Removal of Antimony from Water Using GEH Sorption Material at Different Filter Bed Volumes

Danka Barloková[1], Ján Ilavský[1], Karol Munka[2]

[1]Dpt. of Sanitary and Environmental Engineering, Faculty of Civil Engineering,
Slovak University of Technology, Bratislava, Slovak republic
[2]Water Research Institute, Bratislava, Slovak republic
E-mails: [1]danka.barlokova@stuba.sk (corresponding author); [1]jan.ilavsky@stuba.sk; [2]munka@vuvh.sk

Abstract. The article presents the results of antimony removal from the water at Dúbrava water resource using GEH sorption material at three different amounts (volumes) of the filter bed. Based on the results of the experiment we calculated the linear dependences of the amount (volume) of the bed and the absorption capacity, the time of contact of water with the material, bed volume (V/V0 ratio), the duration of filtration and the adsorbed antimony volume in the filter bed. These values were determined for antimony concentrations of 5 μg/L at the outlet from the filter columns, i.e. for limit concentrations of antimony in drinking water, with an average concentration of antimony in raw water being 90.3 μg/L and the average filtration rate being in the range from 5.3 to 5.4 m/h.

Keywords: drinking water, filtration, iron-based sorption materials, removal of antimony, medium height.

Conference topic: Water engineering.

Introduction

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 (Mohan, Pittman 2007; Ilavský et al. 2015; Westerhoff et al. 2005; Rubel 2003; Sperlich et al. 2005; Saha et al. 2005; Jekel, Seith 2000; Guan et al. 2008; Biela, Kučera 2016). The most frequently reported results are from experiments using ferrous sorption materials (oxides, oxihydroxides, or hydroxides of iron), also known as GEH, Bayoxide E33, CFH12, CFH18, Everzit As, etc. They were manufactured and tested in particular for the removal of arsenic from water. 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:
a) the concentration of the contaminant in the water,
b) the concentration of the contaminant after treatment,
c) the amount of treated water expressed as filtration rate, whereby:

filtration rate [m/h] = flow rate [m³/h] / filter area (cross-section) [m²],

d) 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 [m³] * 60 / flow rate [m³/h],*

e) 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,
f) density (kg/m³). 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.
g) the total surface area (BET) in m²/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 sorption materials indicate this value together with adsorption capacity as data to characterize the effectiveness of the sorption process.
3. Filter length L_F us 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:

a) water pH (lower pH increased sorptive capacity and lifetime of the medium),
b) 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,
c) 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,
d) 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,
e) specific surface area and pore size distribution of the sorption material,
f) 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 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, sulphate, phosphate, fluoride, organics, etc. (Nguyen *et al.* 2011; Zeng *et al.* 2008).

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.

Material and methods

Dúbrava Water Resource

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 source consisted of three springs (Brdáre, Močidlo, Škripeň). Currently only the Škripeň spring, which does not contain antimony, is used as the drinking water supply for the residents (villages of Dúbrava, Ľubela and Gótovany). The other sources are contaminated with Sb.

Based on data from the operational control of water quality provided by the Water Company of the Region of Liptov, the highest antimony contamination was detected in the water from Brdáre spring, whose concentrations ranged from 80.3 to 91.3 µg/L. Antimony concentrations in water from the spring Močidlo were determined lower by about 10 µg/L than in the water from the spring Brdáre (70.6 to 82.0 µg/L). Other heavy metals are not present in the given location.

The main causes of the increased concentration of antimony in the Močidlo and Brdáre springs are considered to be the existence of the Dúbrava bearing, as well as a high concentration of antimony in mine waters, the washing of the tailing rock heap and the sludge bed, which contain highly antimony-enriched rocks, along with rain water, which supplied the groundwater and Križianky surface flow (Munka *et al.* 1999).

