high treatment effect was observed for turbidity. First values increased 5–8 NTU as a result of post-production particulate leaching. But since the 8th day till the end of the cycle, the turbidity values were 1 NTU.

A similar relationship was observed for COD-Mn. Its value ranged around 7.0 mg O_2/L at the beginning of the first cycle up to 4.8 mg O_2/L at the end, as well as from 5.7 to 3.2 mg O_2/L in the second filter cycle. Parameters there were less removed on Birm deposit were ammonium nitrogen and hardness. The hardness in filtered water in both test cycles remained at a similar level, that is, within limits of 1.25–1.89 meq/L. Removal of ammonia nitrogen from the water on Birm deposit also showed no dependence on the duration of the filter work and was stabilized at the level of 0.78–1.12 mg/L throughout the entire experiment. It exceeded almost twice the permitted level.

3.5. Effectiveness of water treatment by natural zeolite

Another tested deposit was natural zeolite (Table 5). In the literature [15], reports on the effectiveness of the ammonium form removal from water in zeolite and organic filters can be found. Other researchers [6,9] argue that zeolites are effective in the process of iron and manganese removal, and may even be used in the construction of natural barriers stopping the heavy metals migrating within the environment [16].

Own studies revealed that the concentration of iron in water after filtration on natural zeolite in the first filtration cycle was in the range from 0.053 to 0.490 mg/L. After washing the deposit of the retained impurities, the iron removal efficiency significantly increased from 49.22% to 90.78%. In the second test cycle, the iron concentration in the filtrate was from 0.068 to 0.156 mg/L. Manganese was equally effectively eliminated on the zeolite. Its concentration in the first test cycle grew from 0.001 to 0.156 mg/L at calculated purification result from 71.43% to 99.82%. In the second test cycle, after filter regeneration, recorded manganese concentrations were higher than in the previous step, that is, from 0.137 to 0.211 mg/L. The analysis of the usefulness of natural and modified zeolite for the removal of iron and manganese was also conducted by Anielak and Arendacz [9]. It was noted that the zeolite was an effective material for the removal of iron and manganese, especially when both elements were present in the water. However, as the initial concentration of iron in solution increased, the effectiveness of its removal decreased from 92% to 68.6%. In the present study, a decrease in the removal effect trend was also observed.

In addition, natural zeolite did not increase the pH of the solution. After the filtration process, the water pH in the 1st test cycle was in the range from 4.80 to 6.55, while in the 2nd cycle pH ranged from 5.57 to 6.77. Rozic et al. [17] emphasize that natural zeolites are the best materials for the retention of ammonium forms both in water and wastewater.

During the present experimental work, high ammonia nitrogen removal efficiency was not confirmed. Its content after filtration on studied natural zeolite ranged from 0.325 to 0.930 mg/L in the first cycle and from 0.267 to 1.015 mg/L

Table 5
Contaminants concentration in the raw water and water filtrated with zeolite bed during both series

	Time (d)	Iron (mg Fe/L)		Manganese (mg Mn/L)		pH		Color (mg Pt/L)		Turbidity (NTU)		Total hardness (mval/L)		Ammonia nitrogen (mg NH_4/L)		COD-Mn (mg O_2/L)	
		Raw water	Filtrated water	Raw water	Filtrated water	Raw water	Filtrated water	Raw water	Filtrated water	Raw water	Filtrated water	Raw water	Filtrated water	Raw water	Filtrated water	Raw water	Filtrated water
I	2	1.14	0.124	0.503	0.009	5.86	6.55	78	78	3	4	3.7	4.1	2.43	0.93	10	7.8
cycle	4	1.378	0.053	0.52	0.001	5.2	5.5	84	25	3	1	3.4	4	2.575	0.858	10.2	10.1
	6	0.973	0.153	0.512	0.008	5.77	6.17	83	86	6	3	3.6	3.62	2.04	0.347	9.4	9.5
	8	1	0.163	0.52	0.013	5.6	6.13	76	46	2	3	2.64	2.88	2.026	0.325	10.1	9.1
	10	1.012	0.172	0.501	0.013	4.25	4.85	76	92	6	9	3.04	3.28	2.552	0.392	10.3	8.5
	12	0.968	0.292	0.546	0.114	4.45	4.8	79	41	2	3	3.52	3.6	2.448	0.5	9.6	9.4
	14	0.965	0.49	0.546	0.156	4.47	4.87	86	27	1	3	3.52	3.76	2.72	0.777	10.2	7.5
II	1	1.085	0.1	0.54	0.137	5.67	5.57	79	31	9	2	4.48	48	2.156	1.015	10.1	10
cycle	2	1.021	0.156	0.55	0.149	6.49	6.06	79	15	1	0	4.8	4.88	2.9	0.267	9.6	9.4
	3	1.039	0.116	0.568	0.155	6.72	6.53	71	10	5	0	4.64	4.48	2.393	0.835	9.9	9.2
	4	1.13	0.078	0.525	0.157	6.35	6.77	77	30	6	7	4.4	4.08	2.9	0.747	9.5	9
	5	1.117	0.068	0.529	0.211	6.32	6.7	72	17	6	2	4.24	4.24	3.1	0.774	10.4	9.5

