Influence of Mining Activities on Quality of Groundwater

J. Ilavský and D. Barloková

Contents

Abstract The increased pollution of water resources leads to a deterioration in the quality of surface water and groundwater, and it initiates the application of various methods for water treatment. The Slovak Technical Standards – STN 75 7111 Water – and the enactment of the Decree of the Ministry of Health of the Slovak Republic No. 151/2004 on requirements for drinking water and monitoring of the quality of drinking water quality have resulted in the reduction of heavy metal concentrations or, for the first time, in defining the limit concentrations for some heavy metals (As, Sb), respectively. Based on this fact, some water resources in Slovakia have become unsuitable for further use, and they require appropriate treatment.

The objective of the study was to verify the sorption properties of some new sorption materials for the removal of antimony (Bayoxide E33, GEH, CFH12). Technological tests were carried out at the facility of the Slovak Water Company

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Liptovský Mikuláš in the locality of Dúbrava. Technological tests have proved that the new sorption materials can be used for reduction of antimony concentration in water to meet the values set under the Decree of the Ministry of Health of the Slovak Republic No. 247/2017 on requirements for drinking water – 5 μg/L.

Keywords Groundwater quality, Removal of antimony, Sorption materials, Water treatment

1 Introduction

One of the primary goals of WHO and its member states is that "all people, whatever their stage of development and their social and economic conditions, have the right to have access to an adequate supply of safe drinking water." A major WHO function to achieve such goals is the responsibility "to propose . . . regulations, and to make recommendations with respect to international health matters . . ." [1].

Since 1998, an intensive attention has been paid to the presence of heavy metals in the water, when standard, STN 75 7111 Drinking Water, was introduced into the Slovak legislation. By transposition of European Directive 98/83/EC and WHO recommendation [2, 3] into our legislation, the limit concentrations of some of the heavy metals (e.g., As, Sb) were decreased, resp., determined for the first time which caused that some of the Slovak water sources has become nonconforming and they need to be adjusted properly for their next use. The risk of the heavy metal presence rests mainly in their tendencies of being accumulated in the tissue of plants and animals. Some metals are quite equally presented in the earth crust from where they may move into the groundwater. Heavy metal occurrence presents the same risks as the risks of industrial or agricultural contaminants. The knowledge about the health aspects of heavy metal presence in drinking water are included in the paper Water Quality and Treatment: A Handbook of Community Water Suppliers [4] and literature [5, 6].

On the map of Slovakia (Fig. 1) are marked places with a higher concentration of antimony in groundwater. In these places are deposits of antimony ore.

The deposits of antimony ore in Slovakia are in five metallogenetic areas – in the Little Carpathians, Low Tatras, Spišsko-Gemerské Rudohorie Mts., Banskoštiavnicko-kremnické Mountains, and Prešov Mountains. The basic minerals of these sites are antimony, which is often accompanied by gold and silver [7].

The Dúbrava deposit contains quartz veins with antimony mineralization – arsenopyrite, Pb–Sb–Bi sulfosalts, sphalerite, tetrahedrite, bournonite, chalkostibit, gold, scheelite, Fe dolomite, and barite. Sb contents in the ore range from 1.5 to 5.0%. From the middle of the eighteenth century until the beginning of the twentieth century, iron ore and antimony were extracted here. The mining was then restored only before the Second World War when it started to grow antimony. The Dúbrava deposit was a significant producer of Sb in the Czechoslovakia in the last four decades until the end of the mining in 1993. In the years 1753–1985, 1,046 kt of

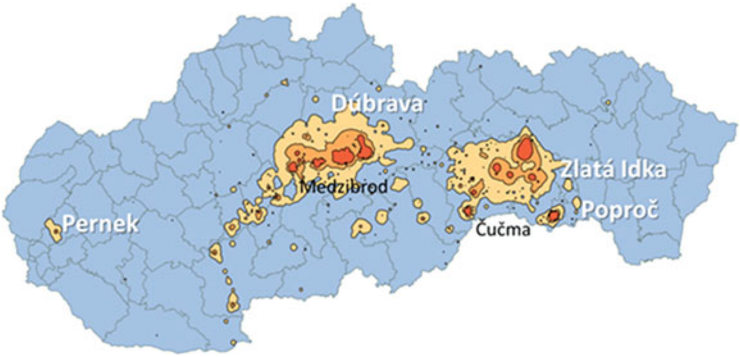

Fig. 1 The occurrence of antimony in Slovakia (https://uvp.geonika.sk/teslo/images/archive/a/a3/20151013103415%21Sb.png)

antimony ore was used on the Dúbrava deposit, of which 1,033 kt after 1945, 27 kt of metal was extracted from the total extracted ore [8].

The abandoned Dúbrava Mine is situated in the northern part of the Low Tatras in the middle of Slovakia. Mine drainage from adits (containing up to 9,300 μg/L of Sb), mine waste dumps, and the leachate from mine tailings contribute Sb and arsenic (As) into nearby Paludzanka Creek and groundwater. Some drinking water resources have been closed due to excessive Sb concentrations; the concentration of Sb in one household well (126 μg/L) far exceeds the Sb drinking water limit of 5 μg/L [9–11].

The Pernek deposit contains antimony mineralization with Au-bearing arsenopyrite and pyrite, bound to black slate, which lie in the environment of actinolitic sands and amphibolites. The mining of antimony and pyrite ores on the Pernek deposit began at the end of the eighteenth century (1790) and lasted with breaks until the early twentieth century (1922).

Pernek–Pezinok mining area is important Sb deposit in the Malé Karpaty Mts. Many dump piles and mine adits left abandoned when the mining activity had stopped. At the present time, these become sources of the surface, groundwater, soils, and stream sediment contamination. Arsenic and antimony are the trace elements transforming and accumulating in several natural components. Sulfide oxidation and silicate weathering are the main processes participating in surface and groundwater chemical composition. The antimony shows an elevated concentration ranging from 1 to 31 μg/L together with elevated concentrations of Ni, Zn, Fe, and sulfates. The stream situated above dump piles is considered to be the site with background values which is confirmed by a relatively low concentration of Fe, As, Sb, Ni, and Zn. The highest concentration of As (0.005 mg/L), Ni (189 μg/L), Zn (161 μg/L), Fe (6.94 mg/L), Mn (0.655 mg/L), and sulfates (488 mg/L) was detected in the mine adit outflow (Pavol). The concentration of Sb was 0.014 mg/L [12, 13].

The Medzibrod deposit is located in the area of the southern slopes of the Ďumbierske Tatry Mts. The monitoring sites are situated in Močiar valley, which is drained by Borovský potok creek. Drainage water from Murgaš mine adit represents a significant source of contamination, where elevated concentrations of sulfates, arsenic (500 μg/L) and antimony (180 μg/L), and high mineralization were detected. The mine waste dumps situated below the mine adit, together with a tailing impoundment, are also the main sources of contamination in this area. The highest concentrations of arsenic and antimony were observed in drainage water from the waste dumps. In spite of the fact that arsenic and antimony are attenuated by dilution and adsorption on ferric iron minerals in stream sediment, elevated concentrations of arsenic and antimony were also found in surface water in Borovský potok creek. Increased amounts of some monitored chemical elements were found in stream sediments of Murgaš adit outflow with a high proportion of Fe oxyhydroxides. Extremely high levels of arsenic (10,250 mg/kg) and antimony were detected in a soil sample in close proximity to the Murgaš mine adit. Significantly elevated contents of monitored elements in stream sediments were found in inflow from Murgaš mine adit where a high portion of Fe oxyhydroxides is present.

