



## The batch tests on new catalytic filtration masses creation by natural materials modification with $\text{MnO}_2$ supporting by electrolysis with the view of Fe and Mn removal

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Received 9 October 2022; Accepted 10 December 2022

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### ABSTRACT

Among the most common and problematic groundwater contaminants are iron and manganese compounds. Specific filter materials are of primary importance in removing them from groundwater. They can be based on natural or modified materials. Modification of the natural materials used for traditional water treatment is one of the factors determining the efficiency of the Fe and Mn removal process, because raw natural media do not effectively remove them from the water. For this reason, research has been carried out on the modification of selected natural materials with coatings that accelerate the removal of iron and manganese from water. In order to shorten the activation time, the coating process was supported with an electrolytic method. The research was conducted on sand and aluminosilicate, which were activated with a  $\text{KMnO}_4$  solution by reducing it with natural reducing agents – coffee and lemon juice. Conducted experiments let to achieve new catalytic masses for Fe and Mn removal from the water. All tested materials were covered with oxidation layer of  $\text{MnO}_2$ . The best materials coated with precipitated  $\text{MnO}_2$  were aluminosilicates of both finer- and larger-grain size. The process of electrolysis allowed a significant reduction in a modification time. After filter columns backfilling with the new modified beds, both aluminosilicates showed the best efficiency in Fe and Mn removal from the water and the most stable  $\text{MnO}_2$  coating. Electrolysis support let to shorten the time of backwash.

*Keywords:* Filtration; Modified materials; Groundwater treatment; Iron and manganese; Electrolysis

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### 1. Introduction

Groundwater has varying chemical status due to the different deposition levels in the ground. Common water contaminants exceeding accepted standards, that is, iron and manganese. These elements are a problem in water treatment management. In accordance with the Directive of the Council of the European Union on the quality of water intended for human consumption 2020/2184 [1] as well as the relevant national regulations of individual EU countries (e.g., in Poland: Regulation of the Minister of Health of 7 December

2017 [2]), the concentration of manganese in water should not exceed 0.05 mg/L and iron 0.2 mg/L. When using groundwater for industrial and municipal purposes, manganese and iron must be removed to the concentrations specified in the aforementioned regulation. Hacker et al. [3] states that the nuisance of elevated manganese and iron compounds is indicated by unpleasant taste and scent. Elevated concentrations also contribute to the formation of dark deposits in the installation and disturb the operation of filters and water meters. For this reason, the process of filtration with special beds is very important. This is the best known method for

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meeting water quality standards [4–8]. Various factors influence groundwater pollution, what bold literature data [9–13]. Skoczko et al. [14], Król and Dudziak [15] and Keken et al. [16] state that naturally occurring water is characterised by specific physical, chemical and biological properties. All these properties affect its suitability for different purposes.

Among the most problematic groundwater contaminants and the most common in groundwater are iron and manganese compounds [17]. According to Canup and Righter [18], the two elements occur side by side in groundwater, with the amount of manganese usually being lower at around 10%–20% of the iron content. In contaminated waters, salts of these elements are found in high concentrations [4,5,8,16,19,20]. According to water quality regulations [1,2], the iron content must not be greater than 0.2 mg·Fe/L and the manganese – not greater than 0.05 mg·Mn/L. Exceeding the permissible concentration – drinking water could contribute to a number of health effects, increased colour and turbidity, unpleasant taste and smell [19,20–22]. Fe and Mn cations are also a disadvantage in the dye, pulp, paper and textile industries [23].

Literature [24–28] states that filter materials are of fundamental importance in the iron and manganese removal from groundwater. They can be composed of natural minerals or can be chemically manufactured. The most commonly used are filter materials with catalytic and/or oxidative properties leading to precipitation of iron and manganese on the grain surface. The catalytic compound is  $MnO_2$ , which is a strong oxidant [29,30]. Removal of iron and manganese is carried out by various methods: filtration, membrane separation, ion exchange, distillation, chemical precipitation, coagulation or sorption [9,13,15,31,32].

The example of naturally activated bed in water treatment station (WTS) is the quartz sand covered with a durable layer of iron and manganese oxides that form an oxidation coating, during aeration and filtration of water contaminated with iron and manganese [22,30,33,34]. Cai et al. [35] report that unprocessed natural materials are also used, which do not require activation and allow effective removal of Fe and Mn. An equally popular method especially in industrial plants and boiler water preparation is filtration based through artificially activated beds based on various patented technologies [36]. Table 1 shows different filtration materials used for Fe and Mn removal from the water.

Modification of filtration materials is one of the decisive factors in the effectiveness of the manganese removal process, as the raw natural media does not effectively remove it from the water. Scientific groups of Karami et al. [33] and Azari et al. [34] also have modified different materials to better remove various substances from the water. They have proved raw materials are inefficient. Beside chemical activation they used technics of modification supporting with physical processes what significantly changed results. Commercially processed filtration masses (e.g., Greensand, Birm, Pyrolox), compared to naturally coated, cannot purify water for longer time without regeneration. Furthermore, the  $MnO_2$  cover is not stable and is washed out during filtration. It does not meet for effective manganese removal, what is confirmed by literature (Table 1). The activation time is also a major disadvantage – the process may last up to six weeks. For this reason, research experiments were

carried out on selected natural minerals modification with specific coating that accelerate the removal of iron and manganese from groundwater. In order to reduce the activation time, the coating process was carried out using an electrolytic method.

## 2. Material and methods

The research was conducted in the laboratory of the Faculty of Civil and Environmental Science at the Bialystok University of Technology. The goal was modification of porous natural minerals with a 5% potassium permanganate solution. Samples of sand, gravel and aluminosilicates of different granulations were prepared:

- fine sand (S1): diameter of 0.2 mm;
- coarse sand, that is, gravel (S2): diameter of 0.8 mm;
- fine aluminosilicate (Z1): diameter of 0.3 mm;
- coarse aluminosilicate (Z2): diameter of 2 mm;

Experiments were conducted on materials' samples weighing app. 500 g placed in 1 litre reactors (Fig. 1). The tested materials were modified with:

- 5% potassium permanganate solution (5 g of  $KMnO_4$  p.d.a. dissolved in 1 L of cold distilled water);
- natural reducing agents;
- coffee infusion (constituting 25% of the activate solution) prepared based on lightly roasted grains, fine-ground; coffee mass was poured in cold distilled water for 24 h, then heated and cooled down;
- lemon juice (5% of the activate solution); prepared based on natural lemon juice dissolved in cold distilled water.

The samples of filter materials were completely soaked in prepared solution ( $KMnO_4$ , coffee and lemon juice solution in the ratio 7:2:1). Above the table surface the excess solution 1 cm was left (Fig. 1).

Investigation stages:

- Stage 1: activation of all tested materials with prepared solution for 7 d,
- Stage 2: electrolytic activation of materials with prepared solution for 7 d,
- Stage 3: activation of materials with prepared solution for 14 d,
- Stage 4: electrolytic activation of materials with prepared solution for 14 d,
- Stage 5: activation of materials with prepared solution for 21 d,
- Stage 6: electrolytic activation of materials with prepared solution for 21 d,
- Stage 7: activation of materials with prepared solution for 28 d,
- Stage 8: electrolytic activation of materials with prepared solution for 28 d.

In each test stage, 4 samples consisting of fine sand, coarse sand, fine aluminosilicate and coarse aluminosilicate were tested. Four test cycles were carried out for each test material.

