Monitoring the effectiveness of advanced sorption materials for removing selected metals from water

Renata Biela, Tomáš Kučera and Mojmír Pěkný

ABSTRACT

There are a number of ways to remove heavy metals from water. Sorption on granular media based on iron oxides and hydroxides is currently the most used option. The experiment was carried out using sorption materials GEH, CFH 0818, CFH 12 and Bayoxide, which are primarily designed to remove arsenic from water. Four columns were prepared with an inner diameter of 4.4 cm for the purpose of the experiment. The thickness of the filtration media was 62 cm on average. Nickel, iron and manganese pollution were simulated in a laboratory. The efficacy of metals removal by four selected sorption materials was compared. During the experiment, the flow rate was set to reach the required retention time of 2.5, 7 and 15 minutes, taking into account the porosity of the media. It was found that the nickel concentration was reduced according to Regulation No. 252/2004, setting the limit value even after the shortest retention time (2.5 min). Longer retention times had no significant effects on nickel removal. The measurements also proved that all sorption materials have the ability to remove iron and manganese from water. Bayoxide sorption material achieved the best results in nickel, iron and manganese removal from water.

Key words | filtration, iron, manganese, nickel, removal, sorption materials, water

Renata Biela (corresponding author)
Tomáš Kučera
Mojmír Pěkný
Faculty of Civil Engineering,
Brno University of Technology, Institute of
   Municipal Water Management,
Žižkova 17,
Brno,
602 00,
Czech Republic
E-mail: biela.r@fce.vutbr.cz

INTRODUCTION

Some uncommon elements can sometimes be present in groundwater and surface water. Metals belong to such elements. Increased concentrations of iron and manganese can be expected in groundwater but higher concentrations of metals such as nickel or arsenic are not typical of this water. Iron and manganese gets into groundwater by dissolving substances from the rock environment. The presence of carbon dioxide in this water helps dissolution. Nickel occurs in the minerals together with arsenic, nickel solubility in water is limited. Nevertheless, water sources exceeding prescribed limits for drinking water in arsenic and nickel concentrations can also be found.

Nickel can be found in minerals usually with sulphur, arsenic and potentially with antimony. It is also included in some of the aluminosilicates (serpentine). Anthropogenic sources of nickel include mainly wastewater from metal surface treatment where it is predominantly complexly bound, and wastewater from colour metallurgy. It is also used in ceramic and glass making industries and for some chemical syntheses as a catalyser. Other potential sources are nickel-plated parts of equipment that can come into contact with water (Pitter 2009).

Perinatal mortality is considered the major risk from nickel in drinking water with the World Health Organization (WHO) guideline set at 20 μg/L (Gray 2008). For the quality of drinking water in the Czech Republic the limit value of nickel is set at 20 μg/L also.

The most widespread iron ores are pyrite, lepidocrocite, magnetic iron ore, limonite, and siderite. Small amounts of iron are also contained in many natural aluminosilicates. Very high concentrations of iron can be found in water containing sulphuric acid originating from oxidation of sulphide

ore of pyrite. Anthropogenic sources of iron in natural and service water are some industrial waters (e.g. from metal pickling, rolling, wire-drawing plants etc.) and corroding processes inside of water mains. Iron is the main metal that forms part of the bottom sediments and may pass into the liquid phase as a result of remobilization processes (Pitter 2009).

The WHO has not yet set a health-based guideline value for iron, because no adverse effects have been found at levels detected in drinking water. Recent studies from India suggest that when iron is ingested with drinking water at higher concentrations it may cause serious problems (Ferrante *et al.* 2014). In compliance with the drinking water ordinance in the Czech Republic, the limiting value for concentration of iron in drinking water amounts to 0.2 mg/L.

Increased concentration of iron in natural water is often accompanied by increased concentration of manganese. Usually there tends to be less manganese than iron. Concentrations of manganese in underground water are higher than in surface water. Anthropogenic sources of manganese can be some industrial wastewater, e.g. from ore processing, metallurgical and chemical plants (Pitter 2009).

