Introduction

Nickel belongs to extra dangerous substances as well as other metals: As, Sn, Cr, Cu, Pb, and Zn. Nickel occurs predominantly as the ion Ni(H₂O)₆²⁺ in natural waters at pH 5-9. Complexes with ligands, such as OH⁻, SO₄²⁻, HCO₃⁻, Cl⁻, and NH₃, are formed to a minor degree in this pH range. Nickel concentrations in groundwater are generally below 20 μg/L and depend on soil use, pH, and sampling depth. Acid rain increases the mobility of nickel in the soil and thus might increase nickel concentrations in groundwater.

The primary source of nickel in drinking water is leaching from metals in contact with drinking water, such as pipes and fittings. Water left standing overnight in plumbing fittings plated with chromium on a base of nickel contained a nickel concentration of 500 μg/L [1-3].

The main EU legal instrument regulating pollution of aquatic environments by nickel and its compounds is Directive 2008/105/EC on environmental quality standards in the field of water policy. According to the Directive, nickel is included in List II – dangerous substances (deleterious effect on aquatic environment). Nickel is also included in the List of Priority Substances (substances posing significant risk to aquatic environments).
The main legislative instrument of the Slovak Republic aimed at issues of hazardous and priority hazardous substances is Water Act No. 364/2004. Nickel is included on List II – hazardous substances and on List III – priority substances.

The most important legal provision concerning the discharge of wastewater containing hazardous and priority hazardous substances is the Regulation of the Government of the Slovak Republic No. 269/2010 establishing the requirements for achieving good water status.

Limit concentration for nickel in surface water is 0.02 mg/L, limit concentration for nickel in streams intended for drinking water abstraction is 0.02 mg/L in the category A1 (water requiring simple physical treatment and disinfection or rapid filtration and disinfection), 0.05 mg/L in category A2 (water requiring physical-chemical treatment and disinfection, e.g. coagulation, flocculation, filtration and chlorine disinfection) and 0.1 mg/L in the category A3 (water requiring intensive physical-chemical treatment and disinfection, e.g. coagulation, flocculation, filtration, adsorption using active carbon, chlorine, and ozone disinfection).

The Regulation of the Government of the Slovak Republic No. 496/2010 establishing the requirements for water intended for human consumption and water quality monitoring sets the permissible limit concentration for heavy metals in drinking water. The limit for nickel categorized as a potential carcinogen is 0.02 mg/L. This limit complies with the recommendations of WHO, the US EPA, and Council Directive 98/83/EU [4, 5].

There are several technological approaches to heavy metal removal in the water treatment process: clarification, ion exchange, membrane processes, adsorption, electrochemical processes, and biological methods rapidly developing at present.

Besides coagulation, adsorption is the most widely used method in the water treatment process. Adsorption is a simple (regarding operation), efficient and cost-effective method of heavy metal removal from water using a wide range of adsorbents. Some kinds of natural materials (zeolites) and wastes from industry and agriculture can be used as cost-effective adsorbents. The most frequently tested heavy metal adsorbents are iron oxides and oxyhydroxides, activated alumina, iron hydroxide-coated sand, activated carbon, media coated with TiO2 or MnO2 film on their surface, zeolites, etc. [6-13].

Efficiency of heavy metal removal by adsorption material depends on the following:

a) water pH (see experimental part)
b) oxidation-reduction potential of a given metal in water
c) concentration of substances in water that have a potential to affect (interfere with) adsorption or modify adsorbent surface loading
d) concentration of substances and colloid particles that can physically block the entry into the particle and the access to grains of adsorption media, respectively
e) specific surface area and distribution of pores of adsorption material
f) hydraulic properties of filtration media in treatment

The first four of the above factors are linked by chemical equilibria between the various aqueous species in the water entering the treatment media; the fourth and last two factors are affected primarily by physical mass transfer processes and media properties.

Literature mostly describes the use of iron oxides and oxyhydroxides for arsenic removal from water. A number of experiments and model studies of the adsorption of arsenic and other heavy metals are described in publications [14-22]. These studies describe sorption processes at different pH value, initial heavy metal ion concentration in water, solid/liquid ratio, particle size of a sorption material, filtration rate, temperature and composition of water to be treated (concentration of iron, manganese, phosphorus, silicon, fluorides, sulphates, organic matter, etc.).

The goal of these experiments was to compare the efficiency of adsorption materials E33, GEH, CFH12, and CFH18 for removal of nickel from water. A special asset of this work is that these materials, which were developed for removal of arsenic from water, were tested for removal of nickel from water for the first time.

Material and Methods

Model tests of nickel removal from water were carried out in the laboratory of the University.