Table 1  
Filtration materials used for Fe and Mn removal – literature review

S. No.	Filtration type	Material	Pollution removed	Features	Efficiency	Literature
1	Bed filtration in treatment plants	Quartz sand	Fe <sup>3+</sup> ; Mn <sup>4+</sup>	Removes mainly solid, larger colloidal agglomerates, turbidity and suspended solids; pre-aeration required	Fe – 15%–82%; Mn – 7%–35%	Cai et al. [35] Lima et al. [36] Inglezakis et al. [37] Adelman et al. [38] Munter et al. [28] Skoczko [39]
		Chalcedonite	Fe <sup>2+ 3+</sup> , Mn <sup>2+ 3+ 4+</sup>	Removes mainly solid larger colloidal agglomerates, turbidity and suspended solids. It becomes more rapidly activated for the removal of manganese	Fe – 11%–86%; Mn – 11%–49%	Phatai et al. [40] Jeż-Walkowiak et al. [41] Lima et al. [36] Munter et al. [28] Kaleta et al. [30]
		Anthracite	Fe <sup>3+</sup> ; Mn <sup>4+</sup>	Removes mainly solid larger colloidal agglomerates, turbidity and suspended solids	Fe – 8%–75%; Mn – 5%–31%	Veressinina et al. [42] Dudziak et al. [31] Zeng et al. [29] Bruins et al. [22]
		Manganese ore	Fe <sup>2+ 3+</sup> , Mn <sup>2+ 3+ 4+</sup> , NH <sub>4</sub> ; organics	Crashed ore reach in MnO <sub>2</sub> called manganese sand is base of many filtration materials; no activation required; fast purification effect	Fe – 19%–95%; Mn – 12%–88%	Jeż-Walkowiak et al. [41] Skoczko [32] Cai et al. [35] Dudziak and Kopańska [4]
2	Filtration with natural materials	Zeolite	Fe <sup>2+ 3+</sup> , Mn <sup>2+ 3+ 4+</sup> ; NH <sub>4</sub>	It has a skeletal structure; allows ion exchange and reversible dehydration; characteristics: high sorption, catalytic and ion exchange capacity; requires aeration	Fe – 12%–86%; Mn – 9%–45%	Munter et al. [28] Lima et al. [36] Kaleta et al. [30]
		Greensand	Fe <sup>2+ 3+</sup> , Mn <sup>2+ 3+ 4+</sup> ; H <sub>2</sub> S	It is an oxidation and filtration bed; it requires KMnO <sub>4</sub> regeneration; if not, the bed will be permanently damaged	Fe – 33%–99%; Mn – 25%–91%	Skoczko [32] Duranceau and Trupiano [26] Jeż-Walkowiak et al. [41]
		Pyrolox	Fe <sup>2+ 3+</sup> , Mn <sup>2+ 3+ 4+</sup> , NH <sub>4</sub> ; organics	It works following the same principles as manganese ore but is pre-activated; a durable material with long life and low abrasion	Fe – 16%–85%; Mn – 12%–69%	Barlokova and Ilavski [43] Veressinina et al. [41] Munter et al. [28]
3	Pre-activated bed filtration	Purolite	Fe <sup>2+ 3+</sup> , Mn <sup>2+ 3+ 4+</sup> ; H <sub>2</sub> S	Manganese zeolite; high oxidation capacity; KMnO <sub>4</sub> regeneration	Fe – 15%–85%; Mn – 9%–65%	Munter et al. [28] Truong et al. [44] Aghoyeh and Khalafi [45]
		Crystal Right	Fe <sup>2+ 3+</sup> , Mn <sup>2+ 3+ 4+</sup> , hardness; acidity	Silica crystalline form; Fe and Mn removed by ion exchange; mechanically resistant; can be disinfected with chlorine	Fe – 37%–81%; Mn – 24%–63%	Christopherson et al. [46] Petkov et al. [47] Szatyłowicz and Skoczko [48] Tao et al. [49]

Table 1 (Continued)

Table 1

S. No.	Filtration type	Material	Pollution removed	Features	Efficiency	Literature
3	Pre-activated bed filtration	Birm	Fe <sup>2+3+</sup> ; Mn <sup>2+3+4+</sup> ; NH <sub>4</sub>	Contains insoluble MnO <sub>2</sub> catalyst, it is amorphous and crystalline silica; requires aeration; organic matter and oils have inhibiting effect; no resistance to chlorination	Fe – 21%–95%; Mn – 10%–85%	Barlokova and Ilavski [43] Kaleta et al. [30] Anielak and Arendacz [25]
		FM	Fe <sup>2+3+</sup> ; Mn <sup>2+3+4+</sup> ; NH <sub>4</sub>	Allows treatment of waters with extremely high Fe and Mn contents; requires aeration and pH adjustment	Fe – 15%–75%; Mn – 8%–62%	Tang et al. [24] Inglezakis et al. [37]
		Defemen	Fe <sup>2+3+</sup> ; Mn <sup>2+3+4+</sup> ; NH <sub>4</sub>	Forms Fe oxides on the surface of grains and sorbs MnO <sub>2</sub> in deeper layers; does not require replacement	Fe – 16%–89%; Mn – 10%–58%	Veressinina et al. [42] Bruins et al. [22] Michel et al. [50]
		G-1	Fe <sup>2+3+</sup> ; Mn <sup>2+3+4+</sup> ; NH <sub>4</sub> ; organics	Effective for removal of Fe and Mn also in organic compounds; combined in layers with sand	Fe – 20%–95%; Mn – 10%–85%	Skoczko [32] García-Mendieta et al. [51]

Source: Own elaboration based on the literature cited in the table.



1) Dry samples

2) Tested materials treated with 5% KMnO<sub>4</sub> solution.

Fig. 1. Preparation of individual series of material samples for each step of activation tests. Source: Own elaboration.

In order to support coating process with MnO<sub>2</sub> and shorten its time the electrolysis process was applied additionally. The schematic of the stand is shown in Fig. 2. A test stand for electrolysis was constructed consisting of a 1-L reactor filled with the tested filter bed (S1, S2, Z1, Z2). Carbon-based electrodes were used for testing. A constant electric current of 12 V and 120 A generated by the electrolyser was passed through samples numbers: 2, 4, 6 and 8. The electrolysed materials were called S1-E, S2-E, Z1-E, Z2-E in this study.

Raw water was prepared from distilled water introducing the following ingredients per 1 L:

- 1.5 g pepton
- 10 g magnesium sulphate,

- 0.1 g manganese(II) sulphate anhydrous,
- 1.6 g ammonium iron(II) sulphate,
- 2 mg-CaO<sub>2</sub>

This made it possible to obtain raw water with constant parameters and a quality close to natural groundwater.

After the specified activation time, the samples were dried and rinsed with water to remove the coloured reactant. The filter material samples were then dried again and back-filled onto the filter columns as presented in Fig. 3. A study was then conducted to determine the treatment efficiency of prepared water with a stable composition corresponding to natural groundwater by filtration through the prepared activated filter materials. The removal efficiency was assessed

on the basis of the water composition by analysis of the water pollution indicators indicated in Directive 2020/2184.

The following contaminant factors were tested in the raw water and the water filtered through activated filter materials: colour, turbidity, conductivity, pH, total iron, total manganese, COD-Mn, total hardness, ammonia nitrogen, nitrate nitrogen (V) and chlorides. The concentration of iron and manganese in the raw and filtered water throughout the particular filter materials was determined by flame atomic absorption spectrometry using a Thermo Scientific iCE3500 atomic absorption spectrometer with deuterium background correction. For the determination of each element, their standard solutions were prepared in 50 cm<sup>3</sup> flasks, allowing a standard curve to be made consisting of 5 measurement points of different concentrations. The reference sample was distilled water.

The study was carried out with a 3-fold repeatability of analyses. Samples for testing were taken once every 24 h. Statistica 12.5 software was used for statistical analyses to calculate statistical values: arithmetic mean, minimum and maximum, median, standard deviation and statistical error, which is the result discrepancy of a unit measurement from the real value. Correlations between individual pollution indicators were also checked using Pearson’s correlation coefficient.

### 3. Results and discussion

In the present study, natural filtration materials were mobilised using KMnO<sub>4</sub> solution for a period of four weeks, whereby each week was analysed separately. The modification process was supported electrolytically using current generated by a constant voltage electrolyser. Particular attention was also paid to the washing time of the investigated beds. Real water treatment station operators highly recommend filter materials that require the possible shortest backwash time. In our study, there was evaluated the efficiency of the filtration process from contaminants presented in the Table 2.

The modification of natural materials is one of the factors determining the efficiency of the iron and manganese removal process, as fresh raw natural material does not effectively eliminate them from the water. The process requires time to build up the bed which depends on local conditions and the degree of required water purification. The activation efficiency depends on several factors:

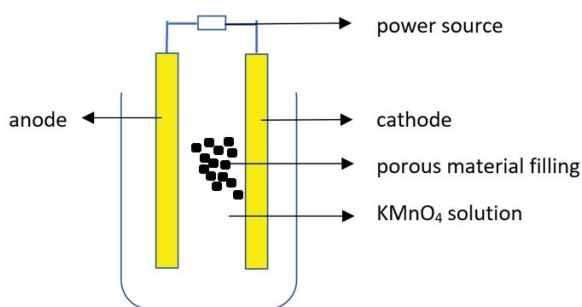


Fig. 2. The stand for the electrolysis process tests. Source: Own elaboration.

the presence of oxidisable or reducible manganese ions, dissolved oxygen content, water pH and the features of the filtration bed. Literature gives examples of different materials modification with different process conditions [9,13,33,39,52]. The Karami et al. [33] evaluated the efficiency of manganese-modified pumice in the treatment of water solutions. It was demonstrated that the removal of the tested contaminants indicated an increase with higher pH value, absorbent dose and contact time.

In the present study, a MnO<sub>2</sub> layer was attempted to be produced from KMnO<sub>4</sub> by electrolytically assisted

Table 2  
Raw water parameters

Pollution parameter	Concentration	Analytical method
Colour	15 mg/L	Spectroscopic
Turbidity	1.5 NTU	Nephelometric
pH	7.2	Potentiometric
COD-Mn	10 mg/L	Permanganate method
Fe total	1.0 mg/L	Atomic absorption spectrometry
Mn total	0.5 mg/L	Atomic absorption spectrometry
Conductivity	1,000 μS/L	Potentiometric
Total hardness	500 mg·CaCO <sub>3</sub> /L	Direct colorimetric titration
NH <sub>4</sub> <sup>+</sup>	2 mg/L	Spectroscopic
NO <sub>3</sub> <sup>-</sup>	10 mg/L	Spectroscopic
Cl <sup>-</sup>	500 mg/L	Mohr’s method

Source: Own elaboration.