Antimony and its basic characteristics

Depending on water pH, the oxidation-reduction potential (the Sb^{3+}/Sb^{5+} ratio) and the oxygen content, antimony is present in the waters such as Sb^{3-}, Sb^0, Sb^{3+} and Sb^{5+} (Sb^{3+} is ten times more toxic than Sb^{5+}), most often in the form of antimonate – as oxoanion $(H_2SbO_4)^-$ or $(HSbO_4)^{2-}$, or it may also be present in the form antimonite (H_3SbO_3) (Pitter 2009).

Antimony is a toxic heavy metal (AWWA 1990; US EPA 1984) which can be compared to arsenic and lead with its effects. Compared with arsenic, antimony poisoning has an easier course, because the antimony compounds are absorbed more slowly. Antimony inhibits some enzyme, affects the metabolism of proteins and carbohydrates, and also infringes on the formation of glycogen in the kidneys. Its ability to accumulate in organisms is low. The World

Health Organization (WHO) and institutions involved in monitoring the carcinogenicity do not yet classify Sb as a carcinogen.

According to WHO, US EPA and the EU directive, the amount of antimony in drinking water is limited by the value 6 µg/L (Drinking Water Directive 1998; US EPA 2017; WHO 2011; WHO 2003); in Slovakia, the permissible concentration of antimony in drinking water is set at 0.005 mg/L by the Government Regulation No. 496/2010 Coll.

The requirement for drinking water is now secured, but due to the lack of quality drinking water in the area there are efforts to use the specified water resources in the future as well, requiring water treatment and the design of its technology.

Pilot-scale experiment

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

The effectiveness of antimony elimination from water was studied on 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 cm and 100 cm.

Model tests of Sb removal were held in the Dúbrava chlorination station building (Fig. 1).

Fig. 1. View of the waterworks building in Dúbrava and used sampling equipment

GEH material was obtained from GEH Wasserchemie, Germany. This is a sorbent material, developed at the University of Berlin in the Department of Water Quality Control for the purpose of removing arsenic from water. It consists of ferric hydroxide and β-FeOOH oxyhydroxide, with a dry content of 57 wt.% (± 10%). The iron content is 610 g/kg (± 10%) in the dry state (Driehaus *et al*. 1998; Westerhoff *et al*. 2005; GEH-Wasserchemie 2017). According to literature, GEH is most often used for the removal of arsenic from water, highly selective towards arsenates (As^{5+}), and therefore requires the initial oxidation in the presence of arsenite (Bissen, Frimmel 2003). The efficiency of removal of As is reduced by increasing the concentration of phosphates and sulphates in the treated water (Westerhoff *et al.* 2008).

Table 1 shows the physical-chemical properties of the GEH material. To complement this we give the chemical composition of the GEH material determined through X-ray microanalysis in Table 2.

Table 1. The physical-chemical properties of the sorption material GEH (GEH-Wasserchemie 2017)

Parameter	GEH
Chemical composition	β-FeOOH + Fe(OH)₃
Physical form	moist granular
Colour	dark brown
Particle size range	0.5–2.0 mm (±10%)
Bulk density, backwashed	1150 (±10%) g/dm³
Specific surface area (BET method)	250–300 m²/g
Empty bed contact time (EBCT)	≥3 min
Grain porosity	72–77 %
Operating pH range	5.5–9.0

Table 2. The chemical composition of the sorption material GEH (Ilavský, Barloková 2012)

Material	Compound in mass [%]						
	Al_2O_3	SiO_2	P_2O_3	SO_x	K_2O	CaO	Fe_2O_3
GEH	1.74	3.05	0.21	0.54	0.08	0.18	91.92

Without undergoing any pre-treatment, 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 column, i.e. for the limit concentration of Sb in drinking water.

Results and discussion

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 3.