The Medzibrod deposit is bunched antimony veins lying in phyllites and black shales, which are sometimes impregnated with pyrite–arsenopyrite ores containing gold, 1–4 ppm. The main mineral ore is antimonite; berthierite, jamesonite, and pyrite are relatively abundant. Between 1938 and 1944, the deposit produced 57 kt of ore containing 2.8 wt% Sb and 4.48 ppm Au. The bearing is considered to be loaded [14, 15].

The Čučma deposit is a quartz vein with antimonite, accompanied by siderite, Fe dolomite, calcite, carbonates, tourmaline, albit, pyrite, arsenopyrite, markazine, pyrothine, chalcopyrite, sphalerite, tetrahedrite, gallate, gold, bismuth, antimony, berthierite, boulangerit, chalkostibit, bournonite, zinckenite, and jamesonite. In the middle ages, gold, silver, and copper ores, later iron, antimony, and manganese ores, were used. The Čučma deposit was obtained from 1918 to 1944 by 204 kt and after 1945 68 kt of antimony ore. Since 1952, mining has been stopped.

In surface water and groundwater, there could be the trace amounts of antimony and arsenic. There are very strict limits for these toxic elements in drinking water (5 μg/L for antimony and 10 μg/L for arsenic). The results of study of arsenic and antimony contamination at the Čučma abandoned deposit are presented in the article [16]. This mining area belongs to the important ore deposits in the south part of Slovenské Rudohorie Mts. The mine water from adits and tailing ponds represent the most important sources of contamination at this area. The maximum value of antimony (7,130 μg/L) was detected in mine water from the Jozef mine adit. The highest content of arsenic (1,350 μg/L) and also high concentrations of Fe and Mn were measured in mining water from the Gabriela mine adit. High concentration of antimony (86 μg/L) was registered in-house wells, as well. Most of the local inhabitants use the contaminated water for drinking purposes. Soil and stream sediments are also contaminated by As, Sb, Cu, Pb, Zn, Ni, Co, Fe, Mn, and Al in this area [16, 17].

The Poproč deposit consists of six cores with ore mineralization, Anna–Agnes, Borovičná hôrka, Barbora, Lazy, Ferdinand, and Libórius, which are located along steep tectonic surfaces. Mining work in modern history began in 1938. The operation was stopped in 1965 and gradually liquidated. The total amount of extracted and processed ore for the years 1939–1965 was about 259 kt. The yield of the flotation treatment plant during the last years of operation was 90.6–93.3% at the concentration of the concentrate 48.35–52.49% Sb and the Au content 3–6 g/t.

Abandoned Sb-deposit Poproč is located in the Gemeric tectonic unit, and hydrothermal mineralization occurs here in the form of veins mainly in phyllites. Stibnite is the most abundant ore mineral; pyrite, arsenopyrite, and few other Pb–Sb–Zn–Cu sulfides are also common. Natural water, soil, stream sediments, and plants in investigated areas of abandoned Sb-deposit Poproč are primarily affected by point sources of contamination (drainage from old mine, tailing impoundments, waste dumps). Weathering of open adits, dumps, and non-isolated tailing impoundments cause many problems such as water, soil, and stream sediment contamination mainly by arsenic and antimony in the area. Extremely high concentrations of Sb and As were observed in natural constituent in the catchments of Olšava river (waters, As max 2,400 μg/L, Sb max 410 μg/L; soils, As max 1,714 mg/kg, Sb max 6,786 mg/kg; stream sediments, As max 5,560 mg/kg, Sb max 1,360 mg/kg), but relatively high values of Fe, Pb, Zn, Mn, Al, and SO_4^{2-} were monitored.

A portion of water extractable fraction of Sb in soil ranges from 0.5 to 3.06% and in the stream sediments from 0.08 to 7.15%. This, however, points to low mobility of Sb, but due to a very high total content, leaching of soils and stream sediments may cause water pollution [18, 19].

Today, it is challenging to distinguish between anthropogenic and natural pollution caused by antimony. The enrichment of antimony occurs by contact of water with rocks, minerals, and soil. In the vicinity of ore deposits, water can be enriched with higher concentrations of antimony. In groundwater the threshold limit value (Sb = 0.005 mg/L) was exceeded, for instance, in the locality of Košice and surroundings (Zlatá Idka, Bukovec water reservoir), Low Tatras in the locality of Dúbrava (Liptovský Mikuláš), Spišsko-Gemerské Rudohorie Mts. (Čučma, Poproč), and in the Little Carpathians (Pernek, Pezinok) [20].

2 Antimony: Effects on the Environment

Concentrations in natural waters not polluted are generally very low (0.1–0.2 μg/L). The increased concentration of antimony was monitored in locality of mining activities. Adverse concentration of antimony 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 water.

The chemistry of antimony and its natural occurrence in some water resources combines to create a strong, widespread human health risk, requiring management and removal from drinking water.

The chemical behavior of antimony is as complicated as that of arsenic, its neighbor in the periodic table. It is speculated that antimony could be a natural contaminant with arsenic in some drinking waters. Soluble forms of antimony (and arsenic) tend to be quite mobile in water, whereas less soluble species are adsorbed into clay or soil particles and sediments, where they are bound to extractable iron and aluminum [21, 22].

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. While there is evidence that some antimony compounds are carcinogenic by inhalation, no such evidence exists for antimony in water. Known health risks by the oral route include an increase in blood cholesterol and a decrease in blood sugar. Findings on health aspects related to the occurrence of some heavy metals in drinking water are summarized in publication [6, 21].

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 [23]. This limit value is in accordance with the WHO recommendations [2] and the EU directive [3].

3 Antimony: Properties and Dissolution Chemistry

Antimony in its elemental form is a silvery white, brittle, fusible, crystalline solid that exhibits poor electrical and heat conductivity properties and vaporizes at low temperatures [24]. Antimony resembles a metal in its appearance and in many of its physical properties, but does not chemically react as a metal. It is also attacked by oxidizing acids and halogens. Antimony and some of its alloys are unusual in that they expand on cooling. Metallic antimony is too brittle to be used alone and, in most cases, has to be incorporated into an alloy or compound.

Antimony and its compounds are industrially crucial because of their usefulness in the manufacture of alloys, paints, paper, plastics, textiles, glass, clay products, and rubber. In recent years, high purity antimony has been used in the production of the semiconductor compound indium antimonide and in the formulation of bismuth telluride-type compound used for thermoelectric applications. Antimony trioxide (Sb_2O_3), the most important antimony compound, is used in halogen-compound flame-retarding formulations for plastics, paints, textiles, and rubbers. Lead–antimony alloys are used in starting–lighting–ignition batteries, ammunition, corrosion-resistant pumps and pipes, tank linings, roofing sheets, solder, cable sheaths, and antifriction bearings [24].

Antimony is present in water as Sb^{3-}, Sb^0, Sb^{3+}, and Sb^{5+} (Sb^{3+} is ten times more toxic than Sb^{5+}), depending on the pH of the water, the oxidation–reduction potential (Sb^{3+}/Sb^{5+} ratio), and the oxygen content. The most common form is antimonate–oxyanion $(H_2SbO_4)^-$ and $(HSbO_4)^{2-}$, or it can be present as antimonite (H_3SbO_3) [21, 25].