in the second. The zeolite was characterized by a low ability to remove color, turbidity, organic pollutants, and total hardness. In the first test cycle, the COD-Mn of water ranged within 7.5 to 10.1 mg O_2/L, and in the second cycle it ranged from 9.0 to 10.0 mg O_2/L. The color of filtered water was in the range from 10 to 92 mg Pt/L in both test cycles. The turbidity of the water ranged from 0 to 9 NTU. A general increase in the hardness of the water was observed for all the test cycle. In the second cycle after the second day of the deposit work, however, there has been a little reduction of the indicator (3.45%–7.27%). This parameter was in the range from 2.88 to 4.10 meq/L during the first cycle of filtration and from 4.08 to 4.88 meq/L in the second cycle.

3.6. *Effectiveness of water treatment by mixed ion-exchange resin*

One of the alternative methods for removing the iron, manganese, and also the hardness from water is the ion exchange on a mixed ion exchange resin (Table 6). In this study, the mixed deposits consisting of a different mixture of weak cation exchanger, strong cation exchanger, weak anion exchanger, natural-origin neutral pellets, and carrier neutral granules were tested. The concentration of iron in the 1st filtration cycle ranged from 0.092 to 0.272 mg Fe/L at the efficiency level from 71.81% to 91.93%. In the second filtration cycle, after the deposit regeneration with a solution of 5% NaCl, the iron content in purified water considerably decreased. Its concentration was as between 0.021 mg Fe/L on the first day of work up to 0.110 mg Fe/L on the 3rd day, and efficiency increased to 98.06%. Throughout the second cycle, the iron concentration does not exceed the permissible value.

Mixed ion masses caused an increase in the pH of the water during the whole filtration period. The degree of ammonia nitrogen elimination increased along with the filtration duration, and after deposit regeneration, this parameter removal efficiency declined. Due to the ion exchanging properties, deposits caused a complete reduction in total and calcium hardness. Mixed ion exchange deposits have proven to be ineffective in reducing the color and turbidity, although after regeneration, some reduction in the increasing of these parameters in water, was observed. The deposit contains mainly cation exchangers, thus it should explain the efficient removal of iron from water. A similar pattern was observed during the manganese removal. Its concentrations were in the range 0.005–0.202 mg/L.

In observing the work of ion exchange resins, pH of the solution is an important parameter, what is noted in the literature as well [13]. After filtration process, the pH of water in the 1st test cycle was in the range from 5.47 to 8.04, whereas in the second cycle the range was from 6.42 to 6.80. Considering the first filtration cycle for all deposit operation time, the pH value was increased. Also in the second cycle, there was an increase in pH of water, but to a lower degree than in the first cycle.

No satisfactory treatment effect was observed for ammonia nitrogen. In the first cycle, its content was within the range of 0.787 to 1.356 mg/L. Removal efficiency ranged from 33.53% to 67.85%. In the second test cycle, the concentration of ammonium nitrogen in water ranged from 2.027 to 2.950 mg/L. After rinsing the deposit, no improvement in the removal of ammonia nitrogen was observed, even a deterioration in removal efficiency, which ranged from 3.45% to 19.28%, was reported.

