Iron-based 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, Bayoxide E33, CFH12) during the process of removing antimony from water. Pilot tests showed that the use of iron-based sorption materials could possibly decrease the antimony content in water to the values limited for drinking water. At an average concentration of antimony in raw water of 58.3 μg/L and the empty bed contact time 6.0 for GEH, 6.4 for Bayoxide E33 and 6.3 for CFH12, the value of bed volume 1,700 for GEH, 715 for Bayoxide E33 and 790 for CFH12 achieved at breakthrough concentration 5 μg Sb/L was determined. Considering the values of bed volume GEH was the most suitable adsorbent for the removal of antimony from water.

Key words | drinking water, iron-based sorption materials, removal of antimony

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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 a drinking water supply, since it contains no antimony. Two other springs are contaminated with antimony from mining activities.

According to the water quality monitoring data provided by the water company of the region of Liptov for the period 2000–2005, the highest contamination from antimony was observed in the water from the Brdáre spring, where the concentrations ranged from 80.3 to 91.3 μg/L. The concentration of antimony in the water from the Močidlo spring was 70.6–82.0 μg/L. Obviously, the best water quality was monitored in the Škripeň spring, where the concentration of antimony was lower than 1 μg/L in every sample taken during the monitoring period. No other heavy metals were present in the Dúbrava water resource.

Antimony is present in water as Sb^{3-}, Sb^{0}, Sb^{3+} and Sb^{5+} (Sb^{3+} is 10 times more toxic than Sb^{5+}), depending on the water pH, the oxidation–reduction potential (Sb^{3+}/Sb^{5+} ratio) and the oxygen concentration. It is found mainly in the form of antimonate as oxyanions $(H_2SbO_4)^-$ and $(HSbO_4)^{2-}$ or it can be present in the form of antimonite (H_3SbO_3) (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. The findings on the health aspects of certain heavy metals in drinking water are included in several publications (USEPA 1984; AWWA 1990).

In Slovakia, an acceptable concentration of heavy metals in drinking water is defined under the Government Regulation No. 496/2010 on Drinking Water. The limit

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concentration for antimony is 5 μg/L. This limit value is in accordance with the WHO Recommendations (WHO 2011) and EU Directive (98/83/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, activated carbon, magnesium hydroxide, media containing CeO_2, TiO_2 or MnO_2 layers on their surface, etc.

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 arsenic removal from water. A number of experiments and model studies on the adsorption of arsenic and other heavy metals are described in various publications (Rubel 2003; Thirunavukkarasu *et al.* 2003; Sperlich *et al.* 2005; Westerhoff *et al.* 2005; Mohan & Pittman 2007; Guan *et al.* 2008; Zeng *et al.* 2008; Cumming *et al.* 2009; Nguyen *et al.* 2011; Vithanagea *et al.* 2013). 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, the temperature and composition of water to be treated (concentration of iron, manganese, phosphorus, silicon, fluorides, sulphates, organic matter, etc.).

The objective of this work was to verify the sorption properties of granular iron-based filter materials (GEH, Bayoxide E33, CFH12) in the Dúbrava water resource during the process of antimony removal from water.

MATERIALS AND METHODS

The pilot tests for removing antimony were carried out at the Dúbrava chlorination plant (Figure 1). For the purpose of these simulation tests, there was a need to convey the water from the Brdáre spring to the chlorination plant through a separate pipe in order to avoid mixing it with the water from the Škripeň spring.

Adsorbents

The GEH was obtained from the supplier (GEH Wasserchemie, Germany). GEH is a sorption material developed by the Department of Water Quality Monitoring of the University of Berlin for the purpose of arsenic removal from water (Driehaus *et al.* 1998; Bathnagar *et al.* 2009; GEH Wasserchemie 2013).

Bayoxide E33 is a granular iron oxide-based medium. It was developed by Severn Trent in cooperation with Bayer AG for the removal of arsenic and other contaminants from water. The advantage of this material is its ability to remove As^{3+} and As^{5+} together with iron and manganese (Naeem *et al.* 2007; Severn Trent Services 2013).

CFH12 is a granular sorption material based on iron oxyhydroxides. It was developed by Kemira Finland as an effective product for the removal of arsenic and other

Figure 1 | Dúbrava chlorination plant and model filtration columns.

contaminants from water by adsorption (Backman *et al.* 2007; Kemwater ProChemie 2013).

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

Model filtration system

The effectiveness of the antimony removal was verified using adsorption columns containing the selected sorption material. The adsorption column was made of glass with a diameter of 5.0 cm. The height of the media ranged from 50 to 52 cm, and the total height of the glass column was 80 cm.

