Influence of mining operations to presence of antimony in water source Dúbrava and possibilities of its removal

Ján Ilavský\(^1\), Danka Barloková and K. Munka\(^2\)

Abstract: The aim of this study was to verify sorption properties of some filtration materials for removal of antimony (Bayoxide E33, GEH, CFH12, CFH18) from the Dúbrava groundwater resource and compare their efficiency. Experiments have proved that the tested sorption materials can be used for reduction of antimony content in water to meet the values set under the Government Regulation No. 496/2010 on drinking water – 5 µg.l\(^{-1}\). The most suitable material for removing antimony from water was GEH.

Key words: drinking water, filtration, sorption materials, removal of antimony, water treatment

Introduction

The Dúbrava water supply resource is situated in the western part of the Low Tatras Mountain Range (Fig. 1). Geological and hydrogeological conditions of this region are very complex where the water of crystalline and Mesozoic basements is interconnected. Higher antimony concentration in the sources of water for the water supply occur mainly due to existence of the antimony deposit in Dúbrava (Sb content in ore varies from 1.5 to 5.0%) and its higher content in granitoids of this part of the Low Tatras Region. In the middle of 18th century antimony ore mining started in this site. Until the end of antimony mining in 1993 deposit Dúbrava was one of the most important producers of Sb in Czechoslovakia. Since 1753 were mined 1046 kt antimony ore, the total mined ore contained 27 kt of antimony. Moreover, the concentration of antimony in mining water was considerably increased at relatively high capacities of wells. Adverse effect comes from the mine tailing piles and sludge lagoon where the rocks rich in antimony were continually washed by the rainwater infiltrating into the groundwater resources or flowing into the surface stream of Križianky. Contaminated water of the Križianka River and water of its alluvial deposits has deteriorated water quality in the springs of Močidlo and Brdáre. In the past, three springs of the Dúbrava water resource (Brdáre, Močidlo, Škripaň) were used for supplying population with drinking water, but today only one spring is used for this purpose (spring Škripaň that does not contain antimony).

Fig. 1 Deposits of antimony ore in Slovakia.

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According to the water quality monitoring data provided by the Water Company of the Region of Liptov, the selected water quality parameters for the separate springs of the Dúbrava water resource are shown in Table 1. The highest contamination from antimony was observed in the water from the Brdáre spring, where the concentrations ranged from 80.3 to 91.3 µg/L. The concentration of antimony in the water from the Močídlo spring was 70.6-82.0 µg/L. Obviously, the best water quality was monitored in the Škripeň spring, where the concentration of antimony was lower than 1 µg/L in every sample taken during the monitoring period. No other heavy metals were present in the Dúbrava water resource.

Tab. 1. Water quality of the Dúbrava water supply resource according to selected parameters for the period 2000-2005.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Močídlo</th>
<th>Škripeň</th>
<th>Brdáre</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>7.65-7.90</td>
<td>7.55-7.95</td>
<td>7.75-7.95</td>
</tr>
<tr>
<td>Alkalinity [mmol/L]</td>
<td>1.7-3.8</td>
<td>1.8-3.8</td>
<td>1.7-2.2</td>
</tr>
<tr>
<td>Conductivity [mS/m]</td>
<td>23.1-38.6</td>
<td>23.0-42.6</td>
<td>22.5-28.7</td>
</tr>
<tr>
<td>Ca²⁺ [mg/L]</td>
<td>30-54</td>
<td>48-52</td>
<td>28-32</td>
</tr>
<tr>
<td>Mg²⁺ [mg/L]</td>
<td>8.5-28.0</td>
<td>15.8-24.3</td>
<td>9.7-15.8</td>
</tr>
<tr>
<td>Sb [µg/L]</td>
<td>70.6-82.0</td>
<td>&lt; 1.0</td>
<td>80.3-91.3</td>
</tr>
</tbody>
</table>

During the pilot tests (2009-2011) was evaluated quality of raw water (Brdáre spring) and were determined concentrations of several other parameters: Cl⁻ [mg/L] 7.2-10.6, NO₃⁻ [mg/L] 2.8-3.4, SO₄²⁻ [mg/L] 10.2-18.6, F⁻ [mg/L] 0.01-0.12, PO₄³⁻ [mg/L] 0.01-0.08, Fe [mg/L] 0.01-0.04.