Table 6
Contaminants concentration in the raw water and water filtrated with ion exchange mix bed Ecomix A during both series

	Time (d)	Iron (mg Fe/L)		Manganese (mg Mn/L)		pH		Color (mg Pt/L)		Turbidity (NTU)		Total hardness (mval/L)		Ammonia nitrogen (mg NH_4/L)		COD-Mn (mg O_2/L)	
		Raw water	Filtrated water	Raw water	Filtrated water	Raw water	Filtrated water	Raw water	Filtrated water	Raw water	Filtrated water	Raw water	Filtrated water	Raw water	Filtrated water	Raw water	Filtrated water
I	2	1.14	0.092	0.503	0.005	5.86	8.04	78	80	3	4	3.7	0	2.43	1.33	10	6.5
cycle	4	1.378	0.123	0.52	0.01	5.2	6.8	84	93	3	9	3.4	0	2.575	1.217	10.2	9.2
	6	0.973	0.103	0.512	0.008	5.77	6.65	83	94	6	5	3.6	0	2.04	1.356	9.4	9.2
	8	1	0.127	0.52	0.01	5.6	6.5	76	53	2	5	2.64	0	2.026	1.249	10.1	9.7
	10	1.012	0.096	0.501	0.075	4.25	5.95	76	66	6	9	3.04	0	2.552	1.143	10.3	9.7
	12	0.968	0.152	0.546	0.103	4.45	5.7	79	59	2	6	3.52	0	2.448	0.787	9.6	7.6
	14	0.965	0.272	0.546	0.202	4.47	5.47	86	61	1	2	3.52	0	2.72	0.993	10.2	9.7
II	1	1.085	0.021	0.54	0.016	5.67	6.42	79	38	9	8	4.48	0	2.156	2.073	10.1	10
cycle	2	1.021	0.043	0.55	0.001	6.49	6.6	79	15	1	2	4.8	0	2.9	2.341	9.6	8.9
	3	1.039	0.11	0.568	0.003	6.72	6.8	71	21	5	0	4.64	0	2.393	2.027	9.9	9.8
	4	1.13	0.086	0.525	0.02	6.35	6.76	77	13	6	2	4.4	0	2.9	2.8	9.5	9.3
	5	1.117	0.058	0.529	0.096	6.32	6.54	72	43	6	8	4.24	0	3.1	2.95	10.4	9.4

Organic impurities were also not satisfactorily removed from the water. In the first cycle, the COD maintained within 6.5–9.7 mg O_2/L, while in the second cycle, it was from 8.9 to 10.0 mg O_2/L. The effect of lowering the oxidation capacity in the 1st filtration cycle was shaped at the level of 2.13%–35%. No improvement in the mixed bed work was recorded after regeneration process. Throughout the whole filtration period in the second test cycle, the efficiency to reduce oxygen consumption was low and ranged from 0.99% to 9.62%. The color of the water after filtration in the 1st test cycle amounted from 53 to 94 mg Pt/L and in the second between 13 and 43 mg Pt/L. The water turbidity in the first filter cycle ranged to about 2–9 NTU, while in the second cycle from 0 to 8 NTU. Carter and Gregorich [18] emphasized the lower efficiency of ion exchange mass for water contaminated with organic compounds with enhanced color and turbidity values. They recommend use of the ion exchange resign for water that is devoid of these impurities. They reported the ion-exchanging capacity reduction of deposits that were used for the purification of water with exceeded COD concentration. The reverse situation was presented for the removal of water hardness. When analyzing the two filtration cycles on mixed ion beds, complete reduction in the total and calcium hardness to 0 meq/L was found.

3.7. Effectiveness of water treatment by anthracite

Poor effect of removing the iron and manganese was showed by anthracite deposit hydrocarbon (Table 7). In the initial phase of the filtration, the material removed the greatest amount of iron, and then its efficiency decreased from 86.23% to 20.41% along with the operation duration. This may be due to a decrease in the pH of water. Lowering to the normative value (0.2 mg Fe/L) was obtained only on the first 4 d of filtration. A similar decline trend of effectiveness along with the cycle duration was observed for ammonium nitrogen removal. Hydrocarbon removed the oxygen consumption of water to very low extent, which did not provide the desired results (5 mg O_2/L).