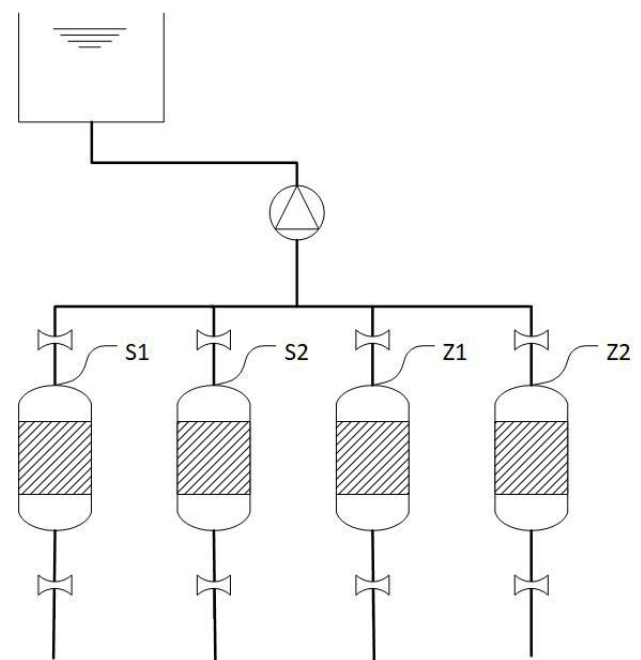
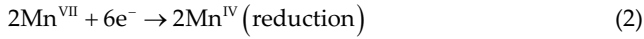
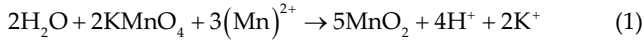


Fig. 3. The stand for filtration process tests. Source: Own elaboration.

reduction. Additional natural reducing agents were used: coffee bean infusion and lemon juice, which were tested by Dinn et al. [53] and Chong et al. [54].



Activation of the materials consisted of coating grains with insoluble in water  $\text{MnO}_2$  (according to the above reaction). The process was assisted by electrolysis. The available literature [35,55,56] reports that the most common process is the oxidation of Mn(II) and Mn(III) ions to produce a  $\text{MnO}_2$  coating. The reduction reaction is less common as it requires additional reducing agents. Wang [55] writes that oxidation, however, occurs at elevated pH and excess of oxygen. Using the solutions and materials described in the ‘Method’ section, we produced 8 different filter materials coated with a layer of  $\text{MnO}_2$  composed on the basis of sand and aluminosilicates: fine-grained and coarse-grained.

After the  $\text{KMnO}_4$  activation process, all materials were washed.

As part of the research, the efficiency of the masses modification was assessed by the effectiveness of water filtration through all the tested beds by reducing the concentrations of contaminants that are typical in groundwater. For technologists and water treatment plant operators, colour is one of the most important contamination control criteria. In the conducted studies, water colour was of great importance, as activation experiments were conducted using a  $\text{KMnO}_4$  solution with a specific colour.

The results obtained for the removal of colour from the tested water are shown in Fig. 4. Water colour, over the course of each test period, showed varying results. The highest values of this parameter reaching over 80 mg-Pt/L were recorded in the water filtered through Z2 activated for 4 weeks without electrolytic support. In contrast, the most effective water colour reduction was achieved by: S1, S2 and Z1, without electrolytic support, which were achieved over 4 weeks of activation and in the 4th cycle of experiments. The colour value varied between 20–30 mg/L. At the same

time, it should be noted that 1st week of testing in 1st cycle of experiments allowed to obtain results within the standard limits, that is, below 10 mg/L – significantly deviating from the others. This was due to the fact that the activation time was so short that the  $\text{MnO}_2$  coating has not yet had time to form from  $\text{KMnO}_4$ . The coloured reagent was easily removed during the rinsing process and did not increase the colour value of the water. As the test time increased, the indicator successively decreased with each test cycle. Increased values were only noticed in the 3rd test cycle. In the 4th cycle, the colour decreased with each successive day of bed operation. In this cycle, the lowest indicator values were recorded for all the filter materials analysed.

Turbidity measurement gives a general picture of the state of water pollution. Its determination is essential in the evaluation of drinking water and water for domestic and industrial purposes. Throughout the study period, the electrolytically activated Z2 filter bed allowed for the most effective removal of water turbidity, with the parameter decreasing from 59 to 7 NTU, as can be seen in Fig. 5 in the 4th filtration cycle. In the Z1 filter bed only chemically activated, the efficiency gradually increased with each cycle and each successive series of tests. However, the electrolytically activated S1 bed has filtered the water most efficiently. In the last cycle, a decrease in turbidity to 1 NTU was observed. A similar result was also achieved the 1st day of the 1st test cycle, when the bed was still fresh, first activated chemically and electrolytically. Effectively flushed out of the residues. Turbidity was also well removed by the electrolytically activated Z1 material. Its lowest values were achieved in the 4th test cycle in all test series. It is worth noting that values not exceeding drinking water standards, that is, below 1 NTU, were recorded in the 1st and 4th series. Activation with  $\text{KMnO}_4$  solution proved to be effective in removing turbidity by Z2. The index decreased successively every day, and result closer to standard level was found in the 4th cycle. Unfortunately, the degree of purification did not allow to reach the target range of 1 NTU, as can be seen in Fig. 5. The worst results in purification were presented by the S2 and S2-E bed. A slight decrease was recorded here and also an increase in the last days of the 4th cycle.

Groundwater is chemically variable due to the different depths in the ground. The most common water

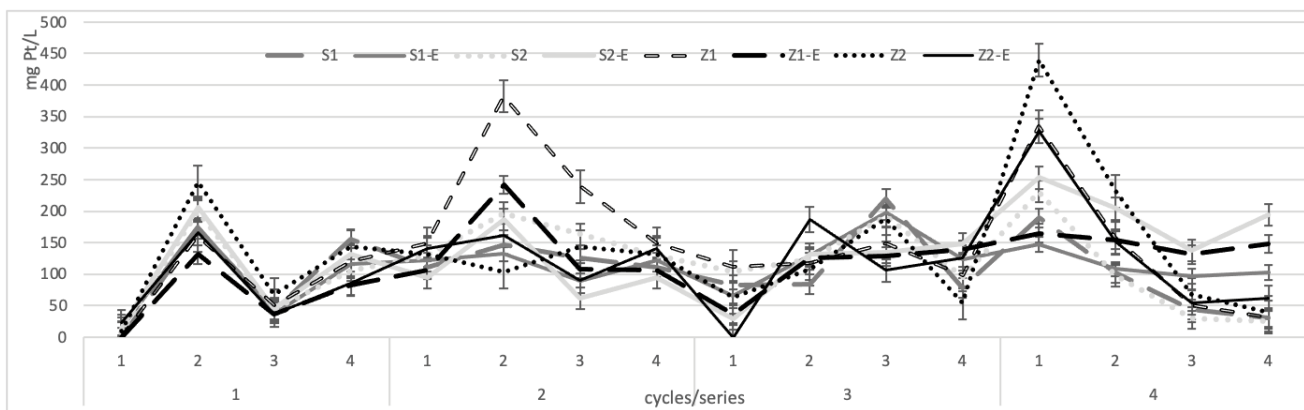


Fig. 4. The results of the colour removal from the water using tested filtration materials.

contaminants exceeding accepted standards are iron and manganese. These elements are a problem in water treatment management. According to Directive (EU) 2020/2184 of the European Parliament and of the Council of 16 December 2020 on the quality of water intended for human consumption, the concentration of iron should not exceed 0.3 mg/L. National standards in some countries, for example, Poland, lower this level to 0.2 mg/L (Journal of Laws 2017, item 2294). Over the whole course of our research with all filtration materials, there was a trend of lowering its concentration in all test cycles and series, as shown in Fig. 6. One of the best filtration material turned out to be Z1-E, which was electrolytically modified. It allowed a reduction in total iron concentration below 0.3 mg/L over the entire test period. Furthermore, only in the first test cycle its concentrations exceeded 0.2 mg/L. All cycles and series succeeded with values within 0.1 mg/L. Electrolytically activated Z2-E was also effective in removing iron from water. The highest Fe concentration in the filtrated water was noted in the first cycle in #2 series, reaching 0.449 mg-Fe/L. As with the previous medium, the best results were achieved in the 4th test cycle in all series. Z2 and Z1, which were not electrolysed, no longer allowed the iron concentrations meet the standards. In the last cycles and series, an increase in iron concentrations in the filtered

water was even noticed compared to the first two test series. The sand and gravel filters did not respond very effectively to both chemical and electrolytic activation. The standard values were exceeded in most of the test cycles. The first series in almost every cycle showed results close to the iron concentration in the raw water. Repeated activation in subsequent series or cycles had no effect. It should be mentioned that the individual test cycles were separated by filters backwashing. Thus, after completing the first series, the beds were washed and another series of modification and subsequent filtration was initiated. The first series of activation in all cycles proved to be insufficient for the tested beds to effectively remove iron from the water. It was only by extending the activation time and electrolytic support that the required degree of water purification was achieved.