Both Sb (III) and Sb (V) ions hydrolyze efficiently in aqueous solution, thus making it difficult to keep antimony ions stable in solution except in highly acidic media [26]. Sb (V) is present as SbO_2^+ or $Sb(OH)_5$ under very acidic conditions, and $[Sb(OH)_6]^-$ or SbO_3^- exists in mildly acidic, neutral, and alkaline conditions (Fig. 2). The antimony pentoxide, Sb_2O_5, is hardly soluble in water and generates the antimonate anion upon dissolution, while the antimony trioxide, Sb_2O_3, also has a relatively low solubility in water [26, 27]. In the pH range 2–12, the solubility of Sb_2O_3 is independent of pH, thus indicating the formation of an undissociated substance and antimony hydroxide $Sb(OH)_3$. Sb (III) exists as SbO^+ or $Sb(OH)_2^+$ in acidic media and as $Sb(OH)_4^-$ or hydrated SbO_2^- in basic media (Fig. 2). At very reducing conditions in the presence of dissolved sulfide, Sb (III) sulfide species will be dominated, e.g., $HSb_2S_4^-$ and $Sb_2S_4^-$, at pH values less than and higher than 11.5, respectively. At low temperatures, antimony chloride complexes such as $SbCl_2^+$, $SbCl^{2+}$, $SbCl_3$(aq), and $SbCl_4^-$ will dominate in chloride-rich acidic aqueous solutions.

Antimony is geochemically categorized as a chalcophile, occurring with sulfur and the heavy metals – lead, copper, and silver. Apart from stibnite (Sb_2S_3) and kermesite (Sb_2S_2O), which are the most common antimony-containing minerals found in hydrothermal deposits, antimony often occurs in minerals in solid solution with arsenic, for example, lead and copper minerals, such as guettardite Pb(Sb, $As)_2S_4^-$, jamesonite $FePb_4Sb_6S_{14}$, and tetrahedrite $Cu_{12}Sb_4S_{13}$ [27]. Tetrahedrite has basically the sphalerite crystallographic arrangement with one-fourth of the Cu replaced by Sb in its structure. As a result of the substantial amount of copper in the

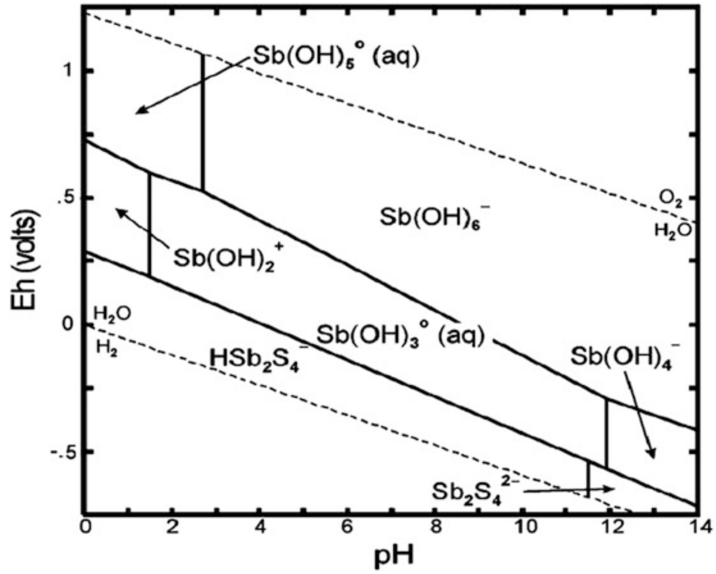

Fig. 2 Eh–pH diagram showing dominant aqueous species of antimony at 25°C and a concentration of 2.90×10^{-10} mg/L [27]

mineral, tetrahedrite is now becoming a potential source of copper, but the antimony content of the mineral is of great concern during the pyro-processing of the ore.

4 Methods of Heavy Metal Removal from Water

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 [28–33].

The most common method for the removal of heavy metals is water clarification – the *precipitation* of metal hydroxides and carbonates. This process is based on the dosing of appropriate agents (lime, iron salt, sodium carbonate, sodium hydroxide, and sulfates) to obtain the optimum pH value of a solution in which an insoluble solid phase of precipitated heavy metal hydroxides or carbonates is formed. The effectiveness of the precipitation depends on the type of contaminant, its concentration, water composition, and the type of agent.

Precipitation seems to be an ideal solution for the treatment of water containing heavy metals, provided that the process is not limited by specific effects that reduce the effectiveness of coagulation. For example, the efficiency of precipitation is lower at a higher concentration of metals in water. If the solution is too diluted, the precipitation will be too slow. The precipitation is also influenced by the pH value. Hydroxides are especially very sensitive to this parameter, and they are not competent enough in acid areas. In addition, the presence of other salts (ions) in water has an adverse effect on the precipitation process. The disadvantages of precipitation are the addition of other chemicals to the treatment process and the high production of sludge that should be processed and stored under specific conditions.

The advantage of precipitation is its relatively low cost compared to other metal removal methods. The coagulants used in this process are easily available. Precipitation can be used for a wide range of metals, and an acceptable level of effectiveness is achieved through its proper operation.

Ion exchange is based on the mutual exchange of ions with the same charge between an ion exchanger (an exchangeable ion) and the treated water (captured ion). The ion exchanger is a material capable of the reverse stoichiometric exchange of cations or anions in a condition of electroneutrality.

The advantage of the ion exchange process is the relatively low cost compared to other methods. The method is tried and tested, and all the components required for its operation are commercially available. It is possible to remove undesirable metals from water using the cation exchanger in a wide range up to the μg/L level.

The disadvantage of ion exchangers is that they disrupt ion exchange due to the high competitiveness of some ions (selenium, fluorine, nitrates, and sulfates) to finding a place in the ion exchanger. In addition, these ions reduce the efficiency due to suspended and organic substances, which may cause fouling of the ion exchanger filter. It is not possible to use the ion exchange method in the treatment of water with a high concentration of metals. Moreover, this method is sensitive to the pH value of the treated water and water quality (alkalinity, concentration of competing ions). The need to dispose of the regenerative agent used and the ion exchanger is also among the disadvantages of this material.

Adsorption processes are based on the adsorption of contaminants on the surface of an adsorption material. The molecules of the contaminant pass from the water environment to the solid adsorbent. It is possible to use activated alumina, iron-activated alumina (Fe-AA), activated carbon, iron-activated carbon, iron oxides, oxyhydroxides, or ferric hydroxide (GEH, CFH12, CFH18, Bayoxide E33, Everzit As), media containing TiO_2, CeO_2, ZrO_2, or MnO_2 layers on their surface, sand covered by iron hydroxide, low-cost materials (zeolites, carbonates, clay, peat, moss, ash, chitosan, sawdust, coconut husk, living or nonliving biomass, etc.), for removal of heavy metals.

Efficiency of heavy metal removal by adsorption material depends on the pH of water; oxidation–reduction potential of a given metal in water; concentration of substances in water that have a potential to affect (interfere with) adsorption or modify adsorbent surface loading; concentration of substances and colloid particles that can physically block the entry into the particle and the access to grains of adsorption media, respectively, specific surface area and distribution of pores of adsorption material; and hydraulic properties of filtration media in treatment (filtration rate, the Empty Bed Contact Time (EBCT), the filter medium height).

Membrane methods belong to a group of diffuse processes in which the selective properties of membranes are used (thin semipermeable films, the thickness of whose walls range from 0.05 to 2.0 mm) to eliminate contaminants from water. Depending on the type of membrane (structure and driving force), it is possible to divide these processes into microfiltration, ultrafiltration, nanofiltration, and reverse osmosis.

Today, *electrochemical methods* are not commonly used in the treatment of water and wastewater. These methods are still in the process of development, but it is important to note that they may become very useful for the removal of metals from water in the future.

Electrodialysis (ED) is a membrane process, by which ions are transported through semipermeable membrane, under the influence of an electric potential. The membranes are cation- or anion-selective, which basically means that either positive ions or negative ions will flow through. Cation-selective membranes are polyelectrolytes with negatively charged matter, which rejects negatively charged ions and allows positively charged ions to flow through.

Biological methods are based on the production of a special microbial culture capable of using heavy metals dissolved in water as a substratum for further microbial growth.

5 Materials Used for Sorption in Removal of Heavy Metals

The literature mostly describes the use of iron oxides, oxyhydroxides, and iron hydroxides, also known as GEH, Bayoxide E33, CFH12, CFH18, Everzit As, etc., for arsenic removal from water. They were manufactured and tested in particular 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 [34–48]. These studies describe sorption processes at different pH values, 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.).