Adsorbents

Bayoxide® E33 is a dry, granular, amber-colored iron oxide composite medium consisting primarily of α-FeOOH. It was developed by Severn Trent in cooperation with Bayer AG for removal of arsenic and other contaminants (antimony, cadmium, chromate, molybdenum, selenium, and vanadium) from water. Bayoxide® E33 will adsorb arsenic in preference to these other ions. The advantage of this material is the ability to remove As(III) and As(V). Bayoxide E33 has a capacity to treat water with As concentration of 1×5000 µg/L [23-25]. Under high pH conditions, high levels of vanadium, phosphate (>1.0 mg/L), and silica (>40 mg/L) can present interference and reduce the media’s adsorption capacity for arsenic.

CFH12 and CFH18 are granular sorption materials on the basis of iron hydroxide (FeOOH). They were developed by Kemira Finland as efficient products for removal of arsenic and other contaminants from water by adsorption. The advantage is their high adsorption capacity and higher efficiency at lower costs, providing that the adsorption capacity is fully used (optimum filtration, backwash, and pH). CFH12 and CFH18 have the same composition but different grain size [26-28].

GEH, obtained from the supplier (GEH Wasserechemie GmbH, Germany), is a high-performance adsorbent developed by the Department of Water Quality Monitoring of the University of Berlin for the purpose of arsenic removal from water. GEH consists of ferric hydroxide and oxyhydroxide with dry solid content 57% (±10%) by mass and 43 to 48% by mass moisture content. Iron content is 610 g/kg (±10%) relative to dry solids [29].
The properties of GEH do not vary significantly from study to study. The density of water-saturated GEH (shipped conditions) has been noted as 1.32 g/cm³ [30] and 1.25 g/cm³ [31]. Surface areas of GEH range from 250-300 m²/g, while porosity has been observed at 72-77% [30] and 75 to 80% [31]. GEH is delivered and provided in water-saturated granular form. The grain size of the GEH obtained from the manufacturer range between 0.2-2 mm.

GEH is an adsorbent for water treatment that permits reduction of As content to well below 10 μg/L without changing the water’s characteristic composition. GEH is generally used in bulk form in large-scale adsorption filters but can also be used by end consumers in cartridge-housed systems. Its adsorption capacity is dependent on the characteristics and composition of the water treated as well as the operating conditions.

U.S. EPA (2000) data provided from [30] noted that GEH is sensitive to influent pH, with arsenic adsorption decreasing with increasing pH.

GEH is highly selective toward arsenate, therefore requiring an initial oxidation step in the presence of arsenite [32]. In this paper, adsorption of arsenate occurred much more rapidly at lower pH values, while in higher pH waters adsorption rates were comparable for both arsenate and arsenite GEH is slightly affected by the presence of sulfate and only when influent pH is below 7. Increasing phosphate concentrations in influent water greatly reduced arsenic removal [30].

The basic physical and chemical properties of these commercial sorption materials are listed in Table 1.

Model Filtration System

Filter columns were originally developed for testing nickel removal with granular sorption materials. It was made of glass and consisted of two parts. An internal column (diameter of 2.8 cm) was filled with adsorption material. The adsorption column was cooled by water from the outside in order to ensure stable temperature of the column (external column was used as coolant). The height of the glass column was 78 cm.

Two commercial media (Bayoxide E33 and GEH or CFH12 and CFH18) were tested in parallel on the same influent water source. Sorption materials were added to columns using drinking water to flush the material down into the columns. Columns were backwashed to remove fine particles by operating the column in upflow mode with drinking water until the effluents ran clear.

Water Source and Chemical Spiking

Drinking water from a water supply system was used for the experiment. Certified reference material containing Ni was added to the water (100 L storage tank), the nickel concentration in the case of sorption materials GEH and Bayoxide E33 ranged from 40.4 to 55.8 μg/L; in the case of CFH12 and CFH18 nickel concentrations in the water ranged from 48.4 to 56.5 μg/L. pH of water was modified to various values.

The results of analysis of drinking (raw) water (before spiking) are listed in Table 2.

Analytical Methods

Nickels samples after passing through columns were collected into plastic bottles and immediately acidified with