Antimony is a toxic heavy metal with effects similar to arsenic and lead. Intoxication with antimony is not as severe as in the case of arsenic because the compounds of antimony are absorbed slowly. Antimony is an inhibitor for some enzymes, has an effect on the metabolism of proteins and carbohydrates, and causes a failure of glycogen production in kidneys. Its ability to accumulate in bodies of organisms is low. Findings on health aspects related to the occurrence of some heavy metals in drinking water are summarized in publication [1,2].

Thus far, the World Health Organization (WHO) and institutes dealing with the monitoring of carcinogenic effects have not classified antimony as a carcinogen.

The limit concentration of antimony in drinking water in Slovakia is 5 µg/L [3]. This limit value is in accordance with the WHO Recommendations [4] and the EU Directive [5].

Antimony is present in water as Sb³⁻, Sb⁰, Sb³⁺ and Sb⁵⁺ (Sb³⁻ is ten times more toxic than Sb⁵⁺), depending on the pH of the water, the oxidation-reduction potential (Sb³⁻/Sb⁵⁺ ratio) and the oxygen content. The most common form is antimonate – oxyanion (H₂SbO₄⁻) and (HSbO₄)²⁻ or it can be present as antimonite (H₃SbO₃). The organic form of antimony is very rare, especially in drinking water [6,7].

There are several technological methods for the removal of heavy metals in water treatment: precipitation (clarification), ion exchange, membrane technologies, adsorption, electrochemical processes and recently also biological methods [8-11].

The current research dealing with the removal of heavy metals via adsorption is aimed at the use of natural materials as well as industrial and agricultural wastes, which can represent cost-effective sorbents [12].

At present, adsorption by iron oxides and oxihydroxides represents an efficient and cost-effective method for the removal of heavy metals from water. A number of experiments and model studies related to heavy metals adsorption are described in publications [13-24]. These studies describe sorption processes at different pH values, the initial concentrations of heavy metal ions in solutions, the solid/liquid ratio, the temperature and the composition of the treated water.

2. Material and methods

2.1 Properties of sorption materials

The objective of this work was to compare the effectiveness of the removal of antimony from the Dúbrava water source with water filtration using the sorption media GEH, CFH12, CFH18 and Bayoxide E33, on the sorption media which, according to the literature, are most often used to remove arsenic from water. Their basic physical and chemical properties are shown in Table 2.
Tab. 2. Physical and chemical properties of selected sorption materials

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Bayoxide E33</th>
<th>CFH12 and CFH18</th>
<th>GEH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Matrix/Active agent</td>
<td>Fe₂O₃&gt;70% and 90,1% α-FeOOH</td>
<td>FeOOH</td>
<td>FeO(OH)₂ and 52-57% β-FeOOH</td>
</tr>
<tr>
<td>Physical Form</td>
<td>dry granular</td>
<td>dry granular</td>
<td>moist granular</td>
</tr>
<tr>
<td>Color</td>
<td>amber</td>
<td>brown-red</td>
<td>dark brown</td>
</tr>
<tr>
<td>Bulk density [g/cm³]</td>
<td>0.45</td>
<td>1.12-1.2</td>
<td>1.22-1.32</td>
</tr>
<tr>
<td>Specific Surface Area [m²/g]</td>
<td>120-200</td>
<td>120</td>
<td>250-300</td>
</tr>
<tr>
<td>Grain Size [mm]</td>
<td>0.5-2.0</td>
<td>0.3-2.5 or 0.8-1.8</td>
<td>0.32-2.0</td>
</tr>
<tr>
<td>Grain porosity [%]</td>
<td>85</td>
<td>72-80</td>
<td>72 - 80</td>
</tr>
</tbody>
</table>

Bayoxide® E33 is a dry, granular amber-coloured iron oxide composite medium, consisting primarily of α-FeOOH. It was developed by Severn Trent in cooperation with Bayer AG for the removal of arsenic and other contaminants (antimony, cadmium, chromate, molybdenum, selenium and vanadium) from water. Bayoxide® E33 prefers to adsorb arsenic from these other ions. The advantage of this material is its ability to remove As³⁺ and As⁵⁺ too. Bayoxide® E33 has a capacity to treat water with As concentration of 11÷5000 µg/L [25,26].

CFH12 and CFH18 are granular sorption materials based on iron hydroxide (FeOOH). They were developed by Kemira Finland as efficient products for the removal of arsenic and other contaminants from water by adsorption. The advantage is their high adsorption capacity and higher efficiency at a lower cost, provided that the adsorption capacity is fully used (optimum filtration, backwash and pH). CFH 12 and CFH18 differ from each other by their grain size and chemical composition (Tab. 3) [27,28].

