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The use of carbonate-silica rock (opoka) to remove iron, manganese and indicator bacteria from groundwater

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Abstract

The study investigated the efficiency of removal of iron, manganese and indicator bacteria from potable groundwater by using carbonate-silica rock (opoka). The tests were performed in a laboratory in three filter columns supplied with water containing increased concentrations of iron and manganese. Two of the columns were filled with carbonate-silica rock with particle sizes of 2–5 mm; retention time for water in the columns was set at 1 h and 2 h. A third column was filled with 1–2 mm rock particles, with hydraulic retention time set at 1 h. High removal efficiencies were determined for iron, manganese and *coliform* bacteria and low removal efficiencies for psychro- and mesophilic bacteria. An increase in the alkalinity of the investigated water was also observed.

Key words: groundwater, iron removal, manganese removal, silica-carbonate rock, water treatment

INTRODUCTION

Supply of good quality water to human populations and industry is becoming a more and more serious problem. Intensive development of various sectors of the economy contributes to the progressive degradation of the environment, including depletion of available water resources [KABATA-PENDIAS, PENDIAS 1993; MOSIEJ *et al.* 2007; OKONIEWSKA *et al.* 2007].

Increasing pollution levels are threatening groundwater reservoirs which are used to supply water to the public. The main sources of contamination of those reservoirs are industrial and municipal wastewater, waste, sludge, pesticides, and fertilizers. The composition of water is significantly affected by natural phenomena resulting from geological structure.

The quality of water is primarily determined by the content of organic and inorganic compounds which influence its organoleptic properties and may

have a toxic or even a carcinogenic activity [ELLIS *et al.* 2000; KOWALIK 1987; OKONIEWSKA 2007; ZAW, CHISWELL 1999]. The most widely occurring components of water, in particular groundwater, are iron and manganese [ELLIS *et al.* 2000; KOWAL, ŚWIDERSKA-BRÓZ 2009]. In water, they are found mainly in the form of carbonates, sulfates, chlorides, humus compounds, and sometimes phosphates [GOUZINIS *et al.* 1998; KONTARI 1988]. They usually come from the natural processes of weathering and leaching of sedimentary and igneous rocks [KOWAL, ŚWIDERSKA-BRÓZ 2009]. Overly high concentrations of iron and manganese in water cause economic and technological problems. Upon contact with air, these elements precipitate in the form of a dark precipitate; the water becomes turbid and colored [HERMANOWICZ *et al.* 1999; TEKERLEKOPOULOU, VAYENAS 2008]. Moreover, their presence in the water can promote the growth of ferruginous and manganese bacteria on pipe walls, leading to corrosion and obstruction of pipes [FUNES *et al.* 2014; GOUZINIS *et al.* 1998; KONTARI 1988].

Both iron and manganese, when present at higher than normal concentrations, can cause health problems. Iron is an important hematopoietic factor, but consumption of water with an increased iron content may contribute to the development of Kashin-Beck disease, which causes degeneration and weakening of bones [MIKOŁAJCZAK 2007]. The consumption of water containing overly high levels of manganese can result in damage to the capillaries and lead to liver cirrhosis [MIKOŁAJCZAK 2007]. Manganese is also toxic to the brain. In particular, manganese accumulated in basal ganglia may cause a neurological syndrome which is a form of parkinsonism [DONALDSON, 1987; TAKEDA 2003].

The removal of iron and manganese from groundwater requires the use of physical, chemical and biological methods or combinations thereof. The most important of these methods are based on oxidation reactions and removal of precipitated compounds in the processes of sedimentation and filtration, biofiltration using the activity of iron- and manganese-oxidizing bacteria, as well as coagulation and adsorption [ANIELAK, ARENDACZ 2007; MAĆKIEWICZ 1998; PACINI *et al.* 2005; PATIL *et al.* 2016; TEKERLEKOPOULOU *et al.* 2013]. The most commonly used adsorbents are natural materials such as activated carbon, zeolite or kaolinite [FUNES *et al.* 2014].

The aim of the present study was to determine the suitability of silica-carbonate rock for the treatment of potable groundwater. The study examined the effectiveness of filters filled with silica-carbonate rock in removing iron, manganese and certain microbial contaminants from contaminated water.