Table 3. The conditions of filtration (the average values)

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 [cm3]	0.982	1.364	1.751
Medium weight [g]	1227.2	1705.8	2189.3
Average flow through column [ml.min-1]	178.0	176.4	173.4
Average filtration rate [m.h-1]	5.44	5.39	5.30

Figure 2 shows the course of the concentration of antimony depending on the filter length of the model facility. The figure also shows the limit value of antimony in drinking water according to Slovak Government Regulation No. 496/2010 (5 µg/L). 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 were additionally calculated through extrapolation.
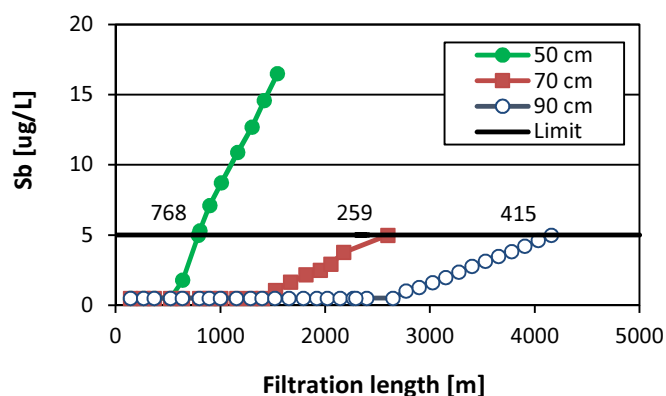

Fig. 2. Compare of efficiency of the materials GEH in the removal of Sb from water

Based on the achieved results, Table 4 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.

Table 4. The chemical composition of the sorption material GEH [24]

Height media	Volume media	Average filtration rate	EBCT	Bed volume (V/V_0)	Filtration length L_F	Amount of adsorbed Sb at filter bed	Adsorption capacity
[cm]	[cm^3]	[m/h]	[min]		[m]	[µg]	[µg/g]
50	981.75	5.44	5.5	1537	768.1	138341	112.7
70	1364.63	5.39	7.7	3736	2596.9	405987	238.0
90	1751.44	5.30	10.1	4659	4155.7	727326	332.6

For mathematical processing and generalization of data in Table 4 we used the linear regression method. Figure 3, 4, and 5 show the equations of lines for GEH adsorption capacities, the V/V_0 ratio (bed volume), the contact time of water with the 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 3 to 5 show that the monitored parameters have a linear relationship, with the exception of 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 indicator, which is used for filter materials, but in the sorption materials this figure is usually not given in literature.
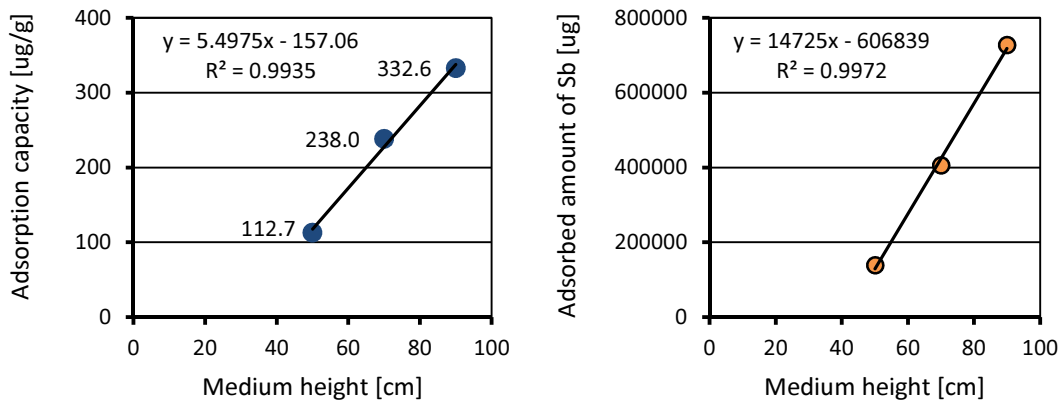