Tab. 3. Chemical composition of selected sorption materials.

<table>
<thead>
<tr>
<th>Material</th>
<th>Compound in mass [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MgO</td>
</tr>
<tr>
<td>E33</td>
<td>0.97</td>
</tr>
<tr>
<td>CFH12</td>
<td>3.75</td>
</tr>
<tr>
<td>CFH18</td>
<td>5.19</td>
</tr>
<tr>
<td>GEH</td>
<td>-</td>
</tr>
</tbody>
</table>

The GEH was obtained from the supplier (GEH Wasserchemie GmbH, Germany). GEH is a high-performance adsorbent developed by the Department of Water Quality Monitoring of the University of Berlin for the purpose of removing arsenic from water. GEH consists of ferric hydroxide and oxyhydroxide with a dry solid content of 57% (±10%) by mass and 43 to 48% by mass moisture content. Its iron content is 610 g/kg (±10%) relative to the 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]. The 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 a water saturated, granular form. The grain size of the GEH obtained from the manufacturer ranges from 0.32 - 2 mm.

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

2.2 Model Filtration System

The pilot tests for removing antimony were carried out at the Dúbrava chlorination plant (Fig. 2). At present, only water from the Škripeň well is conveyed into the storage tank of the chlorination plant. After disinfection, the water is gravitationally distributed to the point of consumption. For the purpose of these simulation tests, there was a need to convey the water from the Brdáre well to the chlorination plant through a separate pipe in order to avoid mixing it with the water from the Škripeň well.
The model tests were divided into two parts. The first part of the model tests was focused on the monitoring of antimony concentrations along the heights (20, 45, 70 and 87 cm) of the adsorption media CFH12 and Bayoxide E33, which were contained in two experimental stainless columns (inner diameter of 35 mm, total height of 120 cm), and the second part of the model tests aimed at the monitoring of the adsorption of antimony using GEH and CHF18 in the same stainless columns. The samples of the treated water were taken from the stainless columns at heights of 20, 45 and 70 cm of the adsorption media and above the adsorption bed, i.e., at the outlet of the treated water. Raw water flowed through the filter system in a bottom-up direction. At the same time, the flow rate at the outlet of each sampling point and the antimony concentration in the samples were monitored.

3. Results and discussion

3.1 Model tests (CFH12, Bayoxide E33)

During the model tests, the antimony concentrations in raw water were in a range of 55 to 62 µg/L (an average of 58.3 µg/L). The filtration rates in the two experimental stainless columns were 4.4 – 4.5 m/h for Bayoxide E33 and 4.1 – 5.6 m/h for CFH12. Figure 3 shows the antimony concentration curves along the height of the CFH12 and Bayoxide E33 media, depending on the on the V/V₀ ratio (bed volume), where “V” is the volume of treated water flowing through at a given time and “V₀” is the volume of the bed.

![Fig. 3. Antimony concentration curves along the height of the CFH12 (left) and Bayoxide E33 (right) media in relation to the bed volume.](image-url)
The results show that the antimony concentration reached the value of 5 µg/L for the media height of 45 cm at the bed volume 250 for both materials. For the 70 cm high adsorption media, the same concentration was reached at the bed volume 650 for CFH12 and the bed volume 720 for Bayoxide E33. Since the model tests of the antimony removal in these two columns had been finished before the antimony concentration in treated water reached the limit value (5 µg/L), the bed volumes were calculated by an extrapolation of the results obtained. When considering the media height of 87 cm, the concentration of antimony would meet the limit value at the bed volume 1350 for CFH 12 and at the bed volume 1750 for Bayoxide E33 (Fig. 4).

Fig. 4. Movement of the adsorption wave (5 µg/L) along the height of the adsorption media CFH12 and Bayoxide E33 in relation to the bed volume (left) or the filtration time (right).

For the above-mentioned antimony concentrations in raw water and the filtration rates, the time of the wave breakthrough with an antimony concentration of 5 µg/L reached 1.90 hours for CFH 12 and 1.34 hours for Bayoxide E33 (media height of 20 cm). For the media height of 45 cm it was 57.7 hours for CFH 12 and 45.4 hours for Bayoxide E33. For the media height of 70 cm it was 120.5 hours for CFH 12 and 140 hours for Bayoxide E33. When considering the media height of 87 cm, the breakthrough wave with the limit concentration would occur after 228 hours for CFH12 and after 318 for Bayoxide E33.

Figure 5 show the amounts of adsorbed antimony along the height of the adsorbents CFH12 and Bayoxide E33 in relation to the bed volume, and the calculated equations of linear regression if we will assume that these curves have a linear progress.