MATERIALS AND METHODS

The studies were conducted in laboratory conditions in three filter columns filled with silica-carbonate rock. Silica-carbonate rock is mainly formed

from small organic debris and is a transition rock between carbonate and silica rocks [BROGOWSKI, RENMAN 2004; PINIŃSKA 2008]. The contents of calcium and silicon in the oxide form are different in different types of silica-carbonate rocks and can vary from 14 to 56% CaO and from 5 to 75% SiO₂ [BROGOWSKI, RENMAN 2004; BUS, KARZMARCZYK 2014; KOZŁOWSKI 1986]. The test rock was obtained from a mine located in the town of Piaski near Lublin, Poland. Prior to use in laboratory tests, the rock was heat-treated (decarbonized) at 900°C. The chemical composition of the rock after heat-treatment, determined using the MiniPal 4 X-ray spectrometer (PANalytical), is shown in Table 1. The material used in the experiments contained 43.3% CaO, 36.1% SiO₂ and 5.9% Al₂O₃ (Tab. 1).

Table 1. Chemical composition of the silica-carbonate rock after heat treatment

Chemical components	Content in a sample, %
CaO	43.336
SiO ₂	36.047
Al ₂ O ₃	5.932
Na ₂ O	2.853
Fe	1.340
TiO ₂	0.960
MgO	0.938
S	0.654
K ₂ O	0.489
P	0.480
Cl	0.237
MnO	0.117

Source: own study.

After heat-treatment and crushing, the material was separated into two fractions with grain size ranges of G₁ = 1–2 mm and G₂ = 2–5 mm. Fractions G₁ and G₂ were characterized by porosities of 0.25 and 0.4, respectively.

All filtration columns were filled with the same amount of silica-carbonate rock (100 cm³) of different particle sizes. The columns had a diameter of 34 mm and the height of the filter beds was 110 mm. The water was fed into the filters with peristaltic pumps at the bottom and travelled vertically upwards (Fig. 1). A different flow rate was set for each filter. Filters were supplied with water by a AQUA-TREND automatic dispenser Doser One Evolution.

Three variants of the experiment were analyzed which differed in particle size of the rock used, hydraulic retention time, and rate of water flow through the substrate:

filter A – fraction G₂ (2–5 mm); retention time $T = 2$ h, flow rate $Q = 20$ cm³·h⁻¹;

filter B – fraction G₁ (1–2 mm); retention time $T = 1$ h, flow rate $Q = 25$ cm³·h⁻¹;

filter C – fraction G₂ (2–5 mm); retention time $T = 1$ h, flow rate $Q = 40$ cm³·h⁻¹.

The study used water from a deep well located in the village of Przegaliny Małe in the commune of Komarówka Podlaska (Lublin province). The water

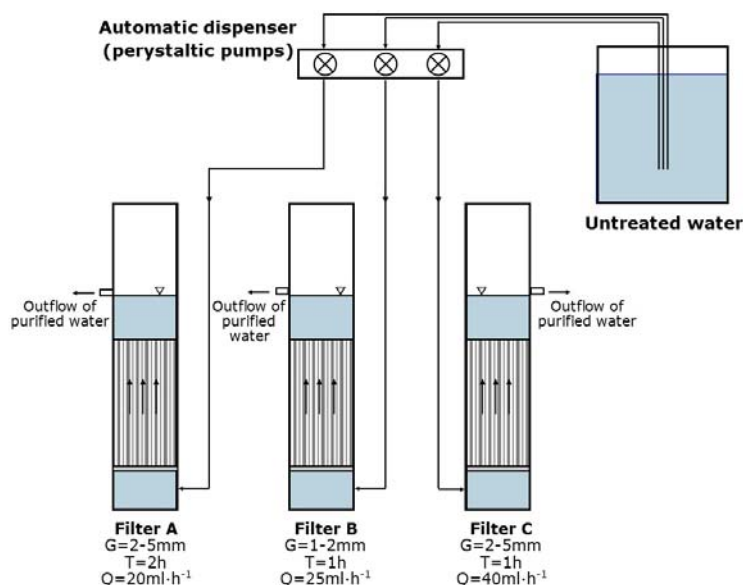


Fig. 1. A schematic of the model system for the treatment of groundwater; source: own elaboration

was characterized by high contents of iron and manganese, which exceeded many times the standards set down for potable water [Rozporządzenie MZ... 2015].