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>RW</th>
<th>Parameter</th>
<th>Unit</th>
<th>RW</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td></td>
<td>7.52</td>
<td>Ca</td>
<td>mg/L</td>
<td>87.8</td>
</tr>
<tr>
<td>Conductivity</td>
<td>mg/L</td>
<td>58</td>
<td>Mg</td>
<td>mg/L</td>
<td>22.1</td>
</tr>
<tr>
<td>Alkalinity</td>
<td>mmol/L</td>
<td>4.81</td>
<td>Ca+Mg</td>
<td>mmol/L</td>
<td>3.10</td>
</tr>
<tr>
<td>COD (Mn)</td>
<td>mg/L</td>
<td>1.14</td>
<td>Fe total</td>
<td>mg/L</td>
<td>0.04</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>mg/L</td>
<td>24.2</td>
<td>Mn</td>
<td>mg/L</td>
<td>0.012</td>
</tr>
<tr>
<td>NO₃⁻</td>
<td>mg/L</td>
<td>12.6</td>
<td>TOC</td>
<td>mg/L</td>
<td>1.6</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>mg/L</td>
<td>49.7</td>
<td>Soluble substances</td>
<td>mg/L</td>
<td>330</td>
</tr>
</tbody>
</table>
highly pure nitric acid (Merck). All bottles were submerged in 10% nitric acid solution over 3 days and triple rinsed with de-ionized water. Agilent 7500CE ICP-MS (ORS technology) was used to determine nickel concentration in solution. The detection limit for Ni by ICP-MS was 2 μg/L.

Results and Discussion

pH Effect

In the first stage of model tests, the efficiency of the sorption materials GEH, CFH12, and Bayoxide E33 was monitored in the nickel removal process in dependence on water pH (8.18, 7.53, 7.01, and 6.54) and filtration rate (from 6.62 to 6.91 m/hour and from 4.38 to 4.58 m/hour) for the same ratio of filtered water volume to filter bed volume V/V₀ (BV).

The efficiency of nickel removal is shown in Figs. 1 and 2, including the concentrations of nickel in raw water and the values measured after passing through the tested filter materials (filter media height 20 cm), depending on pH, filtration rate, and volume of filtered water.

Figs. 1 and 2 show that the most suitable material for removal of nickel is Bayoxide E33, which can be used for water with wide pH range (6.54 to 8.18), but its efficiency increases with decreasing pH value of water. Material CFH12 achieved the best result in pH 7, for GEH material was the most effective area of water pH 7.5 (at pH 6.5 we achieved the lowest efficiency).

Laboratory Column Test

In the following stage of experiments, the efficiency of nickel removal from water using the sorption materials GEH, CFH12, CFH18, and Bayoxide E33 was monitored for filtration rates in the range 5.84-5.89 m/hour, and the height of filter media in the column of 58 cm. The concentration of nickel in raw water was in the range 40 to 56 μg/L, the temperature of raw water was in the interval from 9 to 14ºC, and the water pH was adjusted to 7.0. The filtration conditions are shown in Table 3.

Fig. 3 shows the nickel concentrations at the outlets from the adsorption column in dependence on the ratio V/V₀.

Fig. 4 shows adsorption capacity of the nickel and the values of the V/V₀ ratio for individual adsorption materials when the limit concentration of nickel (20 μg/L) was achieved at the outlets of media.

According to the obtained results presented in Figs. 3 and 4, it can be stated that Bayoxide E33 is the most suitable for nickel removal as compared to other tested sorption materials. For Bayoxide E33, the nickel concentration of 20 μg/L at the outlet of the media with a height of 58 cm was reached for the ratio V/V₀=4808. The value for CFH12 was V/V₀=1409, for CFH18 V/V₀=3007, and for GEH V/V₀=3218. In these conditions the adsorption capacity for

Table 3. Filtration conditions.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>E33</th>
<th>CFH12</th>
<th>CFH18</th>
<th>GEH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grain size [mm]</td>
<td>0.5-2.0</td>
<td>0.5-2.0</td>
<td>0.8-1.8</td>
<td>0.32-2.0</td>
</tr>
<tr>
<td>Medium height [cm]</td>
<td>58</td>
<td>58</td>
<td>58</td>
<td>58</td>
</tr>
<tr>
<td>Volume of adsorption column [cm³]</td>
<td>357.14</td>
<td>357.14</td>
<td>357.14</td>
<td>357.14</td>
</tr>
<tr>
<td>Mass of sorption material [g]</td>
<td>354</td>
<td>470</td>
<td>435</td>
<td>418</td>
</tr>
<tr>
<td>Average concentration Ni in raw water [μg/L]</td>
<td>48.5</td>
<td>51.1</td>
<td>51.1</td>
<td>48.5</td>
</tr>
<tr>
<td>Average flow-through column [ml/min]</td>
<td>60.39</td>
<td>60.25</td>
<td>60.12</td>
<td>60.08</td>
</tr>
<tr>
<td>Average filtration rate [m/hour]</td>
<td>5.885</td>
<td>5.871</td>
<td>5.858</td>
<td>5.854</td>
</tr>
<tr>
<td>Empty bed contact time (EBCT) [min]</td>
<td>5.914</td>
<td>5.928</td>
<td>5.940</td>
<td>5.944</td>
</tr>
<tr>
<td>Total filtration time [hour]</td>
<td>497</td>
<td>480</td>
<td>480</td>
<td>497</td>
</tr>
<tr>
<td>Total amount of water passed through filtration column [m³]</td>
<td>1.798</td>
<td>1.715</td>
<td>1.724</td>
<td>1.789</td>
</tr>
</tbody>
</table>
Bayoxide was 198.4 μg/g, CFH18 107.5 μg/g, GEH 97.5 μg/g, and CFH12 38.1 μg/g.