The WHO health-based guideline value for drinking water was 400 μg Mn/L and the tolerable daily intake was 60 μg Mn/kg body weight (Ferrante *et al.* 2014). In a later edition, the WHO published that 'this health-based value is well above concentrations of manganese normally found in drinking water; it is not considered necessary to derive a formal guideline value' (WHO 2011). In the Czech Republic, the limiting value for concentration of manganese in drinking water amounts to 0.05 mg/L.

The laboratory of the Institute of Municipal Water Management at the Faculty of Civil Engineering of the Brno University of Technology (BUT) focused on removing nickel from water by filtration using various sorption materials. Four filtration materials were used which were primarily designed to remove arsenic from water: CFH 0818, CFH 12, GEH and Bayoxide E33. Besides the efficiency of removing nickel from water, iron and manganese removal efficiency was examined during the filtration, because water was simulated from a ground source with these elements. The aims were: to determine how sorption materials remove selected metals (primarily nickel) from water and to determine which of the sorption materials is the best for nickel, iron and manganese removal.

REVIEW OF LITERATURE

Toxic heavy metals are exposed to the natural eco-system and subsequently are accumulated in the human body through either direct intake or food chains. Therefore, heavy metals should be eliminated from the environment (Balintova *et al.* 2016). There are several technological methods for the removal of heavy metals and metalloids in water treatment: precipitation, ion exchange, membrane technologies, adsorption, electrochemical processes, and recently also biological methods (Illavský *et al.* 2015).

Most specialist articles deal with the removal of arsenic from water applying various methods, for example coagulation (Hering *et al.* 1997), adsorption (Smith 1998), iron impregnated sand (Vaishya 2003), moving bed active filtration (Newcombe *et al.* 2006) and so on.

Every method of heavy metals removal from water has some advantages and disadvantages. For example, the coagulation with iron salt and alum is relatively inexpensive but generates heavy metal-rich sludge. The water treatment technology with iron based surfaces is easily controlled and relatively inexpensive but is not normally regenerated and used material may be classed as toxic waste. Ion exchange selectively removes low levels of metal ions from contaminated aquifer, despite high concentrations of natural components. Waters rich in iron and manganese may require pre-treatment to prevent media clogging. The method is moderately expensive and the regeneration produces metal-rich brine. Membrane technologies have high heavy metals removal efficiency but pretreatment is usually required. The technologies are relatively expensive, especially if operated at high pressures (Bufa-Dörr *et al.* 2012).

Electrochemical methods have a long history as water treatment technologies for removal of a wide range of pollutants. However, these methods have never become accepted as a 'mainstream' of water treatment technology. These treatment technologies are most suitable for decentralized water treatment and supply drinking water for small communities in remote areas (Gyliene 2012).

Sorption is a simple, effective, and economically reasonable method for removal of heavy metals, especially due to the option of using a broad spectrum of substances with absorbing capacity – sorbents. Some natural materials (zeolites), but also industrial and agricultural waste, can be used as affordable sorbents. The most tested heavy metal sorbents are oxides and hydroxides of iron, iron hydroxide-coated sand, activated charcoal, media with TiO_2 or MnO_2 layer on the surface and others (Pěkný 2013).

METHODS

Description of using sorption materials

The sorption material CFH is produced in two modifications, CFH 0818 and CFH 12, that are based on iron oxide hydroxide and are used to remove mainly As, Se, P, Ag, Ni, Pb, Mo, Si, V, Cu and other metals from water. Sorbents have the shape of granules, whose properties are very similar and they mainly differ in terms of granularity. The sorption material CFH 0818 has finer grains than material CFH 12. They are manufactured by Kemira based in Finland. The distributor of the material in the CR is Kemwater ProChemie s.r.o. based in Bakov nad Jizerou (Vosáhlo 2012). The materials at 1,000-fold magnification are shown in Figures 1 and 2.

