READ-As and GEH sorption materials for the removal of antimony from water

Ján Ilavský, Danka Barloková, Pavol Hudec and Karol Munka

ABSTRACT

The objective of this work was to verify the sorption properties of granular filter materials (GEH, READ-As) during the process of removing antimony from water. The pilot tests showed that the use of sorption materials could possibly decrease the antimony content in water to the values limited for drinking water (5 μg/L Sb). A more suitable adsorbent for removing antimony was READ-As. At a concentration of antimony in raw water ranging from 21.5 to 31.1 μg/L, a filtration rate of 5.58 m/h, the value of the bed volume of 3,967, and the adsorption capacity of 128.4 μg/g, which was achieved at a breakthrough concentration of 5 μg Sb/L, were determined. The surface characteristics of the sorption materials used through the physical adsorption of nitrogen, mercury porosimetry, X-ray microanalysis, and scanning electron microscopy (SEM) were studied.

Key words | drinking water, filtration, removal of antimony, sorption materials, surface properties of materials

INTRODUCTION

The Dúbrava group water supply system in Slovakia was built in connection with the construction of the Liptovská Mara Water Reservoir. The group water supply system was supplied with water from the Dúbrava water resource (capacity of about 40 L/s). The water resource included three springs (Brdáre, Močidlo, and Škripeň). Škripeň is currently the only spring used for the drinking water supply, since it contains no antimony. The two other springs are contaminated with antimony.

A deposit of antimony ore is considered to be the main cause of the increased antimony concentrations in the springs of Močidlo and Brdáre. Furthermore, a high concentration of antimony in water from mining activities as well as from rain falling on antimony-rich waste rock piles and a sludge-settling pond has led to higher concentrations of antimony in the relevant water resources.

Antimony is present in water as Sb(III) and Sb(V), depending on the water pH, the oxidation-reduction potential, the Sb(III)/Sb(V) ratio and the concentration of oxygen. It is found mainly in the form of antimonate as oxyanions (H₂SbO₄)⁻ and (HSbO₄)²⁻ or it can be present in the form of antimonite (H₃SbO₃) (WHO 2003).

Antimony is a toxic heavy metal with effects similar to those of arsenic and lead. Intoxication by antimony is not as severe as that from arsenic, since the antimony compounds are absorbed more slowly. Findings on the health aspects of certain heavy metals in drinking water are included in several publications (AWWA 1990; US EPA 1984). The World Health Organization (WHO) and institutions dealing with the monitoring of carcinogenity have not yet classified antimony as a carcinogen.

In Slovakia, an acceptable concentration of heavy metals in drinking water is defined under Government Regulation No. 496/2010 on drinking water. The limit concentration for antimony is 5 μg/L. This limit value is in accordance with the WHO recommendations (WHO 2011) and EU Directive (98/85/EC 1998).

There are several technological methods for removing heavy metal in the water treatment process: precipitation,
ion exchange, membrane processes, adsorption, electrochemical processes, and biological methods.

Adsorption using an appropriate sorption material is preferred for water treatment when considering small water resources. Sorption is a simple (regarding its operation) and effective method of heavy metal removal, mainly because of the wide range of sorption materials that can be used in this process. The most frequently tested sorbents are as follows: iron oxides and oxyhydroxides, activated alumina, sand covered by iron hydroxide, and media containing TiO₂ or MnO₂ layers on their surface, etc. (Bailey et al. 1999).

There are very few references related to the removal of antimony from water by sorption materials. The literature mostly describes the use of iron oxides and oxyhydroxides for the removal of arsenic from water. A number of experiments and model studies on the adsorption of arsenic and other heavy metals are described in various publications (Jekel & Seith 2000; US EPA 2003; Rubel 2003; Sperlich et al. 2005; Mohan & Pittman 2007; Westerhoff et al. 2008; Guan et al. 2008; Zeng et al. 2008; Nguyen et al. 2011). These studies describe sorption processes at different pH values, the initial heavy metal ion concentrations in water, the solid/liquid ratio, the particle size of a sorption material, and the temperature and composition of the water to be treated (concentration of iron, manganese, phosphorus, silicon, fluorides, sulfates, organic matter, etc.).

The objective of this work was to verify the sorption properties of granular filter materials (GEH, READ-As) in the Dúbrava water resource during the process of removing antimony from the water.

## MATERIALS AND METHODS

### Properties of sorption materials

The GEH was obtained from a supplier (GEH Wasserchemie, Osnabrück, Germany). GEH is a sorption material developed by the Chair of Water Quality Control at the Technical 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 43–48% by mass moisture content, GEH is not regenerated (Driehaus et al. 1998; GEH Wasserchemie, 2014). GEH is highly selective toward arsenate; therefore, it requires an initial oxidation step in the presence of arsenite. Increasing phosphate and sulfate concentrations in influent water greatly reduces arsenic removal (Driehaus et al. 1998).