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 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 As^{3+} and As^{5+} too. Bayoxide® E33 has a capacity to treat water with As concentration of 11 ÷ 5,000 μg/L [49–51].

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 (Table 1) [52–54].

GEH was obtained from the supplier (GEH Wasserchemie GmbH, Germany). GEH is a high-performance adsorbent developed by the Department of Water

Table 1 Physical and chemical properties of selected sorption materials

Parameter	Bayoxide E33	CFH12 a CFH18	GEH
Matrix/active agent	$Fe_2O_3 > 70\%$ and 90.1% α-FeOOH	FeOOH, $Fe^{3+} > 40\%$	52–57% $Fe(OH)_3$ and β-FeOOH
Material description	Dry granular media	Dry granular media	Moist granular media
Color	Amber	Brown red	Dark brown
Bulk density ($g\ cm^{-3}$)	0.45	1.12–1.2	1.22–1.29
Specific surface area ($m^2\ g^{-1}$)	120–200	120	250–300
Grain size (mm)	0.5–2.0	0.32–2.5 or 0.5–1.8	0.32–2.0
Grain porosity (%)	85	72–80	72–77
pH	6.0–8.0	6.5–7.5	5.5–9.0

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 43–48% by mass moisture content. Its iron content is 610 g/kg (±10%) relative to the dry solids [55].

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/cm^3 [56] and 1.25 g/cm^3 [57]. The surface areas of GEH range from 250 to 300 m^2/g, while porosity has been observed at 72–77% [56] and 75–80% [57]. GEH is delivered and provided in a water-saturated, granular form. The grain size of the GEH obtained from the manufacturer ranges from 0.2 to 2 mm.

GEH is highly selective toward arsenate; therefore, it requires an initial oxidation step in the presence of arsenite. In paper [58], 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 dramatically reduces arsenic removal [56].

Chemical composition was determined by the Institute of Inorganic Chemistry of the Faculty of Chemical and Food Technology of the Slovak University of Technology using the methods of X-ray microanalysis, SEM, and X-ray phase analysis; the values are listed in Table 2.

The shape and the external surface of sorption materials GEH, CFH12, and Bayoxide E33 were taken by scanning electron microscope. Figures 3 and 4 illustrate differences in the character of surfaces [59].

Table 2 Chemical composition of selected sorption materials

	Compound in mass (%)								
Material	MgO	Al_2O_3	SiO_2	P_2O_3	SO_x	K_2O	CaO	TiO_2	Fe_2O_3 (FeOOH)
E33	0.97	6.59	12.75	0.34	0.31	0.37	2.01	0.91	75.28
CFH12	3.75	0.45	1.18	–	8.49	0.27	2.72	0.50	82.65
CFH18	5.19	0.48	1.47	0.28	4.58	–	1.41	0.30	86.29
GEH	–	1.74	3.05	0.21	0.54	0.08	0.18	–	91.92

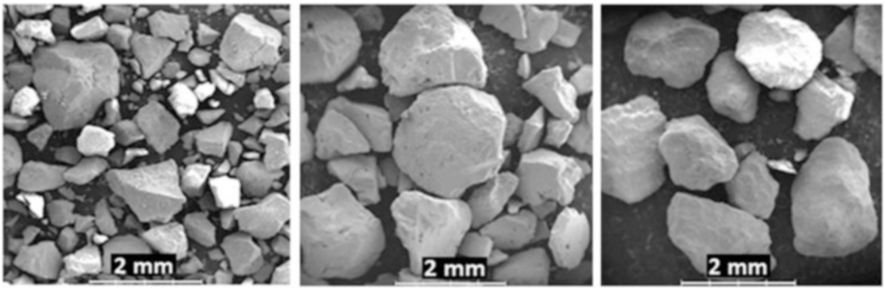

Fig. 3 The microstructure of GEH, Bayoxide E33, and CFH12 (40× magnification)

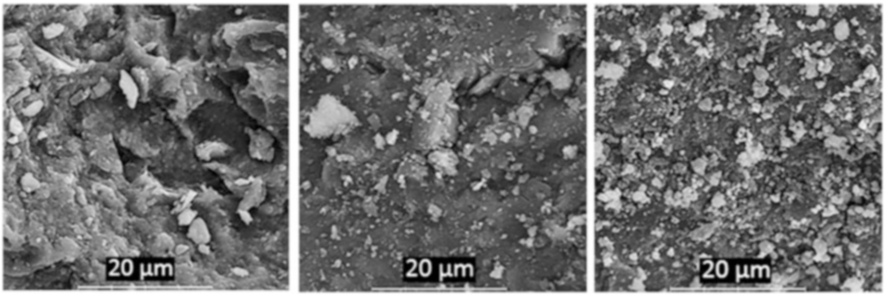

Fig. 4 The microstructure of GEH, Bayoxide E33, and CFH12 (5,000× magnification)

5.1 Activated Carbon

The most widely used adsorbent for water treatment is activated carbon. It is a well-known adsorbent due to its extended surface area, microporous structure, high adsorption capacity, and high degree of surface reactivity.

The structure consists of a distorted three-dimensional array of aromatic sheets and strips of primary hexagonal graphic crystallites. This structure creates angular pores between the sheets of molecular dimensions. Pore size ranges from 1 to 1,000 nm, and the extensive porosity is responsible for the high surface area of the material usually 500–1,500 m^2/g. Commercial activated carbon is manufactured from only a few carbon sources: wood, peat, coal, oil products, and nut shells.

The final pore structure depends on the nature of the starting material and the activation process. Macro- and mesopores can generally be regarded as the highways into the carbon particle and are crucial for kinetics. The micropores usually constitute the largest proportion of the internal surface of the activated carbon and contribute most to the total pore volume. Activated carbon has both chemical and physical effects on the substance where it is used as a treatment agent [60].

Adsorption is the most studied of these properties in activated carbon. Heavy metal removal by adsorption using commercial activated carbon has been widely used [61–64]. However, high costs of activated carbon and 10–15% loss during regeneration limit its use. This has led to a search for cheaper carbonaceous substitutes [60].

5.2 Activated Alumina

Activated alumina is a commercial filter media made by treating aluminum ore so that it becomes porous and highly adsorptive. It can also be described as a granulated form of aluminum oxide. Activated alumina is used for removing a variety of contaminants (fluoride, heavy metals, etc.) from water [65]. The medium requires periodic cleaning with an appropriate regenerator such as alum or acid in order to remain effective. Activated alumina has been used as an effective adsorbent especially for point of use applications.

There is more literature on the use of activated alumina for arsenic removal. The principle is that the soluble arsenic (AsO_4^{3-} and AsO_3^{3-}) in the water can be adsorbed on the surface of the AA[am-$Al(OH)_3$] and occupies the aluminous octahedron crystal lattice sites [66]. The maximum adsorptive capacity of AA is 5–24 (mg As adsorbed/g media) at equilibrium arsenic concentrations of 0.05–0.2 ppm [67, 68].

5.3 *Low-Cost Adsorbents*

Consequently, low-cost adsorbents have drawn attention to many researchers, and characteristics as well as application of many such adsorbents are reported. Some of the reported low-cost sorbents include bark-/tannin-rich materials, lignin, chitin/chitosan, eggshell, dead biomass, seaweed/algae/alginate, xanthate, zeolite, clay, ash, peat moss, bone gelatin beads, leaf mold, moss, iron-oxide-coated sand, sawdust, modified wool, modified cotton, coconut husk, rice husk, tea waste, agricultural waste (fly ash powder, bagasse, waste straw dust, sawdust, and coconut coir), eucalyptus and neem leaves, cast-iron filings (wastes from mechanical workshops, lathes), steel wool (commercially available, used for cleaning of wood surfaces prior to polishing), etc. [60, 69–71].