The sorption material GEH based on granulated iron hydroxide is suitable for economical and efficient removal of arsenic and antimony from water. The material was developed by Berlin University, Department of Water Quality. It is manufactured by the German company GEH-Wasserchemie GmbH. It is imported to the CR by Inform-Consult Aqua s.r.o. Příbram (Vosáhlo 2012). The treatment technology consists of the adsorption of the contaminant on granulated iron hydroxide (GEH sorbent) in a reactor through which the treated water flow flows. The adsorption capacity of the material depends on the operating conditions (Biela 2015). The material at 1,000-fold magnification is shown in Figure 3.

Bayoxide is a dry crystalline granulated sorbent based on iron oxide. It was developed by Severn Trent in cooperation with Bayer AG and produced by LANXESS
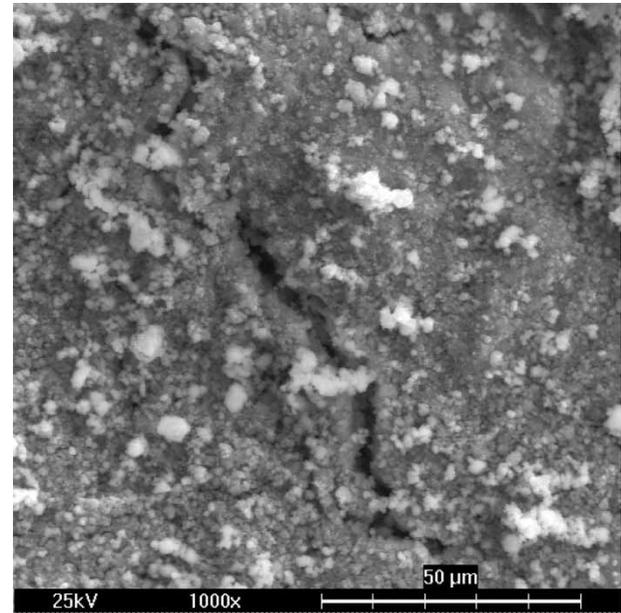

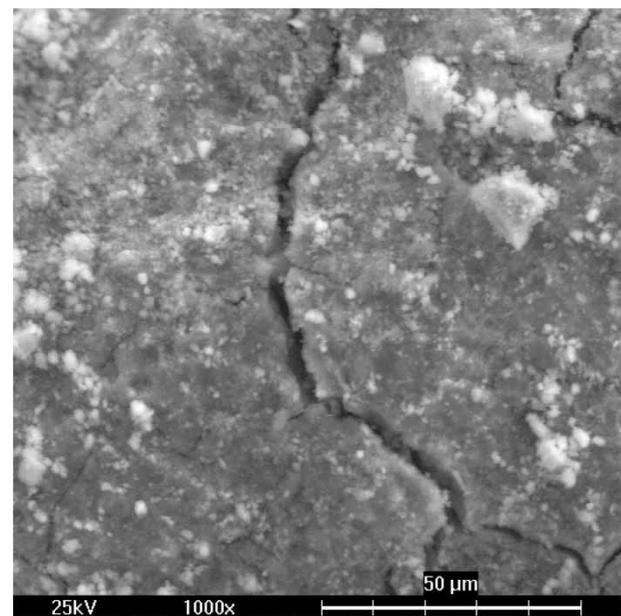**Figure 1** │ Sorption material CFH 0818 at 1,000-fold magnification.

Figure 2 │ Sorption material CFH 12 at 1,000-fold magnification.