READ-As was obtained from S-Metalltech. It was developed by Nihon Kaisui Co., Ltd in Japan. READ-As is a granular hydrous cerium oxide adsorbent (88% CeO₂ and 12% ethylene-vinyl alcohol copolymer), which displays a high degree of selectivity for arsenic ions under a broad range of conditions and effectively adsorbs both arsenite and arsenate. The oxidation of arsenite to arsenate is not needed for arsenic removal nor is an adjustment of the pH required before or after treatment. This material can be regenerated by the addition of 25% sodium hydroxide, then 12% sodium hypochlorite solution and finally, washing with water. Regenerated material needs neutralization with 35% HCl and has to be washed with water before using.

Depending on the amount of the adsorbent and the water chemistry, the regeneration of the adsorbent saturated with arsenic should be accomplished in 4–12 months. The sorbent can be used for eight to 14 regeneration cycles. This waste material is not hazardous (Shin Nihon Salt Co., Ltd 2000; Jain & Singh 2012; S-Metalltech 2014).

Table 1 includes the basic physical–chemical properties of the materials used in the test.

### Characterization techniques

The textural properties of the sorption materials were studied through the physical adsorption of nitrogen at the temperature of liquid nitrogen (−197 °C) by the volumetric method using ASAP 2400 (Micromeritics). The samples were activated

<table>
<thead>
<tr>
<th>Parameter</th>
<th>READ-As</th>
<th>GEH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Matrix/active agent</td>
<td>CeO₂·nH₂O</td>
<td>Fe(OH)₃ + 52-57% β – FeOOH</td>
</tr>
<tr>
<td>Physical form</td>
<td>Moist granular</td>
<td>Moist granular</td>
</tr>
<tr>
<td>Color</td>
<td>Yellow</td>
<td>Dark brown</td>
</tr>
<tr>
<td>Bulk density (g/cm³)</td>
<td>0.76</td>
<td>1.22-1.29</td>
</tr>
<tr>
<td>Grain size (mm)</td>
<td>0.3–1.0</td>
<td>0.32–2.0</td>
</tr>
</tbody>
</table>
The adsorption data were processed using a standard Brunauer–Emmett–Teller (BET)-isotherm with the linearization in the range of $0.05 \leq p/p_0 \leq 0.3$ (specific surface area $S_{BET}$). The desorption branches of the isotherms were used for calculating the pore size distribution by the standard Barrett-Joyner-Halenda (BJH) method (maximum on the pore size distribution curve $R_p$). The total pore volume ($V_a$) was estimated from the nitrogen-adsorbed quantity at a relative pressure of $p/p_0 = 0.99$.

The meso-macroporous texture was verified by mercury porosimetry using AutoPore IV 9500 (Micromeritics).

The sorption materials were analyzed with a Jeol JXA-840A X-ray microanalyzer using the energy dispersive spectroscopy (EDS) system. The samples were evaporated with a thin carbon layer to ensure their electrical conductivity. The quantitative analysis of every sample was determined in three different areas, and the mean value was then calculated. The microstructure was observed by scanning electron microscopy (SEM, TESLA BS 300).

**Table 2 | Results of RW analysis (analysis of some selected parameters)**

<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>8.2</td>
<td>Fe total</td>
<td>mg/L</td>
<td>0.06</td>
</tr>
<tr>
<td>Conductivity</td>
<td>mS/m</td>
<td>22.4</td>
<td>Mn</td>
<td>mg/L</td>
<td>0.001</td>
</tr>
<tr>
<td>Alkalinity (ANC)</td>
<td>mmol/L</td>
<td>2.871</td>
<td>Ca$^{2+}$</td>
<td>mg/L</td>
<td>28.86</td>
</tr>
<tr>
<td>Acidity (BNC)</td>
<td>mmol/L</td>
<td>0.139</td>
<td>Mg$^{2+}$</td>
<td>mg/L</td>
<td>16.14</td>
</tr>
<tr>
<td>TOC</td>
<td>mg/L</td>
<td>0.64</td>
<td>SO$_4^{2-}$</td>
<td>mg/L</td>
<td>15.38</td>
</tr>
<tr>
<td>TDS</td>
<td>mg/L</td>
<td>190</td>
<td>F$^-$</td>
<td>mg/L</td>
<td>0.05</td>
</tr>
<tr>
<td>Sb</td>
<td>μg/L</td>
<td>31.0</td>
<td>PO$_4^{3-}$</td>
<td>mg/L</td>
<td>0.02</td>
</tr>
</tbody>
</table>

TOC: total organic carbon; TDS: total dissolved solids.