When groundwater is used for industrial and municipal purposes, it is necessary, in addition to iron, to remove manganese from the water to the standard value of 0.05 mg/L indicated in Directive 2020/2184 [1] and most national standards [2]. The concentration of manganese in water depends on its solubility and chemical composition. The highest concentrations of this element can be observed in highly acidified waters (e.g., swamp waters), in zones of sulphide deposition or in thermal springs. The nuisance of elevated manganese compounds is demonstrated by an unpleasant

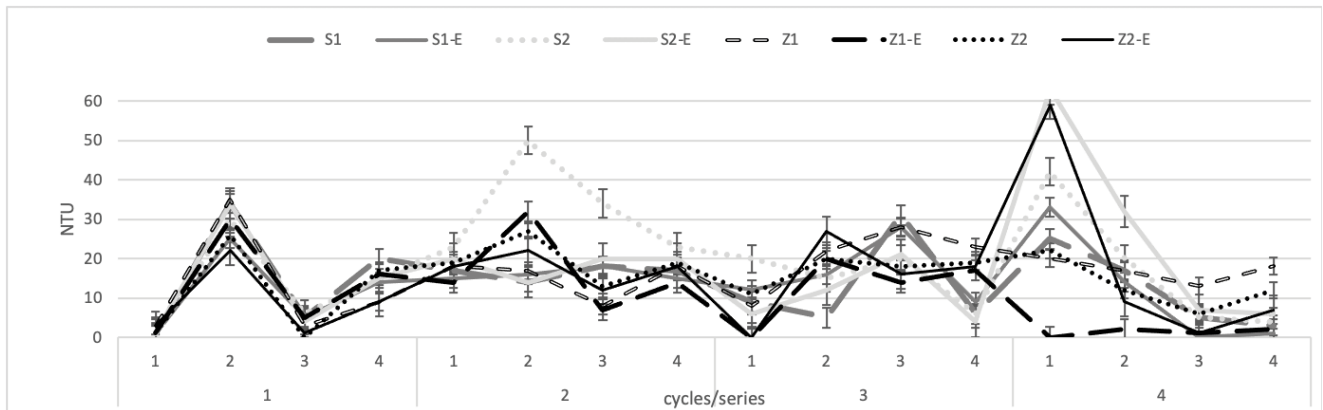


Fig. 5. The results of the turbidity removal from the water using tested filtration materials.

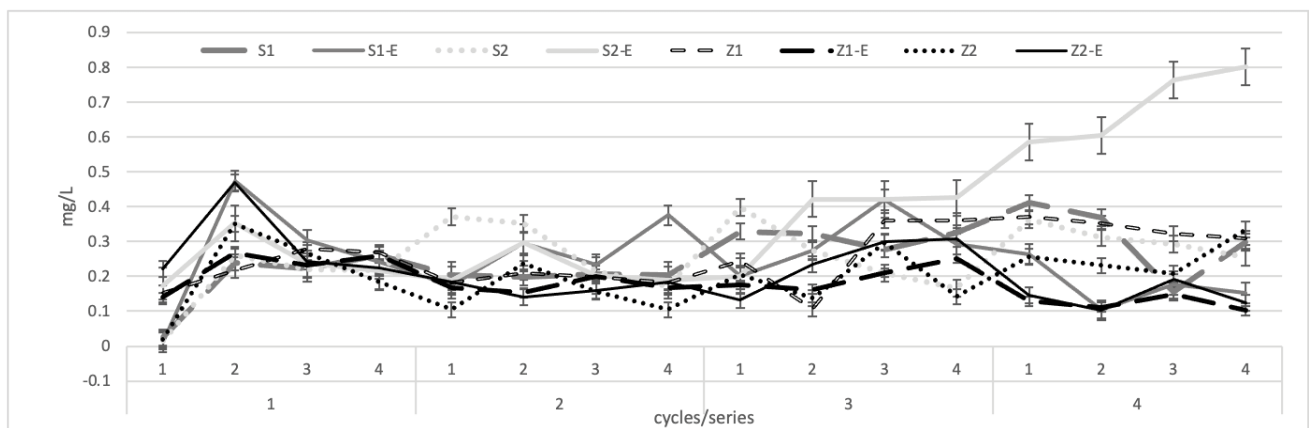


Fig. 6. The results of the removal of total Fe from the water using tested filtration materials.

taste and odour and the formation of dark precipitates in the water supply equipment and installations. It should be bolded that it also interferes with the operation of different devices and installation equipment, that is, filters and water meters. As stated in the first part of the manuscript [24–28], manganese is difficult to remove from water by traditional filtration methods at neutral pH. However, manganese dioxide is used as a catalyst for the Mn removal process [26,28,32,41,43]. Oxidation beds (high manganese ores), do not require additional activation, so the effects of water purification from Fe and Mn compounds can be obtained from the beginning of the filter operation [4,32,35,41]. Kaleta et al. [30] noted that iron and manganese compounds retained in an oxidation bed, using the phenomena of adsorption and catalytic oxidation, are much more strongly bound to the grain surface of this bed than Fe(III) hydroxides fed in the form of flocs [28,41]. It is important that the removal of manganese is not inhibited by iron, which will penetrate the catalytic bed. For this reason, in this study, a lower than average concentration of iron, that is, 0.5 mg/L, and an elevated concentration of manganese, that is, 0.5 mg/L, was introduced into the prepared raw water. The modification of the beds, which was the aim of this study, led to the formation of a  $\text{MnO}_2$  cover on the grains of tested filter materials. Such process may improve water purification in real water supply systems too. Catalytic activated beds are specifically intended for the elimination of manganese compounds from water and excessive amounts of iron as well that remain after first-stage filtration, as noted by Tang et al. [24]. In our own research, the first series of the first cycle was notable for significantly elevated concentrations of manganese in the water flowing out from the filters compared to the raw water. The obtained results are shown in Fig. 7. All beds were still raw and fresh, the  $\text{MnO}_2$  was not formed properly, while the short activation time did not allow for its deposition. The increased amounts of Mn in the filtrated water represented of both dissolved Mn(II) and precipitated Mn(IV) recognized as turbidity. In subsequent series and subsequent cycles, tested materials gradually became more effective. Trends in manganese concentration in the filtered water were similar to iron concentration. Sand and gravel showed the lowest efficiency. In the first test cycle and the first and second series, the S1 and

S2 beds filtered water that contained manganese concentrations higher than standards. This relationship was found for these beds in each subsequent test cycle and the first two series, where manganese concentrations ranged from 0.04–0.1 mg/L. Series #1 represented a 1-week activation, while series #2 represented a 2-week activation. In the case of sand bodies, which are not highly porous, secondary flushing of retained manganese in the water may have occurred. The prolongation of the activation time and its repeatability in successive batches allowed to achieve concentrations within 0.006–0.01 mg/L, which meets standard.  $\text{KMnO}_4$  activation of aluminosilicates (Z1 and Z2) gave better results than sand. After the first two cycles in series #1 and #2, total manganese was determined in the water within 0.1 mg/L. In the subsequent series of first cycles, the concentration decreased to 0.002–0.005 mg/L. Further cycles repeated after filters backwashing and the last series in these cycles resulted in a lowering of manganese to 0.0 mg/L. The electrolytic modification support was the most noticeable when observing changes in the concentration of manganese in the filtered water. Each successive filtration cycle after filter bed washing provided better results. Special attention should be paid to the last series (#3 and #4) of the individual test cycles. In series #3, the manganese concentration for each tested bed decreased from 0.04 to 0.002 mg/L, with Z1-E and Z2-E reaching 0.0 mg/L in the last cycles. In series #4, on the other hand, where the activation time was 4 weeks, Mn concentration in the filtered water was reduced to 0.0 mg/L from the beginning of the experimental run.

Elevated content of organic pollutants is difficult to reduce in traditional filtration processes. What is more, it is often advisable to protect WTS devices. The experiments carried out in this study demonstrate that filter beds capable of removing iron and manganese from water are not sensitive to elevated levels of organic pollutants described as COD-Mn. This indicator is commonly performed for the determination of organic pollutants in water. In our study, the changes in its values are shown in Fig. 8. COD-Mn reached values of up to 8 mg/L for each of the samples. This appeared to be the case at the start of each new test cycle after filter washing. The backwash and short activation times failed to effectively retain organic contaminants in the bed. As mentioned before, there was 10 mg/L of COD-Mn in the raw water. Thus,