Deutschland GmbH, Leverkusen in Germany. It is produced in two variants, Bayoxide E33 and Bayoxide E33P (Konečný 2016). The difference is that Bayoxide E33 is granulated whereas Bayoxide E33P is produced in the form of tablets. The material was designed to remove arsenic and its advantage is the removal of As^{III} and As^{V} along with
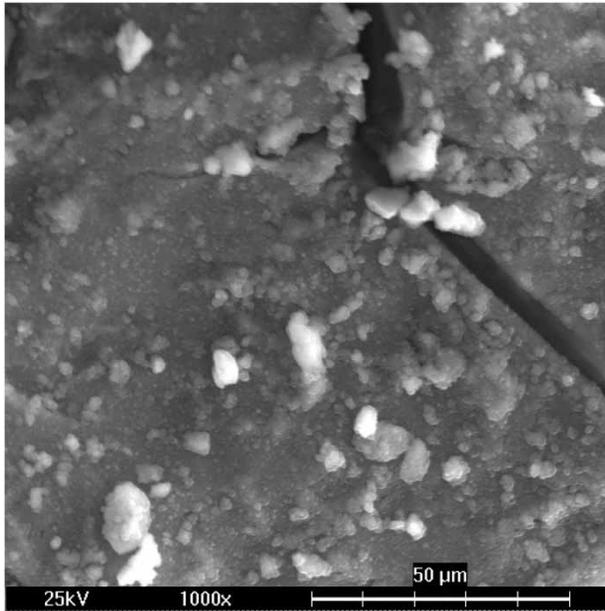
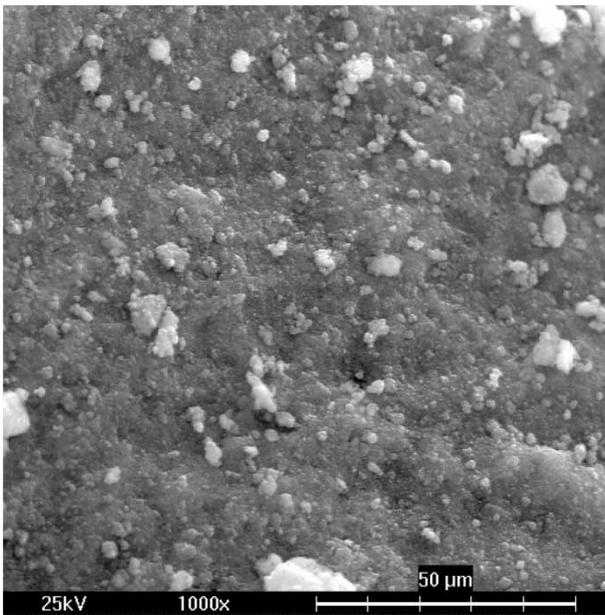**Figure 3** | Sorption material GEH at 1,000-fold magnification.

Figure 4 | Sorption material Bayoxide E33 at 1,000-fold magnification.

the removal of iron and manganese. The producer gives water treatment capacity at the arsenic content of 11–5,000 µg/L and iron content of 50–10,000 µg/L (Biela 2016). The sorption material Bayoxide E33 at 1,000-fold magnification is shown in Figure 4. An overview of sorption materials properties is shown in Table 1.

Description of measurement

Each sorption material was poured into a glass tube with an inner diameter of 4.4 cm, with a drainage layer at the bottom consisting of stones, diameter of 1–2 cm, followed by a layer of glass beads, diameter of 4 mm, and then a layer of beads, diameter of 2 mm. This prevented the escape of loose material from the column during filtration. The height of the filtration medium was 62 cm on average. The filtration columns were fixed to the wall next to each other.

The entire filtration system consisted of a vessel with raw water, pump, flow meter, set of filtration columns and vessels for the filtrate. The filtration system scheme for one column is shown in Figure 5.

Before starting the filtration, the filtration material was processed as instructed by the producer. After that, the filters were flushed with tap water, in a reverse direction from filtration, i.e. bottom up, where the flush water was discharged into the sewerage. During the flushing, the flow-rate through the column was selected so as to avoid the filtration material in suspension being flushed out. The filter flushing usually lasted until clear water started flowing out of the column.

Raw water with increased concentration of nickel, iron and manganese (Table 2) was simulated in a laboratory by adding chemical concentrates (single parameter standard solutions from the company Hach Lange) of these metals into drinking water from the Brno public water supply system. Turbidity and pH was also measured in raw water. The turbidity was measured in FNU (1 FNU =1 NTU).