**Analytical method**

Antimony samples were collected into plastic bottles and immediately acidified with highly pure nitric acid (Merck). All bottles were submerged in 10% nitric acid solution over 3 days and triple rinsed with deionized water. Agilent 7500CE inductively coupled plasma mass spectrometry (ICP-MS) (ORS technology) was used to determine antimony concentration in solution. The detection limit for Sb by ICP-MS was 1 μg/L.

**RESULTS AND DISCUSSION**

Within the frame of the experiments the chemical composition and surface properties of the sorption materials used were studied. The chemical composition was determined using the X-ray microanalysis method; the values are listed in Table 3.

The shape and external surface of the READ-As and GEH sorption materials were scanned by an electron microscope. Figures 1 and 2 illustrate the differences in the character of the surfaces.

Table 4 includes the surface properties of sorption materials determined by physical adsorption of nitrogen and mercury porosimetry.

The adsorption isotherms of the READ-As and GEH samples (Figure 3) are significantly different. The GEH sample, which has a specific surface area of 190 m$^2$/g and a total pore volume of almost 0.3 cm$^3$/g, is a typically mesoporous material with a hysteresis loop on a nitrogen adsorption–desorption isotherm at a relative pressure of $p/p_0 = 0.6$–0.8, resulting in a relatively sharp
pore distribution calculated from the desorption branch of the nitrogen isotherm (Figure 4, left) with a maximum at a pore radius of about $R_p = 2.35$ nm (diameter 4.7 nm). This texture is also supported by the results from the mercury porosimetry (Figure 5, left) which shows a pore structure with a pore radius smaller than about 2.5 nm. Such a texture also corresponds to the relatively smooth surface visible on the SEM pictures, even at the highest magnification (Figure 2).

On the other hand, the texture of the READ-As with a specific surface area of only 42.8 m$^2$/g is completely different. The nitrogen adsorption isotherm (Figure 3) shows a narrow hysteresis loop at a relative pressure of over 0.7, indicating the presence of mesopores of a much wider diameter. The adsorption isotherm shows a rapid increase in the relative pressure over 0.9, which corresponds to the presence of

Table 3 | Chemical composition of selected sorption materials

<table>
<thead>
<tr>
<th>Compound in mass (%)</th>
<th>Al$_2$O$_3$</th>
<th>SiO$_2$</th>
<th>P$_2$O$_3$</th>
<th>SO$_x$</th>
<th>Cl$_2$O</th>
<th>K$_2$O</th>
<th>CaO</th>
<th>CeO$_2$</th>
<th>Fe$_2$O$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>READ-As</td>
<td>–</td>
<td>1.30</td>
<td>–</td>
<td>–</td>
<td>0.59</td>
<td>–</td>
<td>–</td>
<td>98.30</td>
<td>–</td>
</tr>
<tr>
<td>GEH</td>
<td>1.74</td>
<td>3.05</td>
<td>0.21</td>
<td>0.54</td>
<td>2.27</td>
<td>0.08</td>
<td>0.18</td>
<td>91.92</td>
<td>–</td>
</tr>
</tbody>
</table>

Table 4 | Texture properties of sorbent materials

<table>
<thead>
<tr>
<th>Physical adsorption of nitrogen</th>
<th>Physical adsorption of nitrogen</th>
<th>Mercury porosimetry</th>
</tr>
</thead>
<tbody>
<tr>
<td>Material</td>
<td>$S_{BET}$ (m$^2$/g)</td>
<td>$V_a$ (cm$^3$/g)</td>
</tr>
<tr>
<td>READ-As</td>
<td>42.8</td>
<td>0.154</td>
</tr>
<tr>
<td>GEH</td>
<td>190</td>
<td>0.295</td>
</tr>
</tbody>
</table>
macropores. The pore size distribution based on nitrogen desorption (Figure 4, right) is relatively wide with a maximum at \( R_p = 20 \) nm (diameter of 40 nm), which is close to the upper limit of the definition of a mesopore. A small maximum at about \( R_p = 1.9 \) nm is an artefact that does not correspond to actual pores (Groen et al. 2003).

What is interesting are the results of the mercury porosimetry of the READ-As sample (Figure 5, right), which shows a double porous structure. The lower pore structure at \( R_p = 20 \) nm precisely supports the results of nitrogen desorption. Moreover, the pore-size distribution from the mercury porosimetry shows a second pore structure in the range of the macropores with a maximum at \( R_p = 80–100 \) nm (a diameter of about 200 nm). The presence of macropores is also clearly seen on the SEM picture of the READ-As sample at the highest magnification. The total pore volume of 0.154 cm\(^3\)/g is thus concentrated in the meso- and macroporous internal pore structures.