5.4 *Adsorbent Properties*

To be suitable for commercial applications, a sorbent should have high selectivity to enable sharp separations; high capacity to minimize the amount of sorbent needed; favorable kinetic and transport properties for rapid sorption; chemical and thermal stability, including extremely low solubility in the contacting fluid, to preserve the amount of sorbent and its properties; hardness and mechanical strength for long life; no tendency to promote undesirable chemical reactions; and the capability of being regenerated when used with commercial feedstocks.

When choosing the right filter, filtering-and-sorption or sorption material, it is always necessary to follow the given application and properties of different types of filter beds. Today there is a large number of publications available, dealing with arsenic or antimony removal from water using different sorption materials [37, 57, 72–80]. The published procedures are thus often adopted and adapted to the specific conditions. Where there is lack sufficient experience (knowledge) in the choice of sorption materials, it must be obtained, experimentally, best through long-term testing – pilot operation experiments.

Important parameters in the choice of sorption materials are [75]:

1. The concentration of the contaminant in the water.
2. The concentration of the contaminant after treatment.
3. The amount of treated water expressed as filtration rate, whereby filtration rate (m/h) = flow rate (m^3/h)/filter area (cross-section) (m^2).
4. Time of contact of water with material, expressed as EBCT (Empty Bed Contact Time); to calculate, we use the formula: contact time [min] = bed volume (m^3) * 6/flow rate (m^3/h).
5. Particle size (grain size) is important for the proper draft of operational flow rates due to the pressure drop and the contact time of the treated water with filtration material and backwash rates.
6. Density (kg/m^3). In the literature we encounter several densities, e.g., apparent density, expressing the max. vibration tapped density, bed density defined as the ratio of mass of a particulate material, and the total volume taken up by it (sum of the volume of the particles, the volume of the interparticle space, and the internal pore volume). Specific weight is used for the calculation of the volume and the weight of the sorption material.
7. The total surface area (BET) in m^2/g expresses the sorptive capacity of the given material, determined by the volumetric method (e.g., by physical adsorption of nitrogen at liquid nitrogen temperature). It is mainly used in the sorption of gases, having limited predicative value for water treatment, as it does not describe the content of micropores and transport pores in the sorbent material, while micropores are responsible for the adsorption. Transport pores serve for the supply of pollutant molecules to the micropores.

Sorption efficiency is reflected in the following parameters:

1. Adsorption capacity [μg/g] is the ratio of the mass of captured (adsorbed) contaminant in the bed [μg] and the weight of the bed in the filter [g], while the mass of adsorbed contaminant need to be determined experimentally.
2. "Bed volume" (BV) is a term often used to compare the efficacy of the technological process or the sorption material, representing the volume of water that flows through the filter bed V divided by the bed filter volume V_0 (the ratio V/V_0). Manufacturers of sorbents report this value together with adsorption capacity as data to characterize the effectiveness of the sorption process.
3. Filter length, L_F, is given in meter or in m^3/m^2 and represents the volume of water that flows through the filter unit area from the beginning of the filtration cycle; the higher the filter length, L_F, the higher the sludge capacity of the filter bed. In the literature for the removal of heavy metals, there is little data with this parameter; however, it needs to be used in characterizing the efficiency of sorption materials.

The following has an impact on the efficiency of removal of metals (As, Sb) from the water through sorption:

1. Water pH (lower pH increased sorptive capacity and lifetime of the medium).

2. The oxidation–reduction potential of the As and Sb (i.e., the ratio of As^{III}/As^{V}, Sb^{III}/Sb^{V}); it is well known that the pentavalent form of As and Sb is more easily removed from the water.
3. The concentration of substances present in the water that may affect (interfere with) the adsorption of As or modify the surface load of the sorption material.
4. Concentration of the substance and the colloidal particles in water that can physically block access of As to the interior of the particles or to the grains of adsorbent media.
5. Specific surface area and pore size distribution of the sorption material.
6. Hydraulic properties of the filter media during treatment (bed volume, filtration rate, the water retention time in the bed).

The first four factors are linked to the chemical equilibrium between the different substances present in the water and the filter material; the fourth and the last two factors are influenced primarily by the physical processes of mass transfer and properties of the used material. The substances whose presence in water can affect the sorption of arsenic and antimony include, for example, other heavy metals (vanadium), iron, manganese, silicate, sulfate, phosphate, fluoride, organics, etc. [81, 82].

The disadvantages of the use of sorption materials in the removal of heavy metals may be the costs associated with purchase, recovery, or disposal. It is therefore necessary to evaluate and compare this method of treatment with the methods used thus far.

6 Removal of Antimony by Adsorption at WR Dúbrava

The Dúbrava water supply resource is situated in the western part of the Low Tatras mountain range. 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 occurs mainly due to existence of the antimony deposit in Dúbrava and its higher content in granitoids of this part of the Low Tatras region. In the middle of the eighteenth 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 1,046 kt antimony ore, the total mined ore contained 27 kt of antimony [8].

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 to the surface stream of Križianky. Contaminated water of the Križianka River and water of its alluvial deposits have deteriorated water quality in the springs of Močidlo and Brdáre. In the past, three springs of the Dúbrava water resource

(Brdáre, Močidlo, Škripeň) were used for supplying population with drinking water (capacity of about 40 L/s), but today only one spring is used for this purpose (spring Škripeň that does not contain antimony). Two other springs are contaminated with antimony [8].

Water quality monitoring data provided by the Water Company of the Region of Liptov indicates the water quality parameters for the separate springs of the Dúbrava water resource and is shown in Table 3. The highest contamination from antimony was observed in water from the Brdáre spring, where the concentrations ranged from 80.3 to 91.3 μg/L. The concentration of antimony in water from the Močidlo spring was 70.6–82.0 μg/L. Apparently, the best water quality was monitored in the Škripeň spring, where the concentration of Sb 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. The groundwater analysis in locality Dúbrava is shown in Table 4.

The pilot tests for removing antimony were carried out at the Dúbrava chlorination plant (Fig. 5). At present, only water from the Škripeň well is conveyed into the storage tank of the chlorination plant. After its 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 [8].

Table 3 Water quality of the Dúbrava water resource according to selected parameters for the period 2000–2005

Parameter	Dúbrava – spring		
	Močidlo	Škripeň	Brdáre
pH	7.65–7.90	7.55–7.95	7.75–7.95
Alkalinity (mmol/L)	1.7–3.8	1.8–3.8	1.7–2.2
Conductivity (mS/m)	23.1–38.6	23.0–42.6	22.5–28.7
Ca^{2+} (mg/L)	30–54	48–52	28–32
Mg^{2+} (mg/L)	8.5–28.0	15.8–24.3	9.7–15.8
Sb (μg/L)	70.6–82.0	<1.0	80.3–91.3

Table 4 Filtration conditions [84]

Parameter	GEH	CFH12	Bayoxide E33
Grain size (mm)	0.32–2.0	1.0–2.0	0.5–2.0
Medium height (cm)	60	60	60
Mass of sorption material (g)	1,324	1,416	998
Average flow through column (mL/min)	147.3	147.8	140.0
Average filtration rate (m/hod)	4.50	4.51	4.27
Total filtration time (hod)	1,174	1,174	1,174
EBTC (min)	8.0	7.97	8.41

Raw water (the Brdáre spring) passed through the filtration system (Fig. 5), and the concentration of antimony was monitored in raw and treated water at the outlets of the filtration columns. Simultaneously, the flow rates were measured at the outlet of each column. A system of several valves was used for feeding the water for the filtration system (from top to bottom) and for the filter backwash (from bottom to top) as well as for regulating the filtration rates.