According to the material balance of nickel in these experiments, Fig. 5 shows the amount of adsorbed nickel depending on the V/V₀ ratio, as well as the amount of adsorbed nickel in adsorption media when the limit concentration Ni (20 μg/L) was achieved at the outlets from the adsorption column (Fig. 6).

Within the framework of experiments, chemical composition of used sorption materials was determined by the Institute of Inorganic Chemistry of the Faculty of Chemical and Food Technology at Slovak University of Technology using the methods of X-ray microanalysis, SEM, and X-ray phase analysis. The values are listed in Table 4 and shown in Figs. 7-9.

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**Fig. 3.** Progress of nickel concentration at the outlets of the adsorption media CFH12 and CFH18 (A) or GFH and Bayoxide E33 (B), depending on the ratio V/V₀ (filtration media height 58 cm, filtration rate 5.84-5.89 m/hour)

**Fig. 4.** Adsorption capacity of nickel and the values of V/V₀ ratios for limit concentration Ni (20 μg/L) at the outlet of adsorption media.

**Fig. 5.** Amount of adsorbed Ni in adsorption media in dependence on filtration time.

**Fig. 6.** Amount of adsorbed nickel in sorption materials when the limit concentration 20 μg/L of Ni at the outlet from the columns was reached.
Table 4. Chemical composition of sorption materials.

<table>
<thead>
<tr>
<th>Material</th>
<th>MgO</th>
<th>Al₂O₃</th>
<th>SiO₂</th>
<th>P₂O₅</th>
<th>SO₃</th>
<th>K₂O</th>
<th>CaO</th>
<th>TiO₂</th>
<th>Fe₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>E33</td>
<td>0.97</td>
<td>6.59</td>
<td>12.75</td>
<td>0.34</td>
<td>0.31</td>
<td>0.37</td>
<td>2.01</td>
<td>0.91</td>
<td>75.28</td>
</tr>
<tr>
<td>CFH12</td>
<td>3.75</td>
<td>0.45</td>
<td>1.18</td>
<td>-</td>
<td>8.49</td>
<td>0.27</td>
<td>2.72</td>
<td>0.50</td>
<td>82.65</td>
</tr>
<tr>
<td>CFH18</td>
<td>5.19</td>
<td>0.48</td>
<td>1.47</td>
<td>0.28</td>
<td>4.58</td>
<td>-</td>
<td>1.41</td>
<td>0.30</td>
<td>86.29</td>
</tr>
<tr>
<td>GFH</td>
<td>-</td>
<td>1.74</td>
<td>3.05</td>
<td>0.21</td>
<td>0.54</td>
<td>0.08</td>
<td>0.18</td>
<td>-</td>
<td>91.92</td>
</tr>
</tbody>
</table>

Fig. 7. X-ray spectra and SEM picture surface of the sample Bayoxide E33.

Fig. 8. X-ray spectra and SEM picture surface of the sample GFH.

Fig. 9. X-ray spectra and SEM picture surface of the sample CFH12.
Conclusions

Laboratory tests of nickel removal from drinking water were performed at the Department of Sanitary and Environmental Engineering. The results proved that the new sorption materials have a capacity to reduce the content of nickel in water to values that meet the requirements set under Slovak Government Regulation No. 496/2010 on drinking water.

Based on the laboratory tests, the most suitable adsorbent for nickel removal is Bayoxide E33. However, its effectiveness increases with decreasing water pH. For this material it is better to treat the water at lower pH, i.e. 6.5 to 7.5.

According to the model tests (concentration of nickel in raw water of about 50 µg/L, filtration rate 5.8 m/hour, concentration Ni 20 µg/L at the outlet of media with a height of 58 cm, pH 7.0), the adsorption capacity of nickel for Bayoxide E33 was set to 198 µg/g and V/V0 ratio = 4808.

The results proved that the materials CFH12, CFH18, and GEH can also be used to decrease the concentration of Ni in drinking water below the limit value of 20 µg/L (Government Regulation No. 496/2010). However, the pH value of water affects the efficiency of nickel removal. In the case of CFH12 the best results were obtained at pH=7.5. The highest efficiency of GEH was reached at water pH above 7.5. The adsorption capacities and V/V0 ratio are lower for these sorption materials.

Acknowledgements

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