Physico-chemical assays of untreated groundwater and water purified in the filters containing silica-carbonate rock were performed over 22 days. Samples for analysis were taken once each day. The contents of iron and manganese, and pH were determined. The assays were performed using commonly applied

methods [HERMANOWICZ *et al.* 1999]. In the tenth day of the experiment water samples were analyzed for counts of *coli-form* bacteria, fecal enterococci and mesophilic and psychophilic bacterial cells in accordance with the methods described in the relevant norms [PN-C-04615-05:1975P; PN-ISO 6222:1999; PN-C-04615-25:2008P].

The results were analyzed statistically using the STATISTICA 10 software package. An analysis of variance (ANOVA) was performed. Data were divided into homogeneous groups using Tukey's procedure at a level of significance of $\alpha = 0.05$. Correlations between the investigated variables were determined by Spearman's correlation coefficient. Water quality was assessed against the legal requirements laid down for consumption-grade water [Rozporządzenie MZ... 2015].

RESULTS

Iron. The iron content in the untreated groundwater used in the experiments ranged from 1.84 to 5.15 $\text{mg}\cdot\text{dm}^{-3}$, with the mean content of 4.10 $\text{mg}\cdot\text{dm}^{-3}$ (Tab. 2, Fig. 2). This value exceeded several times the admissible level for potable water [Rozporządzenie MZ... 2015].

Table 2. Values of selected quality indicators of the test groundwater

Parameter	Untreated water			Purified water									Limit values
	min	max	\bar{x}	filter A			filter B			filter C			
				min	max	\bar{x}	min	max	\bar{x}	min	max	\bar{x}	
Iron, $\text{mg}\cdot\text{dm}^{-3}$	1.84	5.15	4.10	0.04	0.46	0.10	0.02	0.67	0.09	0.06	0.31	0.14	0.2
Manganese, $\text{mg}\cdot\text{dm}^{-3}$	0.02	0.91	0.31	0.01	0.02	0.01	0.01	0.01	0.01	0.01	0.07	0.02	0.05
pH	7.47	8.40	–	9.77	11.66	–	10.13	11.83	–	8.16	11.20	–	6.5–9.5

Source: own study.

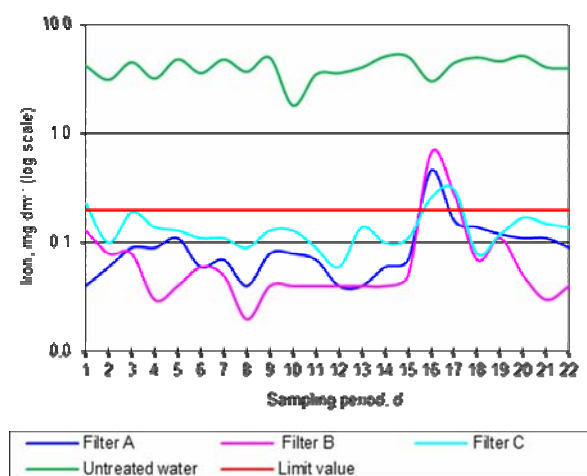


Fig. 2. Concentrations of iron in groundwater samples vs. the reference value; source: own study

The analysis of water treated in the filters filled with silica-carbonate rock indicated that this material could potentially be used to remove iron from groundwater. Iron content in water purified in filter bed A ($G = 2-5 \text{ mm}$, $T = 2 \text{ h}$, $Q = 20 \text{ cm}^3\cdot\text{h}^{-1}$) ranged between 0.04 and 0.46 $\text{mg}\cdot\text{dm}^{-3}$, with a mean of 0.10 $\text{mg}\cdot\text{dm}^{-3}$. In the water discharged from filter B ($G = 1-2 \text{ mm}$, $T = 1 \text{ h}$, $Q = 25 \text{ cm}^3\cdot\text{h}^{-1}$), iron concentrations ranged from 0.02 to 0.67 $\text{mg}\cdot\text{dm}^{-3}$. The mean concentration of iron in this sample was 0.09 $\text{mg}\cdot\text{dm}^{-3}$. In water flowing through filter C ($G = 2-5 \text{ mm}$, $T = 1 \text{ h}$, $Q = 40 \text{ cm}^3\cdot\text{h}^{-1}$), the concentration of iron fell to 0.06–0.31 $\text{mg}\cdot\text{dm}^{-3}$, with a mean value of 0.14 $\text{mg}\cdot\text{dm}^{-3}$ (Tab. 2). The exceeding of limit value of iron in purified water was incidental and therefore difficult to explain with specific causes. The most stable results were obtained for filter A, in which the limit value of 0.2 $\text{mg}\cdot\text{dm}^{-3}$ set down in the Ordinance of the Minis-