The aim of first pilot-scale experiment was to verify the sorption properties of granular iron-based filter materials (GEH, CFH12, Bayoxide E33) in the Dúbrava water resource during the process of antimony removal from water.

In order to verify the effectiveness of the antimony elimination process, tree adsorption columns filled with the sorption material were used. The adsorption column was made of glass material with a diameter of 5.0 cm and medium height of 60.0 cm. The adsorption column with a volume of 1,178.1 cm^3 covered an area of 19.635 cm^2. Water flowed through the column from the top to the bottom. The water discharge was measured continually, and the filtration rate achieved approximately 4.5 m/h [84]. The amount of water flowing through the column was monitored using a water meter placed in front of the column inlet. The filtration conditions are shown in Table 5.

Antimony samples after passing through columns were collected into plastic bottles and immediately acidified with highly pure nitric acid (Merck). All bottles

Fig. 5 Dúbrava chlorination plant and model filtration columns

Table 5 Analysis of groundwater in the area of Dúbrava [84]

Parameter	Unit	RW	Parameter	Unit	RW
pH		7.53	NH_4^+	mg/L	0
Conductivity	mS/m	21	Fe total	mg/L	0.02
Color	mg/L Pt	2	Mn	mg/L	0.001
Turbidity	ZF	0	Cl^-	mg/L	8.23
$ANC_{4.5}$	mmol/L	2.962	NO_3^-	mg/L	5.12
$BNC_{8.3}$	mmol/L	0	SO_4^{2-}	mg/L	21.85
Ca + Mg	mmol/L	1.175	F^-	mg/L	0.18
TDS (105°C)	mg/L	100	COD_{Mn}	mg/L	0.42

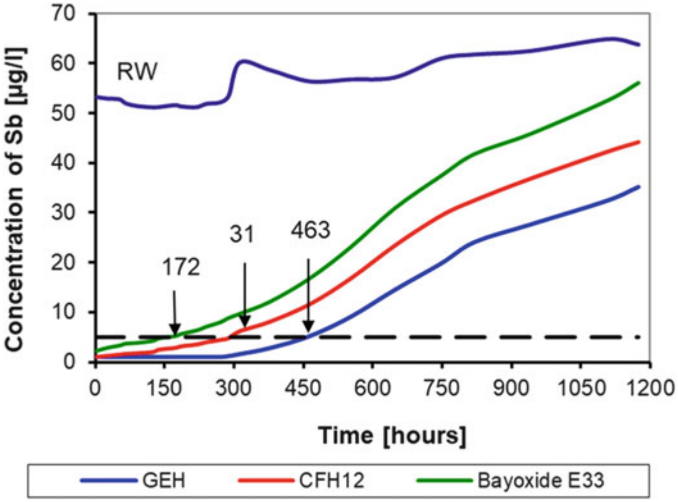

Fig. 6 Removal of Sb from water depending on operational time at breakthrough concentration 5 µg Sb/L (raw water concentration) [84]

were submerged in 10% nitric acid solution over 3 days and triple rinsed with deionized water. Agilent 7500CE ICP-MS (ORS technology) was used to determine antimony concentration in solution. The detection limit for Sb by ICP-MS was 1 µg/L [84, 85].

The results of the technological process are shown in Figs. 6 and 7; there is demonstrated relationship between antimony concentration and operational time or bed volumes treated (volume of the water passed through filtration column to volume of the adsorption column). Figure 6 shows the breakthrough curves of antimony as a function of water volumes treated in for each sorption material when reaching the limit concentration of antimony (5 µg/L). The effectiveness of the monitored sorption materials in the antimony removal process can be seen.

On the basis of the results obtained, it can be stated that all materials used are suitable for removal of antimony from water, although it is recommended in the literature to remove arsenic from water. The antimony removal efficiency is shown in Table 6.

For GEH sorption material has exceeded the value of 5 mg/L Sb after 463 h of operation of the filter device. The amount of water that has passed through this filtering device during this period is 4.088 m^3, i.e., 3,470 times the volume of the medium of GEH. For the sorption material CFH12 (Kemira), the limit value was exceeded after 312 h of operation, with the amount of water that exceeded the filter device during this time period of 2.85 m^3, i.e., 2,421 times the volume of the filter material CFH12. In the Bayoxide E33 sorption material, the limit value was exceeded after 172 h of operation, with the amount of water that exceeded the filter device during this time period of 1.50 m^3, i.e., 1,273 times the volume of the filter medium Bayoxide E33.

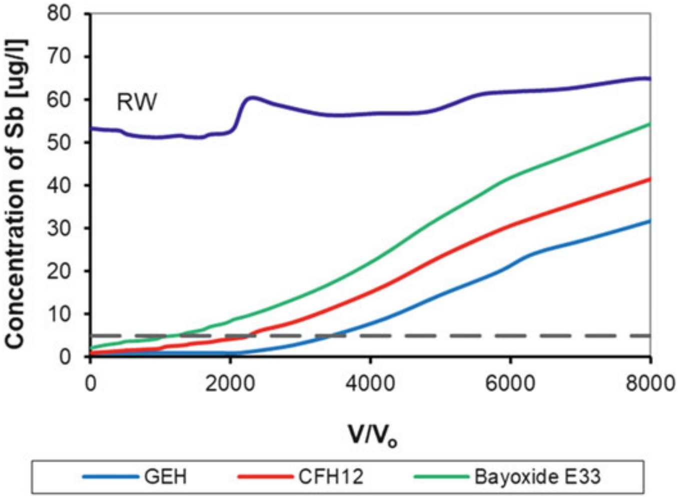

Fig. 7 Removal of Sb from water depending on the bed volume (volume of filtered water *V* to the volume of the filtration media (V_0) at breakthrough concentration 5 μg Sb/L (raw water concentration)) [84]

Table 6 Antimony removal efficiency of the water during filtration–adsorption

Parameter	GEH	CFH12	Bayoxide E33
Total time of filtration (h)	1,174	1,174	1,174
Filtration time (hod) at breakthrough concentration 5 μg Sb/L	463	312	172
Total amount of water passed through filtration column (m^3)	10.11	10.08	9.74
Amount of water passed through filtration column at breakthrough concentration 5 μg Sb/L (m^3)	4.088	2.852	1.460
Bed volume (V/V_0)	3,470	2,421	1,274

The adsorption capacity of the individual adsorbents was calculated based on the condition of not exceeding the antimony limit on the effluent from the filters (Fig. 8). Under the given operating conditions (average antimony concentration in raw water 55.6 μg/L, filtration rate 4.5 m/h) and weight of 1,324 g of GEH in column was adsorbed 222.16 mg of antimony. In the column with CFH12 (weight of 1,416 g) was adsorbed 149.71 mg of antimony, and in the column with 998 g of Bayoxide E33 was adsorbed 90.77 mg of antimony. From these results, the adsorption capacity of the GEH filter material was 167.8 μg/g, CFH12 105.7 μg/g, and Bayoxide E33 90.9 μg/g.

Considering the minimum differences in the filtration rates and based on the results presented in Figs. 6, 7, and 8, it can be concluded that GEH is the most suitable material for antimony removal compared to the other sorbents used in the test.