Fig. 3. Adsorption capacities and the amount of adsorbed antimony at three different filter bed heights
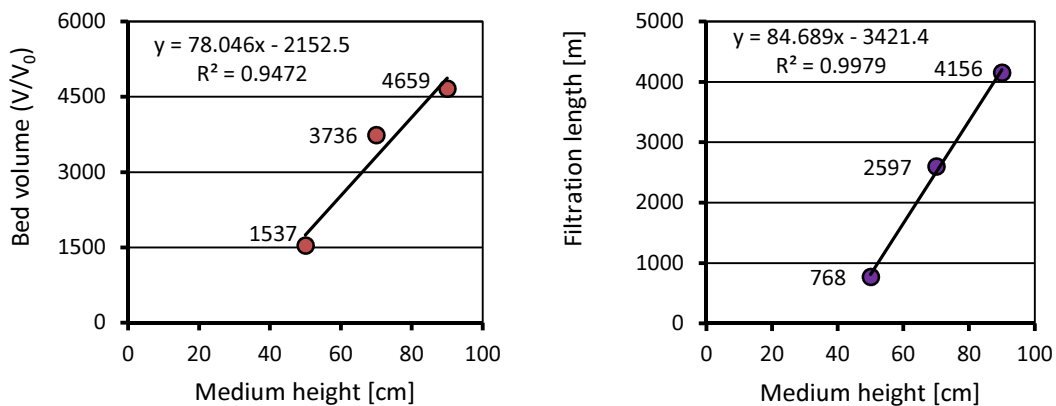set for 5 µg/L of Sb at the outlet from the column

Fig. 4. V/V_0 ratio (bed volume) and the filter length (L_F) for three different filter bed heights
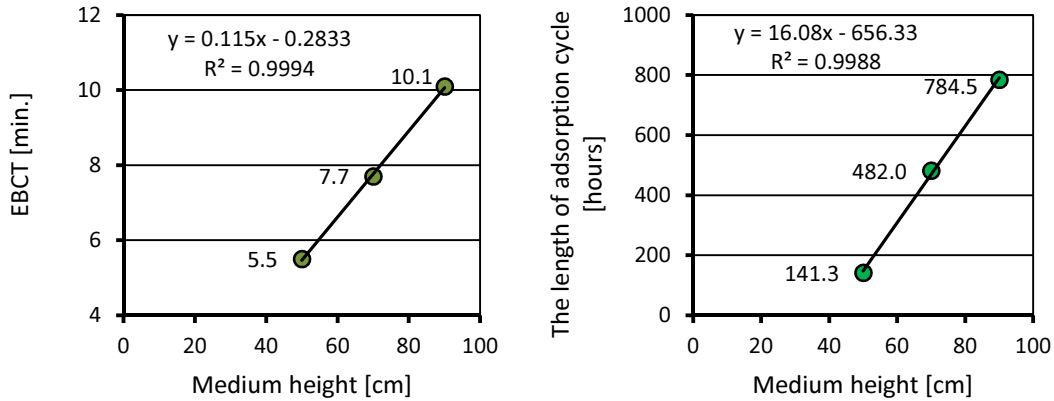(for 5 µg/L of Sb at the outlet from the column)

Fig. 5. 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

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 determined by Slovak Government Regulation No. 496/2010 for drinking water.

Model tests were intended to monitor the effectiveness of antimony removal from water for three different heights of bed with GEH material in the column, 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.

In the known flow and estimate of the appropriate contact time, we can propose the volume (height) of the adsorption column bed, determine the efficiency of antimony removal from the water, expressed either as bed volume (the V/V_0 ratio) or as a filter length LF 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.

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 1273 hours and for 150 cm it would be about 1756 hours. If we compare it with real results, the increase in bed height from 90 cm to 150 cm, i.e. about 60 cm, would extend the length of the work cycle to about 2 times (from 784.5 hours to 1756 hours).

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.

Contribution

D. Barlokova declares involvement in conception and design of the work, participation in field measurements, revising the article. J. Ilavský and K. Munka declare involvement in drafting the article, participation in field measurements, analysis, interpretation of data.

Disclosure statement

The authors declare that they do not have any competing financial, professional, or personal interests from other parties.

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