Fig. 5. A comparison of the amount of antimony adsorbed along the height of the CFH12 (left) and Bayoxide E33 (right) depending on the bed volume.
The mass balance of the antimony adsorption for the separate adsorbent layers shows the following results for CFH12: out of the total adsorbed antimony, 49.2 % was adsorbed in the layer of 0-20 cm; 31.4 % in the layer of 20-45 cm; 14.4 % in the layer of 45-70 cm and only 5.0 % in the layer of 70-87 cm. The mass balance of the antimony adsorption for the separate adsorbent layers shows the following results for Bayoxide E33: out of the total adsorbed antimony, 58.6 % was adsorbed in the layer of 0-20 cm; 27.4 % in the layer of 20-45 cm; 8.9 % in the layer of 45-70 cm and only 5.1 % in the layer of 70-87 cm (Fig. 6). The results show that the sorption capacity of the adsorbents was not exhausted.

![Fig. 6](image1.png) ![Fig. 7](image2.png)

**Fig. 6.** A comparison of the percentage of the total Sb adsorbed in the separate layers of CFH12 and E33.

**Fig. 7.** Average adsorption capacity at different heights of CFH12 and Bayoxide E33 (in µg/g).

Figure 7 presents the adsorption capacities of the separate layers for CFH12 and Bayoxide E33 as well as the adsorption capacities for the whole volume of the media. As the mass balance of both adsorption materials demonstrated no significant difference in the adsorbed amounts of antimony in the separate layers of the media, the more than 2 times higher adsorption capacity of Bayoxide E33 over CFH12 was caused by the 2.5 times lower apparent density of Bayoxide E33 (0.45 g/cm³ and 1.12 g/cm³, respectively). The lower effectiveness of the Sb removal by CFH12 was caused by the higher mass and hydraulic loading rates of this material during the filtration process as well as by its higher granularity.

### 3.2 Model tests (GEH, CFH18)

During the model tests, the antimony concentrations in the raw water were in a range from 78.4 to 108 µg/L (an average of 90.3 µg/L). This represents an increase of more than 60% when compared to the first stage. The filtration rates in the stainless steel column containing GEH were between 5.6 and 5.9 m/h (average of 5.7 m/h). The filtration rates in the second column containing CFH18 were slightly higher in the range of 5.7-6.1 m/h (average of 5.9 m/h). The total height of the GEH and CFH18 media was 91 cm and 94 cm respectively. Figure 8 shows the antimony concentration curves along the height of the GEH and CFH18 media, depending on the bed volume.

These dependencies indicate that the antimony concentration reached the value of 5 µg/L for the media height of 45 cm at 541 the bed volume for GEH, and at 169 the bed volume for CFH18, for the 70 cm high GEH media at the bed volume 1788 and for CFH18 at the bed volume 473, for the 91 cm high GEH media the concentration of antimony did not exceed the limit value of 5 µg/L during the operation of the filtration system (403 hours). With regard to the CFH18 (media height of 94 cm), the limit value was exceeded after 175 hours of operation at the bed volume 1103. The concentration of antimony in the water treated by GEH would reach the limit value under the same conditions after 672 hours of operation at the bed volume 4256 (the values were calculated using an extrapolation of the results obtained).

For the above-mentioned antimony concentrations in the raw water and relevant filtration rates, the time of the adsorption wave breakthrough with an antimony concentration of 5 µg/L was 86 hours for GEH and 26 hours for CFH18 at a media height of 45 cm, while for the 70 cm high media, it was 285 hours (GEH) and 74 hours (CFH18).
Fig. 8. Antimony concentration curves along the height of the GEH (left) and CFH18 (right) media, depending on the bed volume.

The movement of the adsorption wave with the limit concentration (5 µg/L) in different layers of the GEH and CFH18, depending on the time of operation and bed volume, is shown in Figure 9. The figures indicate a significant difference in the effectiveness of the sorption materials.

Fig. 9. The movement of the adsorption wave with a concentration of 5 µg/L along the height of the media GEH and CFH18, depending on the filtration time (left) or the bed volume (right).

Figure 10 shows the amounts of adsorbed antimony along the height of the media GEH and CFH18 in relation to the bed volume, and the calculated equations of linear regression if we will assume that these curves have a linear progress.