ter of Health was exceeded only one-fold [Rozporządzenie MZ... 2015]. To compare, in filters B and C, the admissible iron level was exceeded two- and three-fold, respectively (Fig. 2). Significantly higher mean concentrations of Fe were obtained for water purified in filter C (Tab. 2).

The mean iron removal efficiencies were very high for all the experimental variants analyzed: filter A – 97.72%, filter B – 98.33%, and filter C – 96.17%. Data analysis using ANOVA showed that the iron removal efficiencies of the tested rock-filled filters differed significantly. Tukey's test demonstrated that the significantly lowest iron removal efficiency was obtained by using filter C, and the highest efficiency was achieved in filter B.

The high efficiency of filters with silica-carbonate rock in removing iron from water can be associated with the sorption capacity of this substrate. Research done so far has demonstrated that silica carbonate rock has a good sorption capacity for phosphorus [BROGOWSKI, RENMAN 2004; BUS, KARCZMARCZYK 2014]. The chemical properties of iron compounds suggest that the reduction of iron concentrations in the analyzed water may have been due to other reasons, in particular, oxidation and precipitation of the element in an insoluble form [KOWAL, ŚWIDERSKA-BRÓŹ 2009]. This last phenomenon leads to the formation, on the adsorbent surface, of a coating of precipitate aggregates which can also contain notable amounts of manganese oxide. The precipitated compounds play an important role in removing iron from water, acting as adsorbents or oxidizing agents; at the same time, however, they can limit the effectiveness of the adsorbent proper [EL-SHERIF *et al.* 2013; KOWAL, ŚWIDERSKA-BRÓŹ 2009].

An important role in the activation of sorption may be played by water alkalinity (Fig. 3) as shown in a study using activated carbon [EL-SHERIF *et al.* 2013]. The pH value determines the rate of oxidation of iron and its precipitation as a hydroxide [KOWAL, ŚWIDERSKA-BRÓŹ 2009]. In the analyzed experiment,

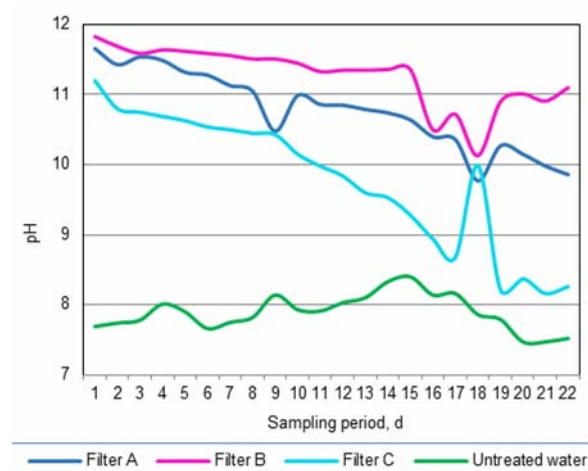


Fig. 3. Changes in the pH of groundwater samples; source: own study

alkalization of water during filtration through a silica-carbonate bed was related to the chemical composition of the substrate and a high content of calcium compounds (Tab. 1). The value of pH in raw water ranged from 7.47 to 8.40, and visibly increased during filtration. The pH of water purified in filter A ranged from 9.77 to 11.66, in filter B – from 10.13 to 11.83, and in filter C – from 8.16 to 11.20 (Tab. 2, Fig. 3). Spearman's rank correlation coefficient between iron removal efficiency and pH was $r_s = 0.68$, which means that the efficiency of removal of iron in the rock-filled filters increased with increasing alkalinity. The same coefficient determined between iron concentrations in purified water and pH was $r_s = -0.78$, which indicates that an increase in the pH of the purified water was accompanied by a simultaneous decrease in iron concentration.