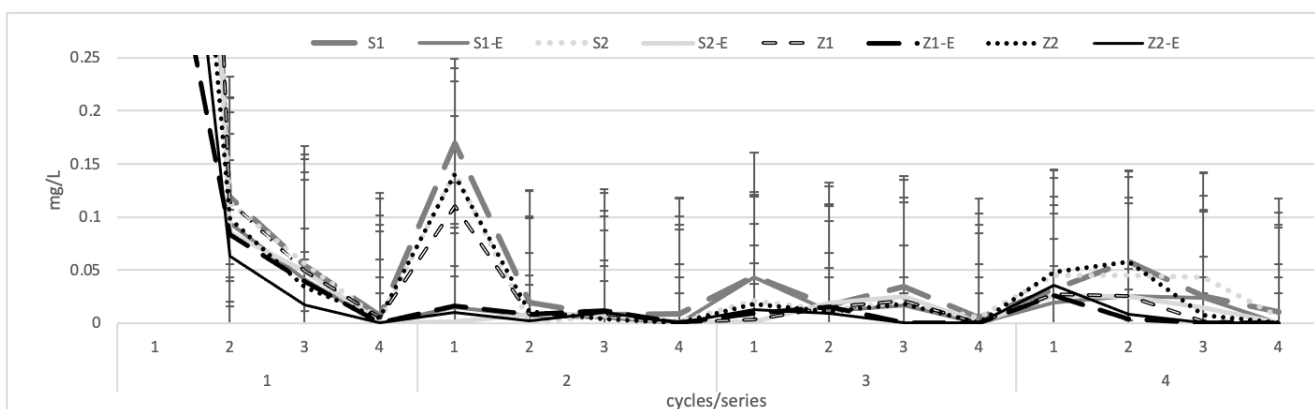


Fig. 7. The results of the removal of total Mn from the water using tested filtration materials.



each time there was a reduction of 10%–30%. This irregularity appeared on the 1st day of all cycles. Then gradually decreasing COD-Mn values were read in the other series and cycles. Only in bed S2 were higher values found, ranging from 5–7.7 mg/L. A linear decrease over the activation time can be read in the beds where activation was assisted electrolytically: S1-E, S2-E, Z1-E and Z2-E. Among all electrolytically-activated materials, the best organic reduction effects were observed for the aluminosilicates. During the last weeks of activation in test cycles #3 and #4, COD-Mn was lowered to 1 mg/L in the filtered water. The non-electrolysed beds showed a lower organic pollution level of less than 5 mg/L.

Elevated iron and manganese concentrations are sometimes accompanied by significant amounts of ammonium nitrogen [38]. It complicates standard water treatment processes. For this reason, the N-NH<sub>4</sub> content in the filtered water was assessed in our study. According to Directive 2020/2184 [1], the N-NH<sub>4</sub> concentration should not exceed 0.38 mg/L (with an ammonium ion concentration of 0.5 mg/L). In the conducted studies, the changes in the concentration of ammonia nitrogen (Fig. 9) were observed. The first series of tests in the first cycle was similar to other analysed pollutants. With the raw water, 2 mg/L of ammonia nitrogen was introduced into the filter columns. Its

concentration at the beginning of the study for all tested materials decreased slightly and oscillated around 1.9 mg/L. The lowest values were recorded for Z1-E and Z2-E, which did not exceed 0.1 mg/L. Ammonia nitrogen was removed from the water equally effectively by Z1 and Z2 media. For all aluminosilicate-based materials, a linear relationship was found in the process of N-NH<sub>4</sub> decrease with activation time. A gradual lowering of the index is also seen in S1 filter. In cycle #3, the indicator decreases to about 0.03 mg/L and stays constant until the last day of the experiments.

Over the course of the research it should also be noted that all tested beds showed the best results after prolonged activation time, that is, 3 and 4 weeks. It is confirmed by the investigations carried out in each of the subsequent test series. Inglezakis et al. [37] and Kaleta et al. [30] write that MnO<sub>2</sub> is a strong oxidant component found in the outer layers of the filter material grains. This is confirmed by Zeng et al. [29] and Lima et al. [55], who indicate that it has a sorption capacity and also acts as an oxidant of Mn(II) ions to Mn(IV). Activated bed with MnO<sub>2</sub> allows the water to be free of manganese without preliminary alkalisation [8,38,41]. It is very common for groundwater treatment technology to use filter materials slowly covered with MnO<sub>2</sub> during filtration process. Literature [22,33,38,50] states, this base on

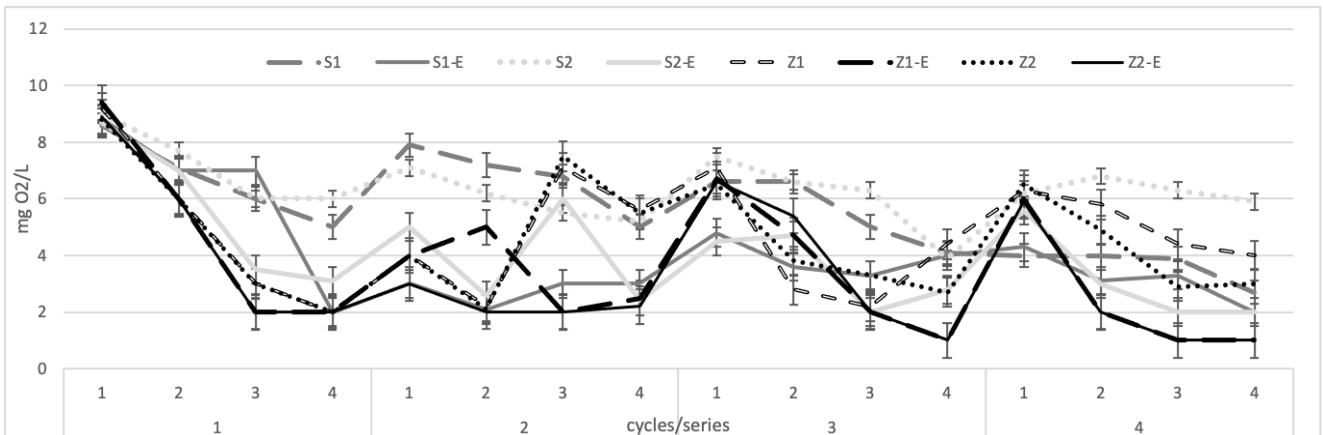


Fig. 8. The results of the removal of organic compounds as COD-Mn from the water using tested filtration materials.

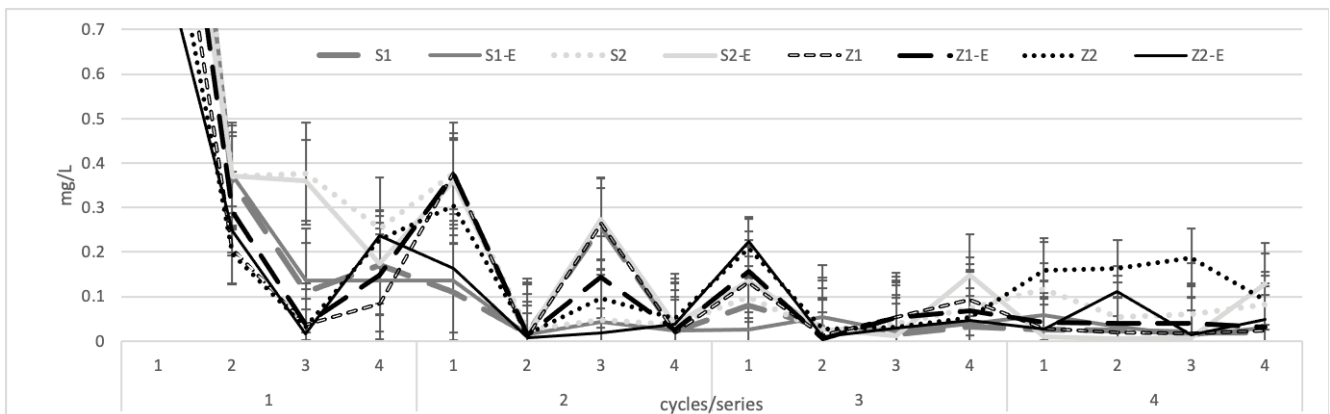


Fig. 9. The results of the removal of N-NH<sub>4</sub><sup>-</sup> from the water using tested filtration materials.

gradual filtration of aerated water containing elevated concentrations of Fe(II) and Mn(II), where their oxides gradually coat the bed grains. These coatings are permanent and create a surface oxidation layer.

Reached own results on Fe and Mn removal show higher efficiency for modified masses. There may be concluded then electrolysis improve the properties of filtration materials and they are able to purify water even better reaching effectivity over 90% for the process of iron and manganese reduction. Raw natural sand tested by many authors [22,28,35,27,38,39] as filtration bed focused on Fe and Mn removal appears as low effective with results max. 61% and 35% Fe and Mn removal, respectively. Scientists [22,28,35,27,38,39] bold that fine sand and gravel are the best materials at filtration water polluted by suspension, turbidity and different types of sediments. Natural aluminosilicate was successful in ammonia form separation from the water and quite high effect of COD decrease. This material is not useful for Fe and Mn removal. As cited in the literature [28,30,36] it is used mostly for nitrogen forms removal. Modification of natural materials brings better response. Modified sand (called manganese sand) reaches some oxidation features and stops iron precipitated form with max. 75% and manganese with 62%. Efficiency of COD and N forms removal is also increased. On the other hand modified aluminosilicate becomes common filtration bed used in groundwater treatment and successful in Fe and Mn removal. It has high effect of COD

and ammonia removal too. Own experiments have shown that longer modification time better filtration materials features for water treatment from impurities presented in Table 3. Additional modification support using electrolysis might be recommended if we want to achieve better filtration efficiency in the shorter time.