The deposit is characterized by a low ability to remove the total and calcium hardness. In some cases, the deposit was broken and parameter values were much elevated, although normative levels were not exceeded. During filtration, the water pH increased, water color was reduced, and the removal percentage ranged from 21.05% to 82.28%. In case of turbidity, in both cycles, the parameter decreased in the initial stage, and then increased to such an extent that it surpassed the content in the raw water. The use of anthracite deposits was studied by Doula [19] and Jez-Walkowiak [20]. In their studies, anthracite was used in combination with quartz sand as the two-bilayer deposit. The underground water was aerated prior to filtration and was characterized by a higher content of iron (up to 1.6 mg/L), manganese (up to 0.29 mg/L), and ammonium nitrogen (up to 1 mg/L). Iron was removed with 91.9%–95.9% efficiency.

3.8. Effectiveness of water treatment by quartz sand

The last and the least efficient deposit studied in the experiments was filtration quartz sand (Table 8). Filtration did not allow to effectively remove most of the parameters, only the turbidity was an indicator that was removed

Table 7
Contaminants concentration in the raw water and water filtrated with anthracite bed during both series

	Time (d)	Iron (mg Fe/L)		Manganese (mg Mn/L)		pH		Color (mg Pt/L)		Turbidity (NTU)		Total hardness (mval/L)		Ammonia nitrogen (mg NH_4/L)		COD-Mn (mg O_2/L)	
		Raw water	Filtrated water	Raw water	Filtrated water	Raw water	Filtrated water	Raw water	Filtrated water	Raw water	Filtrated water	Raw water	Filtrated water	Raw water	Filtrated water	Raw water	Filtrated water
I	2	1.14	0.157	0.503	0.015	5.86	7.07	78	87	3	4	3.7	3.51	2.43	0.630	10	9.5
cycle	4	1.378	0.200	0.52	0.004	5.2	5.60	84	40	3	2	3.4	3.80	2.575	0.848	10.2	9.7
	6	0.973	0.449	0.512	0.009	5.77	6.37	83	98	6	3	3.6	3.44	2.04	1.635	9.4	9.3
	8	1	0.488	0.52	0.008	5.6	6.11	76	25	2	0	2.64	2.64	2.026	1.088	10.1	9.7
	10	1.012	0.730	0.501	0.061	4.25	4.68	76	60	6	1	3.04	3.12	2.552	1.284	10.3	8.5
	12	0.968	0.664	0.546	0.075	4.45	4.99	79	30	2	3	3.52	3.52	2.448	1.367	9.6	8.8
	14	0.965	0.700	0.546	0.169	4.47	4.88	86	30	1	6	3.52	3.84	2.72	1.555	10.2	9.7
II	1	1.085	0.297	0.54	0.297	5.67	5.62	79	49	9	4	4.48	5.20	2.156	1.426	10.1	10.1
cycle	2	1.021	0.344	0.55	0.15	6.49	6.16	79	14	1	0	4.8	4.80	2.9	1.479	9.6	9.4
	3	1.039	0.753	0.568	0.153	6.72	6.67	71	18	5	0	4.64	4.64	2.393	1.565	9.9	9.6
	4	1.13	0.882	0.525	0.152	6.35	6.45	77	40	6	7	4.4	4.64	2.9	1.446	9.5	9.3
	5	1.117	0.889	0.529	0.241	6.32	6.41	72	27	6	3	4.24	4.56	3.1	2.326	10.4	9.7

Table 8
Contaminants concentration in the raw water and water filtrated with quartz sand bed during both series