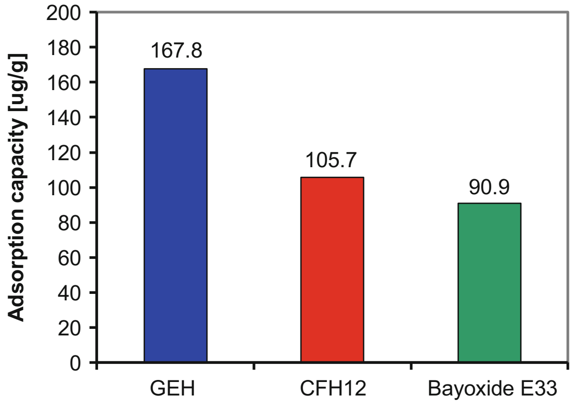

Fig. 8 Adsorption capacity of adsorbents used (v μg/g) [84]

Table 7 The values of bed volume and adsorption capacity of GEH material for different concentration of Sb in raw water, filtration rates, heights media, and EBCT

Material	Concentration of Sb (μg/L) in RW	Average filtration rate (m/h)	Height media (mm)	EBCT (min)	Bed volume (V/V_0)	Adsorption capacity (μg/g)
GEH	55.6	4.5	60	8.0	3,470	167.8
GEH	58.3	5.0	50	6.0	1,700	83.6
GEH	58.3	5.5	53	6.2	2,260	103.7
GEH	72.6	5.5	52	5.7	1,610	81.4
GEH	81.4	3.4	51	9.1	2,030	145
GEH	81.4	5.6	51	5.4	1,342	96.9

In Table 7 are summarized the results of other experiments conducted in the Dúbrava with material GEH [8, 20, 59, 83–85]. The table contains the bed volume and the adsorption capacity for the various antimony concentrations in the treated water and the filtration rate used, the filter media height, and the contact time treated water with the filter media GEH at the breakthrough concentration of 5 μg Sb/L.

If the need to water for the Liptovský Mikuláš region is increased there, it will be possible to use water from the Dúbrava water source. For removal of antimony from the water, we recommend using closed filters with a GEH filling and a filtration speed of 4.5 m/h. After further studies, it will be possible to carry out an economic assessment of the whole technological process and arrive at clear conclusions about the use of GEH materials in water treatment processes.

The aim of the second pilot-scale experiment was to compare the efficacy of antimony removal from water at the Dúbrava water resource using three different heights (50, 70, 90 cm) of filter beds with GEH material.

The effectiveness of antimony elimination from water was studied in a model facility, where raw water passed through three adsorption columns filled with GEH material in a direction from top to bottom. The adsorption column was made of glass, the column diameter was 5.0 cm, and the column height was 80 and 100 cm [75].

Without undergoing any pretreatment, the raw water passed through filtration equipment, while the concentration of antimony was monitored in raw and treated water at the outlet from individual filter columns. At the same time, the water flow at the outlet of each column was also monitored. Technological tests were aimed at verifying the possibilities of using GEH sorption material for water treatment–removal of Sb.

The results of the model tests were used to evaluate the courses of antimony concentration at the outlet from the columns from the time of the model facility operation, depending on the filter length, L_F (expressed in m^3/m^2, or in meters), and bed volume (BV). Based on the material balance of antimony in model facilities, we calculated the amounts of adsorbed antimony; from these data we calculated the adsorption capacities in μg/g. All published results are related to the concentrations of 5 μg/L of Sb at the outlet from the column, i.e., for the limit concentration of Sb in drinking water [75].

Within the given model tests, the concentration of antimony in raw water ranged from 90 to 108 μg/L Sb (average 90.3 μg/L Sb). The filtration rate in the case of a column with a bed height of 50 cm ranged at 5.3–5.6 m/h; at 70 cm bed height, it ranged from 5.1 to 5.5 m/h; and at 90 cm bed height, it ranged from 5.0 to 5.5 m/h. Filtration conditions are shown in Table 8.

Figure 9 shows the course of the concentration of antimony depending on the operational time of the model facility. The figure also shows the limit value of antimony in drinking water according to the Decree of the Ministry of Health of the Slovak Republic No. 247/2017 for drinking water (5 μg/L) [86]. Given that the experiments have been completed prior to reaching a concentration of 5 μg/L of Sb at the outlet from the columns for a medium height of 70 and 90 cm, the remaining value of the Sb concentration was additionally calculated through extrapolation.

Based on the achieved results, Table 9 summarizes the measured and calculated values for the removal of antimony from water using the GEH material and three adsorption bed heights, and the results are related to the value of 5 μg/L Sb at the outlet from the filter bed.

For mathematical processing and generalization of data in Table 4, we used the linear regression method. Figures 10, 11, and 12 show the equations of lines for GEH adsorption capacities, the V/V_0 ratio (bed volume), the contact time of water with the

Table 8 The conditions of filtration (the average values) [75]

Parameter	GEH		
Grain size (mm)	0.32–2.0	0.32–2.0	0.32–2.0
Medium height (cm)	50	70	90
Medium volume (cm^3)	0.982	1.364	1.751
Medium weight (g)	1,227.2	1,705.8	2,189.3
Average flow through column (mL/min)	178.0	176.4	173.4
Average filtration rate (m/h)	5.44	5.39	5.30
Total filtration time (h)	423	423	423
Filtration time (h) at breakthrough concentration 5 μg Sb/L	147	483	784

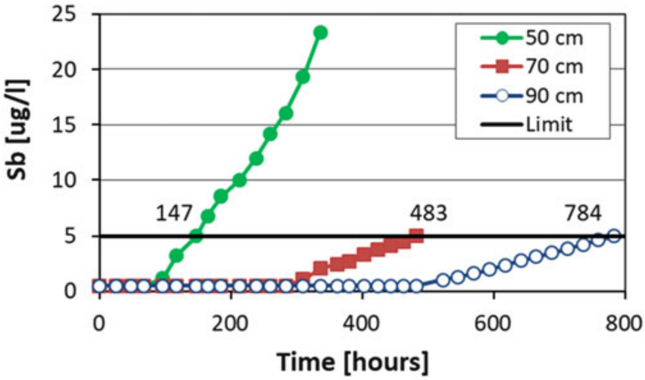

Fig. 9 Compare of efficiency of the materials GEH in the removal of Sb from water

Table 9 Measured and calculated values the sorption of antimony from water [75]

Height media (cm)	Volume media (cm^3)	Average filtration rate (m/h)	EBCT (min)	Bed volume (V/V_0)	Filtration length L_F (m)	Amount of adsorbed Sb at filter bed (μg)	Adsorption capacity (μg/g)
50	981.75	5.44	5.5	1,537	768.1	138,341	112.7
70	1,364.63	5.39	7.7	3,736	2,596.9	405,987	238.0
90	1,751.44	5.30	10.1	4,659	4,155.7	727,326	332.6

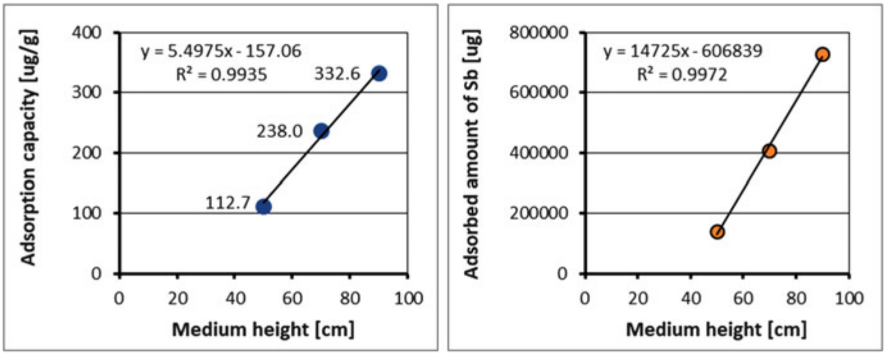

Fig. 10 Adsorption capacities and the amount of adsorbed antimony at three different filter bed heights set for 5 μg/L of Sb at the outlet from the column [75]

filter bed material, and the value of the filter length, L_F, for 5 μg/L Sb at the outlet of the individual columns for 50, 70, and 90 cm bed height.