There are many ways of natural materials modification. In the present study, experiments were performed on the activation of filter materials with  $\text{KMnO}_4$  solution with electrolytic support and the reduction of Mn(VII) to Mn(IV) using natural reductants such as coffee infusion and lemon juice. On the other hand, Azari et al. [34] investigated modification of carbon nanotubes for the reduction method of the conversion of divalent iron to zero-valent iron and a co-precipitation of iron particles on investigated carbon nanotubes. The process was assisted by a magnetic field. The modified carbon nanotubes were found to have a high potential for rapid and efficient removal of nitrogen forms from water and then easy separation from solution using a magnetic field. Another research team [52] tested the adsorption of specific contaminants on ultrasound-assisted iron oxide and graphene oxide nanocomposites. Our own experiments have based on other physical process of electrolysis and reduction of  $\text{KMnO}_4$  to  $\text{MnO}_2$  by natural reductants – coffee infusion and lemon juice. Similar reductants were previously conducted by Dinn et al. [53] and Chong et al. [54]. The advantage of these reductants is that the reactions can be carried out at room temperature in any equipment and

Table 3  
Own results comparison to other investigated materials

	Material	Fe removal effect (%)	Mn removal effect (%)	COD removal effect (%)	$\text{NH}_4$ removal effect (%)	source
1	Sand	15–61	7–35	5–40	5–27	Cai et al. [35] Bruins et al. [22] Inglezakis et al. [37] Adelman et al. [38] Munter et al. [28] Skoczko [39]
2	Modified sand	15–75	8–62	8–55	5–35	Tang et al. [24] Inglezakis et al. [37]
3	S1	61–88	87–99	25–77	77–91	Own exp.
4	S2	59–85	86–99	15–71	79–90	Own exp.
5	S1-E	76–98	87–100	32–80	80–94	Own exp.
6	S2-E	66–97	91–100	30–80	81–92	Own exp.
7	Aluminosilicate	12–86	9–45	9–58	15–65	Munter et al. [28] Lima et al. [36] Kaleta et al. [30]
8	Modified aluminosilicate	15–85	9–65	12–77	21–80	Munter et al. [28] Truong et al. [44] Aghoyeh and Khalafi [45]
9	Z1	62–93	89–98	31–82	82–95	Own exp.
10	Z2	70–91	91–100	28–90	81–93	Own exp.
11	Z1-E	83–93	86–100	40–90	85–98	Own exp.
12	Z2-E	80–99	94–100	38–90	88–97	Own exp.

Source: Own elaboration based on own results and the literature cited in the table.

devices. They are not harmful to human health nor to the environment and are easy to flush out excessive amounts. Duffy et al. [57] mention they are low-cost reactants, so they can be used on a large scale. Activation within our own research has produced new  $\text{MnO}_2$ -layered deposits from natural sand, gravel and aluminosilicates. Electrolysis carried out in parallel on separate samples of the materials helped to fix the oxide layer on the surface of the grains and to accelerate its precipitation reaction. The electrolytic method to produce  $\text{MnO}_2$  was previously tested by many researchers mainly in the field of metallurgy [27,58–60]. This included the oxidation of Mn(II) to Mn(IV). According to Wang [60], the preparation of a purified  $\text{MnSO}_4$  solution is the first element needed to electrolytic  $\text{MnO}_2$  layer creation. The produced fine-grained precipitate had a very high specific surface area, which can be used in processes such as purification of various solutions mainly from heavy metals. The sludge was mostly precipitated on the cathode, as confirmed by Mahmudi et al. [60]. No additional filling with porous material was used in the reactor as in our study. This feature has made the our studies described in the article different from others. The manganese oxide production process was successful, especially after the 3rd and 4th test cycles. The full period of research carried out therefore included four activation phases per cycle and four test cycles, translating into a total of sixteen activation phases. The entire process allowed  $\text{MnO}_2$  coatings to be produced on a neutral natural material with sand and aluminosilicate. It was observed that the efficiency depended on several factors: the content of Mn(IV) ions, which were introduced in significant excess, the presence of reducing substances and, above all, the structure and skeleton of the natural material.

It was noted through experimentation on the water filtration through newly generated catalytic beds that the chemical composition of the coatings depends on the chemical composition of the water, and that certain ions in the water reduce the effectiveness of the beds. This is the case with hydrated iron oxides or  $\text{CaCO}_3$  particles. By their presence, they limit the coating's contact with  $\text{MnO}_2$ , depositing limescale and residues that limit grain contact with the water. In the criteria for assessing the suitability of filter materials,

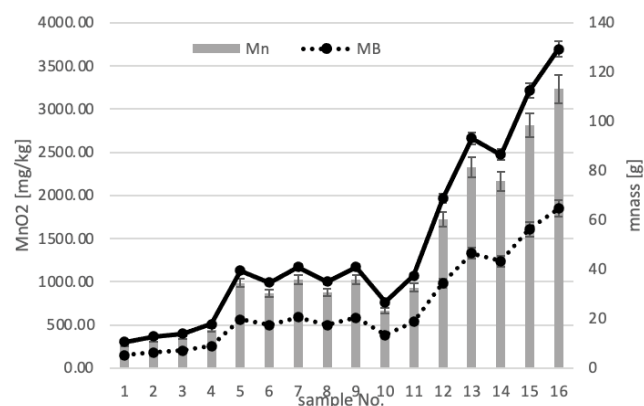


Fig. 10. The amount of created  $\text{MnO}_2$  on tested materials grains. Source: own investigation.

the time of materials auto-activation is important, as highlighted by Li et al.. The process occurs under the influence of manganese ions in the form of  $\text{KMnO}_4$ . As part of the research the mass of precipitated  $\text{MnO}_2$  on individual filter beds was additionally, as shown in Fig. 10. The initial test series was not associated with significant precipitation of the  $\text{MnO}_2$  coating. Among the four tested materials, the least amount of manganese coating was deposited on the coarse gravel and filter sand (S1, S2). In the first test cycle it was below 300 mg  $\text{MnO}_2$ /kg, while in the second test cycle it was 868 mg/kg and 968 mg/kg, respectively. A marked increase in the deposited catalytic layer was observed in the 3rd and 4th test cycles. In the case of aluminosilicates, a high grain coating effect was achieved for Z1 and Z2 as well. It was noticeable especially in the #3 and #4 test cycle. For fine aluminosilicate Z1 the coating mass reached 2800 mg/kg and for coarse aluminosilicate Z2 – 3,233 mg/kg.

Backwashing is one of the most important operations during the service of the filter materials. As a result, it ensures optimal filtrate quality.

The washing time of the filter beds indicated in Table 4 was not constant and varied for each material. Porous beds not electrolytically modified were the longest rinsed from the  $\text{KMnO}_4$  solution. It is worth noting that the electrolysis process significantly reduced the final washing time for the sand (S1) from 95–8 min after 4 weeks of electrolytic activation support. A similarly short final washing time was for the fine aluminosilicate (Z1), which showed a clear filtrate after 9 min. The Z2 bed was the most difficult to rinse. The initial rinsing time reached almost 3 h, but was reduced to 80 min after 4 weeks of chemical activation and its electrolytic assistance.

In practice, filtration material washing with potassium permanganate solution is carried out every 3–6 months and it is called bed regeneration. It is often not well made due to the difficulty of removing the excess of the  $\text{KMnO}_4$  which has characteristic purple colour. The stability of new coating is also rarely tested. Wrong conservation leads to worse removal effects and oxidation properties lost by the filtration bed. On the other, proper activation and regeneration of the bed with  $\text{KMnO}_4$  allows to obtain good results in the removal of manganese and iron forms from waters [55–61].

Table 4

Washing time of the tested filter materials until the reactant is fully washed out

Cycles/ series	Washing time of filter materials (min)							
	1		2		3		4	
	N	E	N	E	N	E	N	E
S1	95	50	92	40	45	35	35	8
S2	105	70	94	65	60	30	55	29
Z1	52	35	43	25	20	15	10	9
Z2	165	150	160	140	150	127	135	80

N – natural conditions; E – electrolysis;  
Source: own investigation.

#### 4. Summary

Groundwater is usually high in soluble forms of Fe(II) and Mn(II) ions. The process of removing them from the water involves oxidising to insoluble forms and separation by filtration. The most effective is filtration through a specific bed of catalytic and/or oxidation nature, where  $\text{MnO}_2$  is one of the components. The active  $\text{MnO}_2$  layer on neutral filter material grains allows both adsorption and oxidation of dissolved manganese, iron, and sometimes ammonium ions, organic pollutants, as well as colour and turbidity in the water. This oxide may cover grains of the filter material during traditional filtration. It can also be produced by oxidation of Mn(II) to Mn(IV) or reduction of Mn(VII) to Mn(IV) by industrial chemical processes. Artificially coated grains are not as durable and effective compared to natural processes. On the other hand natural modification takes time up to 4–6 weeks what is a major disadvantage.

For this reason, research was carried out on the chemical activation of selected natural minerals (sand, gravel and aluminosilicates of different granulations) with coatings that accelerate the removal of iron and manganese from groundwater. In order to shorten the activation time, the coating process was supported by an electrolysis. Chemical activation based on  $\text{KMnO}_4$  reduction to  $\text{MnO}_2$  using natural reducing agents – lightly roasted coffee and lemon juice. The studies were conducted in 4 series from 1 to 4 weeks and in 4 test cycles separated by filter backwashing. The half of the samples were modified only chemically and the half – chemically and physically with electrolysis (12 V and 120 A).