	Time (d)	Iron (mg Fe/L)		Manganese (mg Mn/L)		pH		Color (mg Pt/L)		Turbidity (NTU)		Total hardness (mval/L)		Ammonia nitrogen (mg NH_4/L)		COD-Mn (mg O_2/L)	
		Raw water	Filtrated water	Raw water	Filtrated water	Raw water	Filtrated water	Raw water	Filtrated water	Raw water	Filtrated water	Raw water	Filtrated water	Raw water	Filtrated water	Raw water	Filtrated water
I cycle	2	1.14	0.546	0.503	0.412	5.86	7.26	78	115	3	5	3.7	3.06	2.43	1.55	10	10
	4	1.378	0.678	0.52	0.398	5.2	7.60	84	75	3	5	3.4	2.89	2.575	1.41	10.2	10
	6	0.973	0.561	0.512	0.386	5.77	6.57	83	83	6	2	3.6	2.56	2.04	1.12	9.4	9.2
	8	1	0.689	0.52	0.391	5.6	6.29	76	41	2	1	2.64	1.45	2.026	1.32	10.1	7.5
	10	1.012	0.730	0.501	0.465	4.25	5.48	76	12	6	1	3.04	2.01	2.552	1.25	10.3	7.8
	12	0.968	0.945	0.546	0.488	4.45	6.08	79	9	2	0	3.52	1.56	2.448	1.88	9.6	7.9
	14	0.965	0.911	0.546	0.511	4.47	6.55	86	70	1	2	3.52	2.85	2.72	1.95	10.2	8.5
II	1	1.085	0.245	0.54	0.329	5.67	7.02	79	15	9	0	4.48	3.45	2.156	1.05	10.1	5.6
cycle	2	1.021	0.341	0.55	0.425	6.49	7.19	79	18	1	0	4.8	3.12	2.9	1.32	9.6	6.5
	3	1.039	0.787	0.568	0.497	6.72	7.85	71	18	5	1	4.64	3.03	2.393	1.25	9.9	7.2
	4	1.13	0.825	0.525	0.498	6.35	7.46	77	10	6	2	4.4	2.5	2.9	1.56	9.5	6.8
	5	1.117	1.02	0.529	0.482	6.32	7.42	72	48	6	2	4.24	2.64	3.1	1.75	10.4	6.2

in 100%, which has resulted in meeting the standard levels. There was also a reduction in some other parameters such as color, ammonia nitrogen, and oxygen consumption, what is often mentioned in the literature [21,22].

4. Conclusion

Based on the study, it was found that none of the analyzed filtration deposits purifies the water to such an extent that all pollution parameters fit the permitted level setup by the drinking water legal regulations [23,24].

Greensand Plus proved to be the most effective material in removing the iron from water, although manganese compounds were retained better by Crystal-Right and Birm. It should be noted that both deposits, that is, Greensand Plus and Birm are recommended for iron and manganese removal from water. Differences in water purification and their exploitation are related to their structure. Greensand Plus is characterized by a fine grain size and is faster clogged than Birm that traps the contaminants both between and within the pores. In addition, it removes the water color, turbidity, and organic pollutants characterized as COD-Mn, the best among all analyzed deposits. Ammonia nitrogen was not effectively removed on any of tested deposits, although Greensand Plus producers argued that this material can be also used to eliminate the ammonium forms. This parameter, in turn, was reduced by Crystal-Right, that has the cation-exchanging properties. That nature of the deposit was also reflected in the reduction of water hardness.

The study used a model raw water so contaminated that had the characteristics of infiltration water, that is, the most taken underground water. Increased color, turbidity, and organic impurities are parameters that are difficult to reduce in the process of filtration. Often, it is recommended to protect the iron and manganese removing as well as ion exchange deposits against them. Nevertheless it is possible to use other water pollution parameters to control the final concentration of basic pollutants – Fe and Mn. Equations of kinetics may be useful at this field. Experiments carried out in frameworks of this research demonstrate that not all deposits capable of removing the iron and manganese from water, are sensitive to elevated values of these parameters.

The presented experiments revealed that single-stage filtration is ineffective. However, the reduction in water pollution, which is required by regulation, can be achieved by using the multi-stage filtration. Based on these results, it can be stated that combining filtration on Greensand Plus and Crystal-Right or Birm and Crystal-Right in a single technological line can bring an increase in the purification effects. In addition, introduction of the zeolite pre-filter and sand can partially stop the color and turbidity of water as well as iron (III) sediments, which can additionally improve the estimated effects.

References

[1] J. Kriš, V. Dubová, Trends in Economical Treatment of Water, in Proc. New Trends in Water Management, Trenčín, 2005, pp. 20–25

[2] M.S. Burger, S.S. Mercer, G.D. Shupe, G.A. Gagnon, Manganese removal during bench-scale biofiltration, Water Res., 42 (2008) 4733–4742.