Compared to other materials used in water filtration, silica-carbonate rock shows very high iron removal efficiency. A study by KALETA *et al.* [2009] has demonstrated that filters filled with quartz sand can deliver a 79% efficiency of iron removal from groundwater. Similar results have been obtained using slow sand filters installed downstream of coarse filters with aeration. Such an installation gave a final concentration of iron in the range of 0.03–0.04 mg·dm⁻³ [PACINI *et al.* 2005]. The efficacy of silica carbonate rock in removing iron from water is comparable to that of active carbon, which can be used to obtain an iron removal efficiency of up to 95% [EL-SHERIF *et al.* 2013].

Manganese. The manganese content in the water supplied to the rock-filled filter varied within a wide range from 0.02 mg·dm⁻³ to 0.91 mg·dm⁻³ (Tab. 2). The mean concentration of manganese for the entire study period (0.31 mg·dm⁻³) considerably exceeded the maximum admissible content in potable water [Rozporządzenie MZ... 2015].

Research carried out by WILMAŃSKI [2014] demonstrates that a high efficiency of manganese removal from groundwater can be achieved by using catalytic masses differing in the percentage content of MnO₂. Manganese removal was observed already on the day following the start-up of the filters. The concentration of manganese fell from 0.36–0.47 mg·dm⁻³ to 0.02–0.03 mg·dm⁻³, but, unfortunately, after about 15 h, it was higher than the limit value [Rozporządzenie MZ... 2015]. This process strongly depends on the time of contact of water with the catalytic material. To obtain the desired water purification efficiency, it is recommended that a two-step filtration process at a high water flow rate is applied [WILMAŃSKI 2014].

Preliminary results obtained in this present study indicate that manganese can be successfully removed from water using silica-carbonate rock. In water purified in filter bed A ($G = 2\text{--}5$ mm, $T = 2$ h, $Q = 20$ cm³·h⁻¹), a constant concentration of manganese of 0.01 mg·dm⁻³ was recorded throughout the study period, with only one exception, when the concentration increased to 0.02 mg·dm⁻³. In water purified in filter

B ($G = 1\text{--}2\text{ mm}$, $T = 1\text{ h}$, $Q = 25\text{ cm}^3\cdot\text{h}^{-1}$), manganese concentration was constant in all experimental series and did not exceed $0.01\text{ mg}\cdot\text{dm}^{-3}$ (Tab. 2, Fig. 4). The concentration of manganese in water outflowing from filter C ($G = 2\text{--}5\text{ mm}$, $T = 1\text{ h}$, $Q = 40\text{ cm}^3\cdot\text{h}^{-1}$) was $0.01\text{ mg}\cdot\text{dm}^{-3}$, but in the final phase of the experiment it started to increase, reaching a maximum value of $0.07\text{ mg}\cdot\text{dm}^{-3}$ (Tab. 2, Fig. 4). Except for one case, all manganese concentrations recorded were below the limit value (Fig. 4).

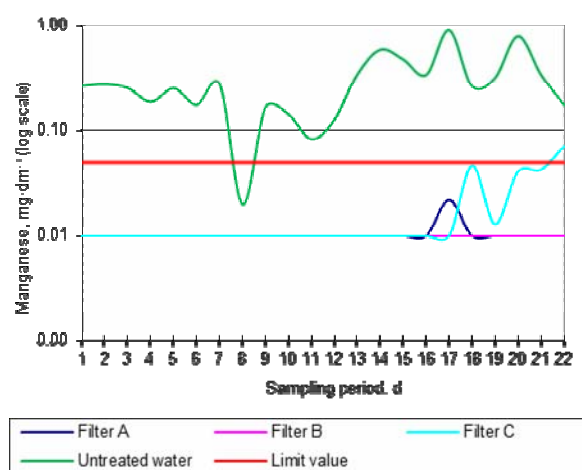


Fig. 4. Concentrations of manganese in groundwater samples vs. the reference value; source: own study