During the measurement, the raw water was pumped via a flow meter with flow rate values set in a way to achieve the required retention time in the columns of 2.5, 7 and 15 minutes. The real retention time takes into account the porosity of the media. Each sorption material has different porosity that was considered when calculating the volume of water in the column and consequently the flow rate for the required retention time. Water filtered through the sorption materials had the following set concentrations of iron, manganese and nickel.

RESULTS

The analyses indicate that all sorption materials achieve excellent results in nickel removal despite its high

Table 1 │ Sorption materials properties overview (Pěkný 2013)

Parameter	Unit	CFH	GEH	Bayoxide E33
Chemical composition	–	Fe-O-OH	$Fe(OH)_3 + \beta$ Fe-O-OH	$Fe_2O_3 + \alpha$ Fe-O-OH
Particle size	mm	1–2	0.2–2	0.5–2
Bulk density	g/cm^3	1.12	1.25	0.45
Specific surface	m^2/g	120	250–300	120–200
pH working range	–	6.5–7.5	5.5–6.5	6.0–8.0
Porosity of the grains	%	72–80	72–77	85
Colour	–	Brown to brown-red	Dark brown to black	Amber
Description	–	Dry granular	Moist granular	Dry granular
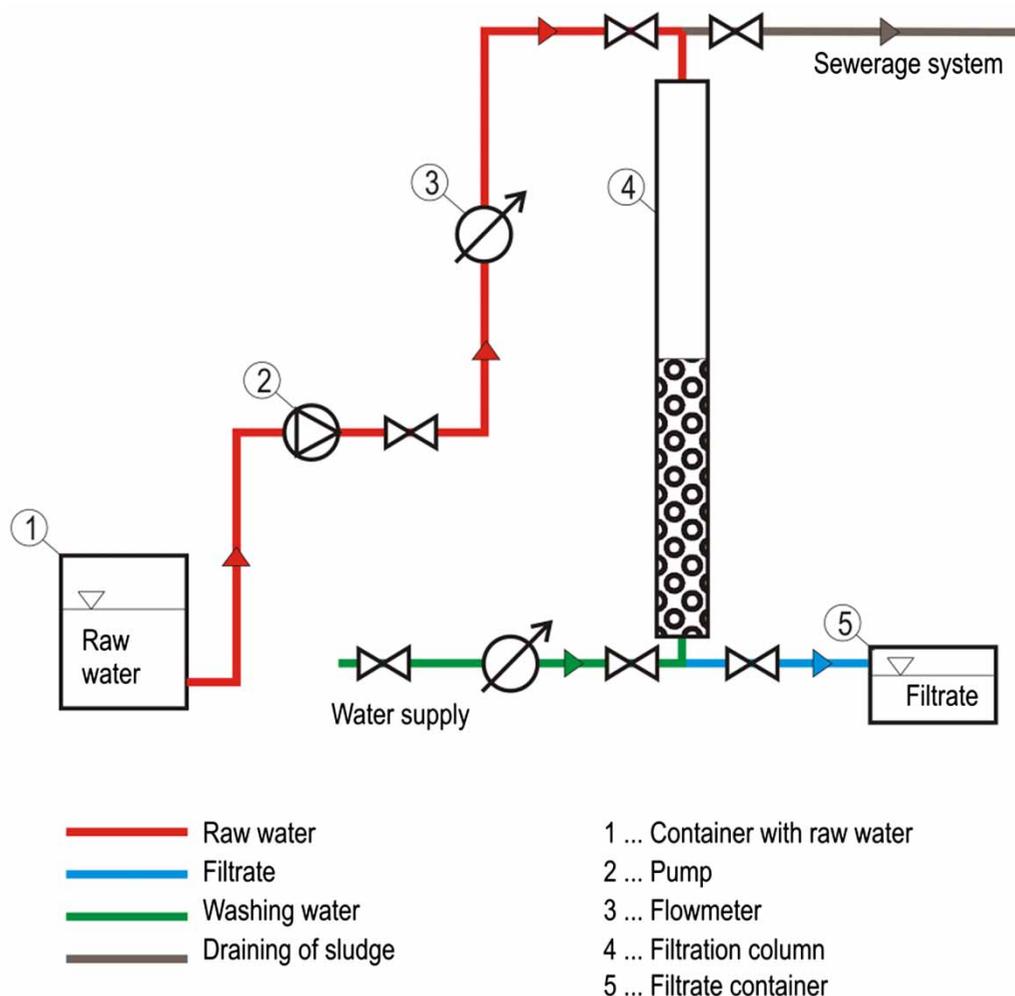
Figure 5 │ Diagram of the filtration system.