Figures 10, 11, and 12 show that the monitored parameters have a linear relationship, except the V/V_0 parameter (bed volume) which does not have a linear relationship, as can be seen not only visually but also based on the standard deviation R^2. Therefore, it is appropriate to supplement this parameter with the filter length

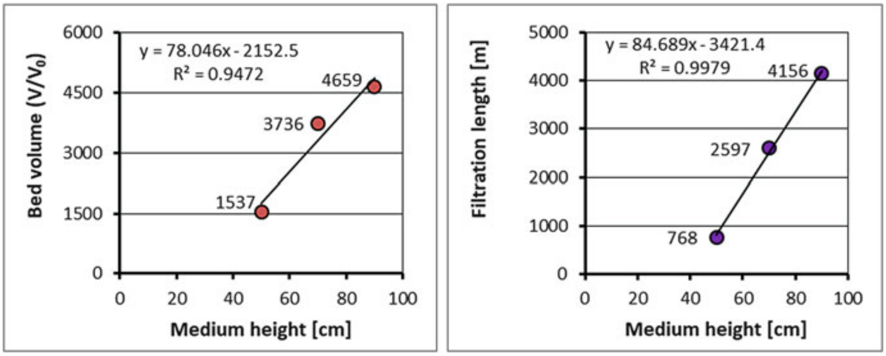

Fig. 11 Bed volume (*V*/V_0 ratio| and the filter length (L_F) for three different filter bed heights (for 5 μg/L of Sb at the outlet from the column) [75]

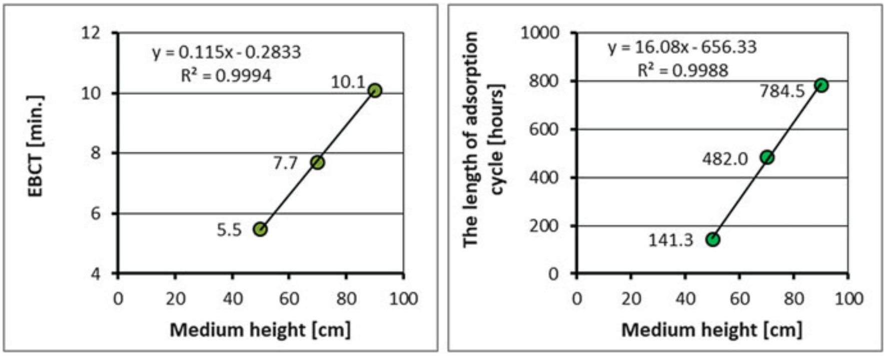

Fig. 12 The Empty Bed Contact Time (EBCT) and the length of the adsorption cycle for individual filter bed heights set for 5 μg/L Sb at the outlet from the column [75]

indicator, which is used for filter materials, but in the sorption materials, this figure is usually not given in the literature [75].

7 Conclusion

The conducted technological tests with underground spring water in the Dúbrava location showed that with the help of the GEH sorption material, we can reduce the antimony content in water to the value 5 μg/L determined by the Decree of the Ministry of Health of the Slovak Republic No. 247/2017, which lays down details on drinking water quality, drinking water quality control, monitoring, and risk management of drinking water supply [82].

Model tests were intended to monitor the effectiveness of antimony removal from water source Dúbrava with three different sorption materials (GEH, CFH12, and Bayoxide E33). From this results show that GEH is the most suitable material for antimony removal compared to the other sorbents used in the test. Therefore, the effectiveness of antimony elimination from water was studied in a model facility, where raw water passed through three adsorption columns filled with GEH material using different height (50, 70, or 90 cm) of filter bed and to determine the most frequently used parameters indicating the effectiveness of sorption (adsorption capacity and bed volume) on the basis of the measured values through linear regression [75].

For the known filtration rate (flow) and concentration of antimony in water, we can propose the volume (height) of the adsorption column bed and determine the efficiency of antimony removal from the water, expressed either as bed volume (the V/V_0 ratio) or as a filter length, L_F, using the linear regression equation. It is also possible to calculate (estimate) the amounts of adsorbed antimony in the filter bed and the adsorption capacities of the materials used for the given technological process of water treatment [75]. If the water contact time (EBCT) with the sorption material in filter column is longer, the higher the antimony removal efficiency from the water will be achieved.

Assuming that the linear relationship will also apply to other filter bed heights (e.g., 120 cm, 150 cm, etc.), we can determine the length of the colon's adsorption cycle (in hours) after which the concentration of Sb at the outlet will achieve just 5 μg/L. For 120 cm bed height, it would be 1,273 h, and for 150 cm it would be about 1,756 h. If we compare it with real results, the increase in bed height from 90 to 150 cm, i.e., about 60 cm, would extend the length of the work cycle to about two times (from 784.5 to 1,756 h) [75]. To increase the efficiency of antimony removal from water source Dúbrava, it is possible to use two filter columns connected in series.

Our results also showed that in addition to the adsorption capacity and the V/V_0 ratio (bed volume), it is necessary to express the efficiency of the used procedure also by the filter length parameter (although this figure is not used for the sorption materials in literature). This is due to the fact that the bed volume parameter did not have a linear dependency for the used heights of adsorption column beds during our experiments [75].

Obtained results confirmed the findings published by foreign authors who consider these sorption materials to be more efficient in arsenic than antimony removal. Therefore, obtained results in this phase of works provide a certain background for usage of monitored filtration (sorption) materials also in antimony removal from water.

This method of water treatment is suitable mainly in localities where water treatment does not include coagulation, sedimentation, and filtration as well as in emergency situations. The advantage of this technology is total reliability, promptness, and simplicity of the operation. The disadvantage can be the cost of sorption materials (6 to 8€/kg) and pH of treated water (lower pH increases the sorption capacity and operational life of the medium). The presence of salts, colloid particles, organic substances, and other heavy metals in treated water can affect antimony adsorption or block the access of antimony to grains of adsorption medium. The disadvantage can be the higher concentrations of metals adsorbed in sorption material (after exhaustion of sorption capacity and replacing of material) and the necessity to dispose of used material on waste dump.

8 Recommendations

Our recommendations are as follows:

1. The results of experiments obtained have proved that the GEH material is more effective for the removal of antimony from the water compared to the Bayoxide E33 and CFH12.
2. The effectiveness of antimony removal from water is significantly lower compared to arsenic removal, the materials used in this work are developed to remove arsenic from water, so new materials need to be found and tested under operating conditions.
3. In general, the effectiveness of heavy metal removal depends on the filtration rate, height (volume) of the filter media (i.e., contact time with sorption materials), and heavy metal concentrations in raw water.
4. To increase the efficiency of heavy metal removal from water source using adsorption, it is necessary to decrease pH value of raw water (lower pH increased sorption capacity and lifetime of the sorption material).
5. It is necessary to increase oxidation potential of the heavy metals (it is well known that the pentavalent form of As and Sb is more easily removed from the water compared to trivalent form of As and Sb) by oxidation (aeration, adding disinfectant agent) of raw water.
6. When choosing the right filter, or sorption material, it is always necessary to follow the given operational conditions and have knowledge of different types of sorption materials (sorption capacity, bed volume, grain size, etc.); the efficiency of sorption materials needs to be experimentally verified by long-term testing – pilot plan experiments.
7. The higher efficiency of heavy metal removal from water will be achieved by increasing the water contact time (EBCT) with the sorption material in filter column (optimal filtration rate needs to be verified).
8. The sorption material used must be sufficiently washed prior to the start of the experiment; it is necessary to remove the dust particles and air bubbles in the filter column.
9. When choosing the right treatment technology for removing of heavy metals, it is necessary to know water quality, heavy metal concentrations in raw water, for what purpose the treated water is to be served, which concentration must be obtained by the selected water treatment, etc. Therefore, pilot tests to verify the effectiveness of heavy metal removal directly on a water source are needed.

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