The mass balance of the antimony adsorption for the different layers of GEH shows that out of the total antimony 40.9% was adsorbed in the layer of 0-20 cm; 40.6% in the layer of 20-45 cm; 15.5% in the layer of 45-70 cm and only 3.0% in the layer of 70-91 cm. The mass balance of the antimony adsorption for the different layers of CFH18 shows that out of the total antimony 31.5% was adsorbed in the layer of 0-20 cm; 41.3 % in the layer of 20-45 cm; 17.8 % in the layer of 45-70cm, and more than 9.6 % in the layer of 70-94 cm (Fig. 11).

Figure 12 shows the average adsorption capacities for the different layers of GEH and CFH18 as well as the adsorption capacities for the whole volume of the sorption media. The results indicate that the adsorption capacities and the amount of antimony adsorbed in some layers of the media are higher for GEH.

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The mass balance of both adsorbents (Fig. 11) and the comparison of the percentage amount of the adsorbed antimony as well as the average adsorption capacities in the different layers of the media (Fig. 12) indicate that there was no significant difference between GEH and CFH18. This is in contrast to the development of the antimony concentration at the outlets of the GEH and CFH18 media, depending on the bed volume (Fig. 8). A significantly higher effectiveness of the antimony removal from the water using GEH can be seen in Figure 9. The figures show the movement of the adsorption wave (5 µg/L) in the different layers of GEH and CFH18 in relation to the filtration time and bed volume.

This difference was caused by the higher mass and hydraulic loading rates (filtration rate, EBCT) and the total height of the CFH18 media. The CFH18 and GEH columns were overloaded in the first two zones (0-20 cm, 20-45 cm), which was demonstrated by the approaching or intersecting curves of these dependencies for the first and second zones (Fig. 10).

The results show that the volumetric loading rate of the GEH and CFH18 columns in the second model tests (loading = 9.2-11.7 µg/L.min) was higher by 100 percent compared to the loading of CFH12 and Bayoxide E33 during the first model tests (loading = 4.5-6.7 µg/L.min). The relationship between the amount of antimony adsorbed by the CFH12 and Bayoxide E33 and the filtration rate indicates that these adsorption media were not overloaded at the above volumetric loading rates (no approaching or intersection of the curves of these
dependencies for the first and second zones of the adsorption media was observed). The same can also be concluded for the GEH and CFH18 sorption materials (when operating under the same loading as the above mentioned materials), since they are more efficient sorption materials than media CFH 12 and Bayoxide E33.

4. Conclusion

The technological tests of the groundwater from the spring in the locality of Dúbrava proved that new iron-based sorption materials GEH, CFH12, CFH18 and Bayoxide E33 can help reduce the concentration of antimony in water below the limit of 5 µg/L (RG of the Slovak Republic No. 496/2010 on Drinking Water).

The model tests were aimed at monitoring the sorption properties of adsorbents along the height of media. The results of the tests showed that the GEH adsorbent is the best material for the removal of antimony from water. For the antimony concentration of 78.4 -108.0 µg/L in raw water (average of 90.3 µg/L) and a filtration rate of 5.6-5.9 m/h, the limit concentration of 5 µg/L at the outlet of the 45 cm high adsorption media was reached at the bed volume 541, at the outlet of the 70 cm high adsorption media was reached at the bed volume 1788. In a case where the media height was 91 cm, the antimony concentration in the treated water would reach the limit value of 5 µg/L after 672 hours of operation at the bed volume 4256. Under these conditions, the adsorption capacity was calculated at 184 µg/g. The adsorption capacities and bed volumes of the other materials used in the test (CFH12, CFH18 and Bayoxide E33) were lower in comparison to GEH.

The effectiveness of sorption materials is expressed their adsorption capacity, but in the cases of use of sorbents with different bulk densities Table 2 is not correct, and the effectiveness of sorption would be suitable to express by using of the bed volume.

The composition of the water from the Brdáre spring had no adverse effects on the adsorption materials. During the model tests of the antimony removal using the above adsorbents, no higher concentrations of iron exceeding the limit for drinking water were measured in the water after the treatment process. Moreover, no effect on the pH value of the treated water was observed when the water from the Brdáre spring passed through the adsorption media.

In the case of increased water demand in the region of Liptovský Mikuláš, it is recommended that water from the Dúbrava resource be treated by using two serial closed filters containing GEH at a filtration rate below 4.5 m/h.

According to the results obtained in the model tests of the antimony removal using the selected adsorption materials, it can be concluded that GEH is the most suitable adsorption material for antimony removal from less contaminated small water resources. The advantage of this technology is the treatment of water directly in a water resource. It is a simple, safe and efficient method of removing antimony from water.

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References

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