The highest efficiency of manganese removal from groundwater was achieved in filters A and B – over 96%, and the lowest in filter C – about 93%. The chemical properties of manganese compounds suggest that this element could have been absorbed by the silica-carbonate rock as well as having undergone oxidation. This is all the more likely given the fact that the water was strongly alkalized while passing through the silica-carbonate bed, and the alkalinity of water is considered to be the primary determinant of manganese oxidation rate [BENEFIELD, MORGAN 1990; FUNES *et al.* 2014]. The lower efficiency of manganese removal in filter C may have been due to the lower pH values (Fig. 3). In later stages of the experiment, an important role may have been played by the compounds forming on the surface of the filter material, including iron (III) hydroxide and manganese (IV) oxide precipitating in the course of iron removal. These compounds have a sorption capacity for manganese and can also act as factors co-precipitating manganese as its oxidants [SOLECKI 1972].

Indicator bacteria. An inherent component of every technological water treatment system is disinfection, which is aimed at eliminating the risks connected with microbial contamination. During routine examination of microbiological quality, water is always tested for *coliform* bacteria. Their presence in water disqualifies it as potable water [Rozporządzenie MZ... 2015]. In the experiment discussed in this paper, the counts of *coliform* bacteria and other indicator microorganisms were determined a single time. Non-

purified water contained $2.4\cdot 10^2\text{--}100\text{ cm}^{-3}$ *coliform* bacteria. Filtering of water through beds A and B resulted in complete elimination of this group of bacteria, which means that this process can be viewed as a good water disinfection method. In filter C, the efficiency of removal of *E. coli* was about 90%, which was not enough to reach the admissible level. It is likely that the biocidal effect of silica-carbonate was due to its high alkalinity [GRABOW *et al.* 1978; SIQUEIRA, LOPES 1999; STARLIPER *et al.* 2015]. STARLIPER and WATTEN [2013] have shown that an almost total elimination of *coliform* bacteria can be achieved already at pH 10.0, and GRABOW *et al.* [1978] have observed this effect at pH over 11.1. The pH values recorded in the effluent from filters A and B were significantly higher than those observed for water discharged from filter C, and usually exceeded pH 10.0 (Fig. 3). The action of a disinfecting agent, apart from its intensity, is significantly affected by the period over which it acts upon the microorganisms [STARLIPER, WATTEN 2013]. In filter C, due to the porosity of the material used and the hydraulic retention time set, the flow rate of water was the highest. Exposure of the microorganisms to the adverse factor was the shortest in this case, which could also have contributed to their greater survival.

Additional indicators of fecal contamination of water are fecal enterococci, which, compared with *coliform* bacteria, can survive longer in water at temperatures in the range of $4\text{--}6^\circ\text{C}$ and are more resistant to disinfectants. Therefore, enterococci tests are used in controlling the efficiency of water disinfection [KROGULSKA 1996; 2003]. Since none of the tested water samples, including non-purified water samples, contained enterococci (Tab. 3) we could not assess whether the use of filters filled with carbonate-silica rock was effective in the elimination of this group of bacteria. Based on the results obtained by GRABOW *et al.* [1978] and STARLIPER and WATTEN [2013], however, such an effect is highly likely.

Table 3. Counts of indicator bacteria in untreated water and in water purified in filters filled with silica-carbonate rock

Parameter measurement unit	Un-treated water	Purified water in filter			Limit values
		A	B	C	
Total coliforms, MPN·100 cm ⁻³	$2.4\cdot 10^2$	0	0	$2.3\cdot 10$	0
Faecal enterococci bacteria, MPN·100 cm ⁻³	0	0	0	0	0
Total number of bacteria at 37°C, cfu·cm ⁻³	$2.5\cdot 10^4$	$3.3\cdot 10^3$	$5\cdot 10^2$	$5.9\cdot 10^3$	20
Total number of bacteria at 22°C, cfu·cm ⁻³	$2.8\cdot 10^4$	$5.1\cdot 10^3$	$3.7\cdot 10^2$	$6.5\cdot 10^4$	100

Source: own study.