concentrations in raw water. Even the shortest retention time (2.5 min) ensures lower nickel concentration in raw water than the highest limit value in drinking water as per Regulation No. 252/2004 Sb. If the retention time was longer, there was no major increase in the nickel concentration reduction. The assumption is that it is contact

Table 2 | Analysis of raw water

t (min)	pH (–)	Turbidity (FNU)	c Fe (mg/L)	c Mn (mg/L)	c Ni (μg/L)
0	7.0	5.76	1.500	0.609	720.0

filtration for nickel, in 2.5 min the concentration of nickel went down from 720 to a maximum of 10 μg/L (for the sorption material GEH).

For sorption material CFH 0818, the nickel concentration in 15 min residence time was higher than in 7 min residence time. The experimental measurement was performed only once, nickel concentrations were determined by an accredited laboratory of the National Health Institute in Brno. After the results were found, the experiment was not performed again, so the measurement was not checked.

The results of the water analyses after filtration through individual sorption materials are shown in Table 3. Figure 6 shows how the effluent concentration of Ni depends on the retention time.

The adsorption capacity of using materials was studied and it was found that material CFH has the adsorption capacity of 4.9 g As per 1 kg adsorption material (Kemira *CFH12, CFH0818*). The adsorption capacity of material GEH depends on working conditions (GEH Arsenentfernung) and the life

Table 3 | Analyses after filtration through the sorption materials CFH, GEH and Bayoxide

t (min)	Turbidity (FNU)	c Fe (mg/L)	c Mn (mg/L)	c Ni (μg/L)
CFH 0818				
2.5	1.43	0.111	0.052	2.0
7	0.66	0.116	0.034	2.0
15	0.41	0.021	0.037	5.0
CFH 12				
2.5	2.54	0.400	0.057	4.0
7	1.45	0.363	0.056	5.0
15	1.21	0.332	0.044	4.0
GEH				
2.5	1.63	0.153	0.155	10.0
7	0.70	0.142	0.153	9.0
15	0.67	0.133	0.150	9.0
Bayoxide E33				
2.5	0.97	0.122	0.055	1.0
7	0.45	0.179	0.047	1.0
15	0.49	0.086	0.038	1.0
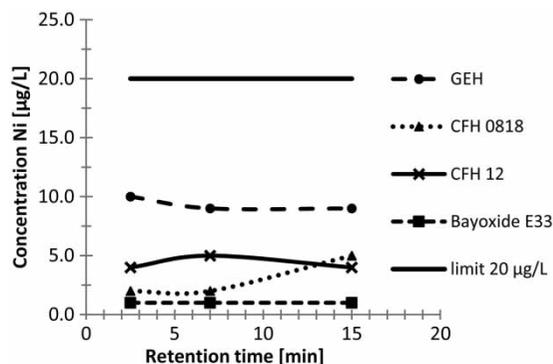
Figure 6 | The dependence of Ni concentration on the retention time.

expectancy of sorption material Bayoxide E33 is dependent on specific water quality and operating levels (Industrie De Nora S.p.A.).