The pilot test was aimed at monitoring the effectiveness of the GEH and READ-As sorption materials for the removal of antimony from water. The antimony concentrations in the RW were in a range from 21.5 to 31.1 \( \mu \)g/L (an average of 27.7 \( \mu \)g/L with a standard deviation ± 3.41). The filtration conditions are shown in Table 5.

Figure 6 shows the breakthrough curves of the antimony as a function of the water volumes treated in terms of bed volumes and the values of the bed volume or the adsorption capacity for each sorption material when reaching the limit concentration of antimony (5 \( \mu \)g/L).

As for the results presented in Figure 6, it can be concluded that READ-As is a more suitable material for antimony removal compared to the GEH sorbent used in the test. The following bed volumes were measured for the antimony concentration at the outlet of the adsorbent media: bed volume 3,967 for the READ-As (the time of the wave breakthrough reached 336 h) and 3,236 for the GEH (the time of the wave breakthrough reached 311 h). The adsorption capacities were as follows: READ-As = 128.4 \( \mu \)g/g and GEH = 63.0 \( \mu \)g/g.

According to the material balance of the antimony in these experiments, the amount of adsorbed antimony in
the adsorption media when reaching the limit concentration of 5 μg/L Sb at the outlet of the media was 92,166 μg for the READ-As and 75,945 μg for the GEH.

The antimony sorption capacity depends also on the quantity and character of adsorption centers on adsorbents where sorption of antimony species proceeds. Because, the chemical character of both adsorbents is very different, it is very hard (or impossible) to compare their adsorption capacities on the basis of measured characteristics.

### Table 5 | Adsorption conditions of the model tests

<table>
<thead>
<tr>
<th>Parameter</th>
<th>READ-As</th>
<th>GEH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grain size (mm)</td>
<td>0.3–1.0</td>
<td>0.32–2.0</td>
</tr>
<tr>
<td>Medium height (cm)</td>
<td>48</td>
<td>49</td>
</tr>
<tr>
<td>Volume of adsorption column (cm³)</td>
<td>942.5</td>
<td>962.1</td>
</tr>
<tr>
<td>Mass of adsorption column (g)</td>
<td>717.5</td>
<td>1204.8</td>
</tr>
<tr>
<td>Average flow through column (mL/min)</td>
<td>182.6</td>
<td>181.8</td>
</tr>
<tr>
<td>Average filtration rate (m/h)</td>
<td>5.58</td>
<td>5.55</td>
</tr>
<tr>
<td>Empty bed contact time (EBCT) (min)</td>
<td>5.16</td>
<td>5.29</td>
</tr>
</tbody>
</table>

### Figure 5 | Pore size distribution for sorption materials GEH (left) and READ-As (right) from mercury porosimetry.

### Figure 6 | Breakthrough curves of antimony (left) and the bed volumes and adsorption capacity achieved (right) at a breakthrough concentration of antimony of 5 μg/L.
CONCLUSIONS

The technological tests performed on the groundwater from the spring in Dúbrava showed that the use of sorption materials can possibly decrease the content of antimony in water to the values limited by Government Regulation No. 496/2010 on drinking water. Based on the pilot tests, a more suitable sorption material for removing antimony from water is the READ-As.

At a concentration of antimony in RW ranging from 21.5 to 31.1 μg/L, the filtration rate of 5.58 m/h and empty bed contact time (EBCT) of 5.16 min, the value of the bed volume 3,967, and the adsorption capacity of 128.4 μg/g achieved at a breakthrough concentration of 5 μg Sb/L, were determined.

The results proved that the GEH materials can also be used to decrease the concentration of Sb in drinking water below the limit value of 5 μg/L. The adsorption capacities and bed volumes are lower for these sorption materials in comparison to the READ-As.

The filtration rate, height of the filter media (i.e., EBCT), and antimony concentrations in RW have an influence on the value of the adsorption capacity and bed volume. Therefore, pilot tests to verify these values directly on a water source are necessary.

The efficiency of antimony removal from water under dynamic conditions affects not only the interaction of the antimony with the surface of the sorption material, but also mainly the pore size (mesopores and macropores), which may affect the rate of internal transport. The internal transport in pores also depends on the ratio between the size of adsorbate species and pore size of adsorbent, so the increase of pore size positively improves the internal transport of antimony species. Therefore, the specific surface of each material and pore size distribution was determined by the physical adsorption of nitrogen. The mercury porosimetry completed the results of the physical adsorption in terms of the presence of macropores. On the basis of these measurements, it can be concluded that the READ-As has a smaller specific surface than the GEH, but the size of the mesopores, moreover, the presence of the macropores, increase the rate of internal transport and, by that, the ability to capture antimony on the surface too.

ACKNOWLEDGEMENTS

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