Microbiological reference criteria for potable water impose limits on total counts of microorganisms growing at $36 \pm 2^\circ\text{C}$ after 48 h of incubation (mesophilic bacteria) and $22 \pm 2^\circ\text{C}$ after 72 h of incubation (psychrophilic bacteria). In accordance with these criteria, the counts of mesophilic and psychrophilic

bacteria in water should not exceed $20 \text{ cfu}\cdot\text{cm}^{-3}$ and $100 \text{ cfu}\cdot\text{cm}^{-3}$, respectively [Rozporządzenie MZ... 2015]. The highest efficiency of reducing the counts of mesophilic and psychrophilic microorganisms was achieved in filter B – about 98%. In contrast, the use of filter A led to an approximately 10-fold reduction in total bacterial counts. Despite the reduction in the number of microorganisms in the water subjected to filtration, none of the purified water samples met the potable water standards (Tab. 3).

The experiments presented in this study, due to their subject matter and duration must be viewed as preliminary. Nevertheless, they point to the potential usefulness of carbonate-silica rock in removing iron, manganese and certain groups of indicator bacteria from groundwater. The results demonstrate that filtration of contaminated water through a silica-carbonate bed allows to obtain purified water with levels of iron, manganese and some indicator bacteria significantly lower than admissible values. The high efficiency of filters filled with silica-carbonate rock may be associated both with the sorption capacity of the test material as well as the conditions it creates during the passage of water through the filter bed. The strongly alkaline pH of treated water can promote the adsorption of iron and manganese ions on the surface of the material and significantly affect their rate of precipitation as insoluble precipitates, as well as exhibiting disinfectant activity. At the same time, the high alkalinity of the substrate is one of the shortcomings of this water purification method, as the pH values recorded exceed the optimum range for drinking water.

CONCLUSIONS

1. Filters filled with thermally-treated silica-carbonate rock exhibit a very high efficiency of removal of soluble forms of iron (96%) and manganese (more than 93%) from groundwater.

2. Filtering of contaminated water through a silica-carbonate bed causes a significant increase in its pH, which can intensify the processes of adsorption of metal ions on the surface of the rock and accelerate their oxidation and precipitation as solid phases.

3. In almost all cases, the concentrations of iron and manganese in the water purified in the rock-filled filters met the standards laid down for potable water.

4. Iron removal efficiency was the lowest for rock particle sizes in the range of 2–5 mm and the hydraulic retention time of 1 h. In the final phase of the experiments, this experimental variant also exhibited a decreased efficiency of manganese removal with the concentration of manganese ions approximating the limit value.

5. Filtration of groundwater through silica-carbonate beds at a relatively low flow rate resulted in complete elimination of *coliform* bacteria, which may suggest that the alkaline pH of the water has a disinfectant action.

6. Filters filled with silica-carbonate rock did not allow to reduce total counts of mesophilic and psychrophilic microorganisms to levels required for potable water.

7. The preliminary results indicate that the application of heat-treated silica-carbonate rock may be an advantageous alternative to other methods of removing iron and manganese from groundwater, at the same time ensuring partial disinfection of the water. A drawback of this water treatment method is that it requires adjustment of the pH to the range specified for potable water.



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**Zastosowanie skały węglanowo-krzemionkowej (opoki) do usuwania żelaza, manganu
i bakterii wskaźnikowych z wód podziemnych**

STRESZCZENIE

W pracy przeanalizowano skuteczność usuwania żelaza, manganu i bakterii wskaźnikowych z wody podziemnej przeznaczonej do picia. Stosowano w tym celu skałę węglanowo-krzemionkową (opokę). Badania wykonano w warunkach laboratoryjnych w trzech kolumnach filtracyjnych zasilanych wodą o zwiększonej zawartości żelaza i manganu. Dwie z kolumn wypełniono skałą węglanowo-krzemionkową (opoką) o granulacji 2–5 mm, czas retencji wody w kolumnach ustalono odpowiednio na 1 i 2 h. Trzecią kolumnę wypełniono skałą o granulacji 1–2 mm, przyjmując czas retencji wody 1 h. Stwierdzono dobre efekty usuwania żelaza i manganu i bakterii grupy *coli* z badanych wód, niewielką skuteczność usuwania bakterii psychro- i mezofilnych, a także zwiększenie zasadowości wody.

Słowa kluczowe: *opoka, usuwanie manganu, usuwanie żelaza, uzdatnianie, wody podziemne*