#### 5. Results of our experiments let to draw conclusions

The minerals that best adsorbed the generated  $\text{MnO}_2$  were aluminosilicates of both finer and larger grain sizes.

- Over the entire test period, the electrolytically activated Z2-E and Z1-E allowed the most effective reduction in turbidity of the water. The lowest values were achieved in the last test cycle, below drinking water standards, that is, below 1 NTU, recorded in the 1st and 4th series.
- The trend in iron removal from water was similar. The best filtration material turned out to be electrolytically activated Z1-E. The concentration of total iron was reduced below the Drinking Water Directive 202/2184 standards. Only in #1 test cycle Fe concentration exceeded 0.2 mg/L, all subsequent cycles and series showed values app. 0.1 mg/L. Electrolytically activated Z2-E was also effective. In contrast, chemically modified filters did not allow meet standard.
- Tested aluminosilicates (Z1, Z2, Z1-E, Z2-E) showed the best efficiency in purifying the water from considered contaminants defined in the Drinking Water Directive 202/2184 L and were able to decrease the manganese content in the water to the permissible value intended for human consumption, that is, below 0.05 mg/. Sand and gravel-based beds showed the lowest efficiency in Mn removing. Special attention should be paid to the last series (#3 and #4). In series #3, the manganese concentration for each tested bed decreased from 0.04 to

0.002 mg/L, with 0.0 mg/L achieved for Z1-E and Z2-E in the last cycles.

- The electrolytically modified aluminosilicates effectively reduced organic contaminants (COD-Mn) in the water. During the last weeks of activation in test cycles #3 and #4, COD-Mn was reduced in the filtered water from 10 to 1 mg/L.
- In natural groundwater, elevated concentrations of iron and manganese are usually accompanied by significant amounts of ammonium ion. Therefore, its content in the filtered water was assessed in the described studies. The lowest values were recorded for Z1-E and Z2-E, which did not exceed 0.1 mg/L. The Z1 and Z2 beds, which were not electrolytically modified, were equally effective in removing ammonium nitrogen from the water reaching concentrations between 0.2–0.3 mg/L. For all aluminosilicate-based media, a linear process dependence of the decrease in ammonium nitrogen concentration with activation time was found.
- Overall, it should also be noted that all beds showed the best results after a longer activation time, that is, 3 and 4 weeks. The first series of activation in all cycles proved to be insufficient for the tested media to effectively remove most contaminants from the water. Only prolonged activation time and electrolytic support allowed to achieve the required levels of water purification.
- $\text{MnO}_2$  coating on tested natural non-manganese minerals was under investigation in the presented study too. The chemical formation and maintenance of the  $\text{MnO}_2$  coating was supported with an electrolysis. As a result, the amount of precipitated manganese oxide on the natural minerals grains was measured after a time from 1 to 4 weeks. The starting test series was not associated with a significant precipitation of the  $\text{MnO}_2$  coating on grains. A clear increase in the deposited catalytic film started in the #3 and was the highest in the #4 test series. High  $\text{MnO}_2$  coating effect was achieved particularly for both aluminosilicates: for Z1-E it reached 2,800 mg/kg and for Z2-E – 3,233 mg/kg.
- From an exploitation point of view, filters washing is one of the most important procedures during the maintenance of a Water Treatment Station. It also ensures optimal filtrate quality. Therefore backwash times for filters filled with modified materials were also observed in the study. The longest rinsing time was spent on  $\text{KMnO}_4$  activation solution from porous media. It is worth noting that the electrolysis significantly reduced the backwash time especially for the sand bed (S1) from 95 min to 8 after 4 weeks of electrolytic activation. A similarly short final washing time was measured for the fine aluminosilicate (Z1), which produced a clear filtrate after 9 min.

#### References

- [1] Revised EU Drinking Water Directive (EU) 2020/2184 from Dec 16th 2020 r.
- [2] Regulation of the Ministry of Health from Dec 7th 2017 r. on Drinking Water (Dz.U. 2017 poz. 2294).
- [3] B.R. Hacker, S.M. Peacock, G.A. Abers, S.D. Holloway, Subduction factory 2. Are intermediate-depth earthquakes in subducting slabs linked to metamorphic dehydration reactions?, *J. Geophys. Res.*, 108 (2003), doi: 10.1029/2001JB001129.