Because the used sorption materials were produced primarily for removing arsenic from water, all information concerning these materials relate specifically to arsenic. The literature (Bufa-Dörr 2012) reports that if pH of water is higher than 7.5, arsenate removal by material CFH falls. At low pH, the adsorption density of arsenic (V) is much higher than that of arsenic (III), but at slightly alkaline pH, adsorption is nearly equal for both oxidation states of arsenic. Alkaline pH reduces the lifetime of CFH. The pH value of water during the experiment was not measured, only raw water. The pH value of raw water 7 was in the pH working range for sorption materials CFH and Bayoxide E33, see Table 1.

The turbidity of raw water was 5.76 FNU and after filtration through sorption materials the turbidity decreased. The limit value of turbidity for drinking water in the Czech Republic is 5 FNU, so it can be said that the sorption materials reduced turbidity below the limit. However, the turbidity of raw water was not too high. In another experiment the measurement of raw water with higher turbidity (11.4 FNU) was simulated and the water was filtered through the same materials. The results were very similar and all sorption materials reduced the turbidity below the limit. It can be said that sorption materials GEH, CFH and Bayoxide E33 are very good at reducing the turbidity from water.

Through measuring, it was also determined how the used sorption materials remove iron and manganese from water. The most effective method for removing iron from

water was indicated to be the sorption material CFH 0818, the sorption material CFH 12 was the least effective; even after 15 min the iron concentration did not fall below the 0.2 mg/L limit for drinking water.

When removing manganese from water, the sorption material CFH 0818 was the most effective. After 7 min the filtrate showed Mn concentration under the 0.05 mg/L limit for drinking water. The least effective for removing manganese from water was the GEH material, the concentration of Mn after filtration through this material remained constantly above the threshold value for drinking water.

For determining the concentrations of iron and manganese a spectrophotometer from the laboratory of the Institute of Municipal Water Management was used.

CONCLUSIONS

Adsorption is seen as an effective technique for removal of heavy metals from water. The adsorption process provides flexible operation and in most cases it will give high-quality treatment. Activated carbon is the most widely used adsorbent for water treatment (Bufa-Dörr 2012), but in recent years new adsorption materials have been made. Tests were carried out in the laboratory of some of these adsorption materials to remove metals from water. The model water was simulated groundwater with an increased content of iron, manganese and nickel. The area of interest was above all to remove nickel from water since it is a heavy metal.

The aim was to determine how the selected sorption materials (made primarily for removing arsenic from water) will remove nickel. Regarding iron and manganese, it is known that the most common method of their removal is oxidation, but the tests were carried out to show how selected materials remove iron and manganese from water.

The best results of nickel removal from water was achieved by Bayoxide E33, which managed to reduce the Ni content during the shortest retention time and such good results were achieved constantly throughout the measurement period. When adsorbent CFH 0818 was used, the Ni concentration increased if a longer retention time was used, but this may have been caused by

measurement inaccuracy. Given the velocity of nickel removal from water, this is contact filtration with respect to all sorption materials. The high nickel concentration in raw water dropped after 2.5 min of contact with CFH 0818, CFH12, GEH and Bayoxide E33 materials with very low nickel concentrations in the filtrates that almost did not change over time.

The measurement also detected that the applied filtration materials also remove iron and manganese from water. Apart from CFH 12, other sorbents removed iron below the limit concentration for drinking water of 0.2 mg/L. The most efficient material for iron removal seems to be sorption material CFH 0818. Manganese removal required a longer retention time than for nickel and iron to ensure the drop below the limit concentration for drinking water (0.05 mg/L). Increased retention time resulted in increased manganese removal efficiency. The material GEH did not cause the manganese concentration to drop even after a contact period of 15 min to reach the limit prescribed value, which was probably caused by inaccurate measurement.

The sorption material Bayoxide E33 is the most effective in removing nickel, but in terms of costs compared with materials CFH and GEH it is the most expensive. The cheapest of all four sorption materials is CFH 0818 (in the Czech Republic). Thus costs have also to be considered when using these materials for the removal of metal in the treatment of drinking water.

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