[3] I. Skoczko, E. Szatylowicz, Studies on the efficiency of groundwater treatment process with adsorption on activated alumina, J. Ecol. Eng., 18 (2017) 211–218.

[4] D. Barloková, J. Ilavský, Iron and manganese removal from small water resources, Polish J. Environ. Stud., 19 (2009) 1117–1122.

[5] M. Granops, Effective methods of iron and manganese removal from the water in water treatment stations in urban areas, Sci. Rev. Environ. Eng. Protect., 14 (2005) 153–160.

[6] N. Tufenkji, M. Elimelech, Correlation equation for predicting single-collector efficiency in physicochemical filtration in saturated porous media, Environ. Sci. Technol., 38 (2004) 529–536.

[7] S. Chatuverdi, N.D. Pragnesh, Removal of iron for safe drinking water, Desalination, 303 (2012) 1–11.

[8] J. Kaleta, D. Papciak, A. Puszarkiewicz, Natural and modified minerals in groundwater treatment, Miner. Mater. Manage., 25 (2009) 51–63.

[9] A.M. Anielak, M. Arendacz, Iron and manganese removal effects using zeolites, Annu. Set Environ. Protect., 9 (2007) 9–18.

[10] V.A. Pacini, A.M. Ingallinella, G. Sanguinetti, Removal of iron and manganese using biological roughing up flow filtration technology, Water Res., 39 (2005) 4463–4475.

[11] A. Sperlich, A. Werner, A. Genz, G. Amy, E. Worch, M. Jekel, Breakthrough behavior of granular ferric hydroxide (GFH) fixed-bed adsorption filters: modeling and experimental approaches, Water Res., 39 (2005) 1190–1198.

[12] J.S. Duranceau, V.M. Trupiano, Evaluation of oxidized media filtration for removing sulfides from groundwater, Desal. Wat. Treat., 28 (2011) 366–377.

[13] E. Pogorni, M. Rzaca, Investigation of the effects of salinity and temperature on the removal of iron from water by aeration, filtration, and coagulation, Pol. J. Environ. Stud., 23 (2014) 2157–2161.

[14] I. Skoczko, J. Piekutin, K. Ignatowicz, Efficiency of manganese removal from water in selected filter beds, Desal. Wat. Treat., 57 (2016) 1611–1619.

[15] A. García-Mendietaa, M. Solache-Ríosa, M.T. Olguína, Evaluation of the sorption properties of a Mexican clinoptilolite-rich tuff for iron, manganese and iron–manganese systems, Microporous Mesoporous Mater., 118 (2009) 489–495.

[16] P.H. Jacobs, T.D. Waite, The role of aqueous iron (II) and manganese (II) in sub-aqueous active barrier systems containing natural clinoptilolite, Chemosphere, 54 (2004) 313–324.

[17] M. Rožić, S. Cerjan-Stefanović, S. Kurajica, V. Vančina, E. Hodžić, Ammoniacal nitrogen removal from water by treatment with clays and zeolites, Water Res., 34 (2000) 3675–3681.

[18] M.R. Carter, E.G. Gregorich, Soil sampling and methods of analysis, 2nd ed., Taylor & Francis Publication, NW, 2008, pp. 1013–1088.

[19] M.K. Doula, Removal of Mn^{2+} ions from drinking water by using clinoptilolite and clinoptilolite-Fe oxide system, Water Res., 40 (2006) 3167–3176.

[20] J. Jez-Walkowiak, Filtration materials in water treatment, Water Wastewater Syst., 11 (2006) 50–52.

[21] A. Funes, J. de Vicente, L. Cruz-Pizarro, I. de Vicente, The influence of pH on manganese removal by magnetic microparticles in solution, Water Res., 53 (2014) 110–122.

[22] D.A. Fungaro, M. Bruno, L.C. Grosche, Adsorption and kinetic studies of methylene blue on zeolite synthesized from fly ash, Desal. Wat. Treat., 2 (2009) 231–239.

[23] The European Drinking Water Directive (DWD), Council Directive 98/83/EC.

[24] Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000: The Water Framework Directive.