- [4] M. Dudziak, D. Kopańska, Occurrence of heavy metals in selected made grounds, *Ecol. Chem. Eng. A*, 22 (2015) 137–149.
- [5] T. Walczykiewicz, Water Resources and Their Use, M. Cygler, R. Miłaszewski, Eds., Materials to Economics Study and Water Resources, Economy & Environment, Białystok, 2008, pp. 11–21.
- [6] M. Włodarczyk-Makuła, A. Nowacka, B. Macherzyński, Comparison of effectiveness of coagulation with aluminum sulfate and pre-hydrolyzed aluminum coagulants, *Desal. Water Treat.*, 52 (2014) 3843–3851.
- [7] S. Myszograj, Z. Sadecka, Realization of national programme of municipal wastewater treatment and the quality of surface water in Poland. *Medycyna Środowiskowa*, 15 (2012) 97–105.
- [8] I. Skoczko, J. Piekutin, K. Ignatowicz, Efficiency of manganese removal from water in selected filter beds, *Desal. Water Treat.*, 57 (2016) 1611–1619.
- [9] E. Wiśniewska, M. Włodarczyk-Makuła, Removal of nitrates and organic compounds from aqueous solutions by zero valent (ZVI) iron reduction coupled with coagulation/precipitation process, *Arch. Environ. Prot.*, 46 (2020) 22–29.
- [10] UN-Water Strategy 2014–2020 from May 8th 2014.
- [11] UN-Water 2030 Strategy from July 1st 2020.
- [12] T. Cichoń, J. Królikowska, Protection of water resources for sustainable development, *Desal. Water Treat.*, 128 (2018) 442–449.
- [13] K. Szymański, B. Janowska, A. Iżewska, R. Sidelko, I. Siebielska, Method of evaluating the impact of landfill leachate on groundwater quality, *Environ. Monit. Assess.*, 190 (2018) 415, doi: 10.1007/s10661-018-6776-2.
- [14] I. Skoczko, J. Piekutin, A. Roszczenko, Iron and manganese removal from groundwater by filtration on selected masses, *Annu. Set. Environ. Prot.*, 17 (2015) 1587–1608.
- [15] M. Król, M. Dudziak, Occurrence and determination of selected micropollutants in water environment regulated by directive 2000/60/WE, *Ecol. Eng. Environ. Technol.*, 19 (2018) 38–47.
- [16] P.E. van Keken, B. Kiefer, S.M. Peacock, High-resolution models of subduction zones: implications for mineral dehydration reactions and the transport of water into the deep mantle, *Geochem. Geophys. Geosyst.*, 3 (2002) 1 of 20–20 of 20, doi: 10.1029/2001GC000256.
- [17] B. Das, P. Hazarika, H. Kalita, D.C. Goswami, H.B. Das, S.N. Dube, R.K. Dutta, Removal of iron from groundwater by ash: a systematic study of traditional methods, *J. Hazard. Mater.*, 141 (2006) 834–841.
- [18] R.M. Canup, K. Righter, Origin of the Earth and Moon, University of Arizona Press, Tucson, AZ, 2000.
- [19] M.J. Adelman, M.L. Weber-Shirk, A.N. Cordero, S.L. Coffey, W.J. Maher, D. Guelig, J.C. Will, S.C. Stodter, M.W. Hurst, L.W. Lion, Stacked filters: novel approach to rapid sand filtration, *J. Environ. Eng.*, 138 (2012) 1–17.
- [20] G.S. Longsdon, Water Filtration Practices: Including Slow Sand Filters and Precoat Filtration, American Water Works Association, 2008.
- [21] S. Environmental Protection Agency Office of Water: Drinking Water Health Advisory for Manganese, 2004.
- [22] J.H. Bruins, B. Petrusevski, Y.M. Slokar, K. Huysman, K. Joris, J.C. Kruijthof, M.D. Kennedy, Factors controlling the ripening of manganese removal filters in conventional aeration-filtration groundwater treatment, *Desal. Water Treat.*, 72 (2017) 22–29.
- [23] E. Kudlek, Decomposition of contaminants of emerging concern in advanced oxidation processes, *Water*, 10 (2018) 955, doi: 10.3390/w10070955.
- [24] W. Tang, L. Wu, J. Gong, G. Ye, X. Zeng, Screening, identification, and removal dynamics of a novel iron-manganese removal strain, *Bio-Med. Mater. Eng.*, 24 (2014) 2049–2056.
- [25] A.M. Anielak, M. Arendacz, Efficiency of iron and manganese removal from the water, *Annu. Set Environ. Prot.*, 9 (2007) 9–18.
- [26] S.J. Duranceau, V.M. Trupiano, Evaluation of oxidized media filtration for removing sulfides from groundwater, *Desal. Water Treat.*, 28 (2011) 366–377.
- [27] A. Biswal, B.C. Tripathy, K. Sanjay, K. Subbaiah, M. Minakshi, Electrolytic manganese dioxide (EMD): a perspective on worldwide production, reserves and its role in electrochemistry, *RSC Adv.*, 5 (2015) 58255–58283.
- [28] R. Munter, P. Overbeck, J. Sutt, Which is the best oxidant for complexed iron removal from groundwater: The Kogalym case, *Ozone: Sci. Eng.*, 30 (2008) 73–80.
- [29] H. Zeng, Y. Yu, T. Qiao, J. Zhang, D. Li, Simultaneous removal of iron, manganese and ammonia from groundwater: upgrading of waterworks in northeast China, *Desal. Water Treat.*, 175 (2020) 196–204.
- [30] J. Kaleta, A. Puskarewicz, D. Papciak, Removal of iron, manganese and nitrogen compounds from underground waters with diverse physical and chemical characteristics, *Environ. Prot. Eng.*, 33 (2007) 5–13.
- [31] M. Dudziak, E. Kudlek, E. Burdzik-Niemiec, Decomposition of micropollutants and changes in the toxicity of water matrices subjected to various oxidation processes, *Desal. Water Treat.*, 117 (2018) 181–187.
- [32] I. Skoczko, Water Filtration, PAN Ed., Warsaw, 2019.
- [33] A. Karami, K. Karimyan, R. Davoodi, M. Karimaei, K. Sharafie, S. Rahimi, T. Khosravi, M. Miri, H. Sharafi, A. Azari, Ali, Application of response surface methodology for statistical analysis, modelling, and optimization of malachite green removal from aqueous solutions by manganese-modified pumice adsorbent, *Desal. Water Treat.*, 89 (2017) 150–161.
- [34] A. Azari, A. Babaie, R. Rezaei-Kalantary, A. Esrafilii, M. Moazzen, B. Kakavandi, Nitrate removal from aqueous solution by carbon nanotubes magnetized with nano zero-valent iron, *J. Mazandaran Univ. Med. Sci.*, 22 (2013) 15–27.
- [35] X. Cai, F. Shen, Y. Zhang, H. Hu, Z. Huang, Y. Yin, J. Liang, Mineralization of organics in hazardous waste sulfuric acid by heiral manganese oxide ore and a combined MnO<sub>2</sub>/activated carbon treatment to produce qualified manganese sulfate, *J. Hazard. Mater.*, 366 (2019) 466–474.
- [36] L.A. Lima, Y.F. Silva, P.L.T. Lima, Iron removal efficiency in irrigation water by a zeolite added to sand media filters, *Desal. Water Treat.*, 220 (2021) 241–245.
- [37] V.J. Inglezakis, M.K. Doula, V. Aggelatou, A.A. Zorpas, Removal of iron and manganese from underground water by use of natural minerals in batch mode treatment, *Desal. Water Treat.*, 18 (2010) 341–346.
- [38] A.J. Adelman, M.L. Weber, P. Shirk, N.C. Anderson, S. Coffey, Stacked filters: novel approach to rapid sand filtration, *J. Environ. Eng.*, 138 (2012) 1–17.
- [39] I. Skoczko, Efficiency estimation of water purification with various filtration materials, *Desal. Water Treat.*, 134 (2018) 99–108.
- [40] P. Phatai, L. Wittayakun, N. Grisdanurak, W.H. Chen, M.W. Wan, C.C. Kan, Removal of manganese ions from synthetic groundwater by oxidation using KMnO<sub>4</sub> and the characterization of produced MnO<sub>2</sub> particles, *Water Sci. Technol.*, 62 (2010) 1719–1726.
- [41] J. Jeż-Walkowiak, Z. Dymaczewski, L. Weber, Iron and manganese removal from groundwater by filtration through a chalcocite bed, *J. Water Supply Res. Technol. AQUA*, 64 (2015) 19–34.
- [42] Y. Veressinina, M. Trapido, V. Ahelik, R. Munter, Catalytic Filtration for the Improvement of Drinking Water Quality, Proceedings of the Estonian Academy of Sciences, Chemistry, 2000, pp. 168–179.
- [43] D. Barlokova, J. Ilavski, Removal of iron and manganese from water using filtration by natural materials, *Pol. J. Environ. Stud.*, 19 (2010) 1117–1122.
- [44] D.Q. Truong, P. Loganathan, L.M. Tran, Removing ammonium from contaminated water using Purolite C100E: batch, column, and household filter studies, *Environ. Sci. Pollut. Res.*, 29 (2022) 16959–16972.
- [45] R.G. Aghoyeh, H. Khalafi, Design of dual column water purification system for industrial gamma irradiator based of PUROLITE® resins, *Ann. Nucl. Energy*, 69 (2014) 90–96.
- [46] S.H. Christopherson, J.L. Anderson, D.M. Gustafson, Evaluation of recirculating sand filter in a cold climate, *Water Sci. Technol.*, 51 (2005) 267–272.
- [47] N. Petkov, M. Holzl, T.H. Metzger, S. Mintova, T. Bein, Ordered micro/mesoporous composite prepared as thin films, *J. Phys. Chem. B*, 109 (2005) 4485–4491.

- [48] E. Szatyłowicz, I. Skoczko, Studies on the efficiency of groundwater treatment process with adsorption on activated alumina, *J. Ecol. Eng.*, 18 (2017) 211–218.
- [49] Y.S. Tao, H. Kanoh, K. Kaneko, ZSM-5 monolith of uniform mesoporous channels, *J. Am. Chem. Soc.*, 125 (2003) 6044–6045.
- [50] M.M. Michel, I. Reczek, D. Papciak, M. Włodarczyk-Makula, T. Siwiec, Y. Trach, Mineral materials coated with and consisting of  $\text{MnO}_x$ —characteristics and application of filter media for groundwater treatment: a review, *Materials*, 13 (2020) 2232, doi: 10.3390/ma13102232.
- [51] A.M. García-Mendieta, M. Solache-Ríos, M.T. Olguín, 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.
- [52] A. Azari, M.H. Mahmoudian, M. Hazrati Niari, I. Es, E. Dehghanifard, A. Kiani, A. Javid, H. Azari, Y. Fakhri, A.M. Khaneghah, Rapid and efficient ultrasonic assisted adsorption of diethyl phthalate onto  $\text{Fe}^{\text{II}}\text{Fe}_2^{\text{III}}\text{O}_4$ @GO: ANN-GA and RSM-DF modeling, isotherm, kinetic and mechanism study, *Microchem. J.*, 150 (2019) 104144, doi: 10.1016/j.microc.2019.104144.
- [53] J. Dinn, J.L. Liu, S. Bashir, Use of natural products as green reducing agents to fabricate highly effective nanodisinfectants, *J. Agric. Food Chem.*, 61 (2013) 2019–2027.
- [54] S. Chong, C.W. Lai, S.B.A. Hamid, Green preparation of reduced graphene oxide using a natural reducing agent, *Ceram. Int.*, 41 (2015) 9505–9513.
- [55] Y. Wang, S. Indrawirawan, X. Duan, H. Sun, H.M. Ang, M.O. Tadé, S. Wang, New insights into heterogeneous generation and evolution processes of sulfate radicals for phenol degradation over one-dimensional  $\alpha\text{-MnO}_2$  nanostructures, *Chem. Eng. J.*, 266 (2015) 12–20.
- [56] D.J. Tarimo, K.O. Oyedotun, A.A. Mirghni, N.F. Sylla, N. Manyala, High energy and excellent stability asymmetric supercapacitor derived from sulphur-reduced graphene oxide/manganese dioxide composite and activated carbon from peanut shell, *Electrochim. Acta*, 353 (2020) 136498, doi: 10.1016/j.electacta.2020.136498.
- [57] P. Duffy, L.A. Reynolds, S.E. Sanders, K.M. Metz, P. Colavita, Natural reducing agents for electroless nanoparticle deposition: mild synthesis of metal/carbon nanostructured microspheres, *Mater. Chem. Phys.*, 140 (2013) 343–349.
- [58] C.X. Li, H. Zhong, S. Wang, Preparation of  $\text{MnO}_2$  and calcium silicate hydrate from electrolytic manganese residue and evaluation of adsorption properties, *J. Cent. South Univ.*, 22 (2015) 2493–2502.
- [59] Patent CN103556172A Method for Deeply Removing Impurities of Manganese Dioxide Electrolyte, 2013.
- [60] J. Wang, B. Peng, L. Chai, Q. Zhang, Q. Liu, Preparation of electrolytic manganese residue-ground granulated blast furnace slag cement, *Powder Technol.*, 241 (2013) 12–18.
- [61] Mahmudi, W. Widiyastuti, P. Nurlilasari, S. Affandi, H. Setiawan, Electrolysis synthesis of  $\text{MnO}_2$  in acidic environment and its electrochemical performance for supercapacitor, *J. Phys.: Conf. Ser.*, 1093 (2018) 012021, doi: 10.1088/1742-6596/1093/1/012021.