Raw water (the Brdáre spring) passed through the filtration system, 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 and for the filter backwash as well as for regulating the filtration rates.

RESULTS AND DISCUSSION

Within the frame of experiments were studied chemical composition and surface properties of used sorption materials. Chemical composition and microstructure were 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.

Table 1 | Physical and chemical properties of the selected sorption materials

Parameter	GEH	Bayoxide E33	CFH12
Matrix/active agent	$Fe(OH)_3$ and 52–57% β-FeOOH	Fe_2O_3 > 70% and 90, 1% α-FeOOH	FeOOH and Fe^{3+} > 40%
Physical form	Moist granular	Dry granular	Dry granular
Bulk density [g/cm^3]	1.22–1.29	0.45	1.12–1.2
Specific surface area [m^2/g]	250–300	120–200	120
Grain size [mm]	0.32–2.0	0.5–2.0	0.5–2.0

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
GEH	–	1.74	3.05	0.21	0.54	0.08	0.18	–	91.92
Bayoxide 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

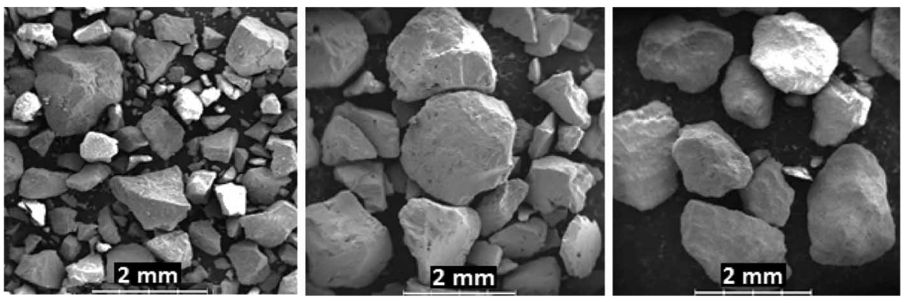

Figure 2 | The microstructure of the GEH, Bayoxide E33 and CFH12 (40× magnification).

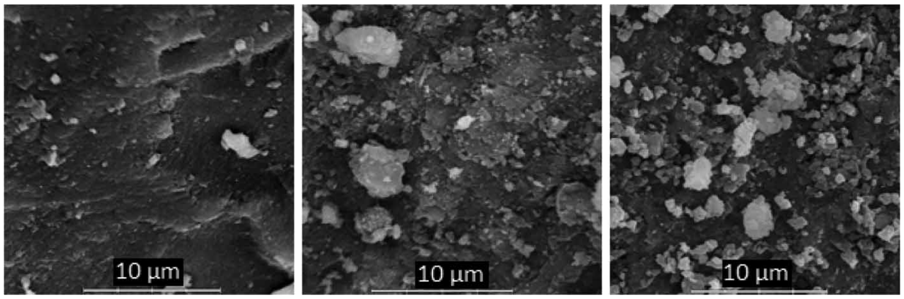

Figure 3 | The microstructure of the GEH, Bayoxide E33 and CFH12 (10,000 × magnification).

Table 3 | Surface properties of sorbent materials

Material	S_{BET} [m^2/g]	V_a [cm^3/g]	D_p [Å]
GEH	190	0.295	47
Bayoxide E33	245	0.447	80
CFH12	110	0.092	22

The shape and the exterior surface of sorption materials GEH, Bayoxide E33 and CFH12 were taken by electron microscope. Tested adsorbents presented in Figure 2 (magnification 40 ×) and in Figure 3 (magnification 10,000 ×) illustrate differences in character of aggregates and differences of surfaces which correspond to their chemical composition (Table 2).

Surface properties of sorption materials (Table 3) were studied through the physical adsorption of nitrogen at the temperature of liquid nitrogen (−197 °C) by the volumetric method using ASAP 2400 (Micromeritics). Before measurement the samples were activated for 15 hours at a temperature of 350 °C and a vacuum of less than 2 Pa. Adsorption data were processed using a standard Brunauer–Emmett–Teller (BET) isotherm with the linearization in the range $0.05 \leq p/p_0 \leq 0.3$ (specific surface area S_{BET}). Desorption branches of isotherms were used for calculation of pore size distribution by the standard Barrett-Joyner-Halenda (BJH) method (maximum on the pore size distribution curve D_p). The total pore volume was estimated from nitrogen adsorbed quantity at relative pressure of $p/p_0 = 0.99$.

Adsorption isotherms of samples Bayoxide E33 and GEH (Figure 4(a)) of type IV show hysteresis loops of H2 type typical for mesoporous materials. Specific surface area S_{BET} is 245 and 190 m^2/g with maximum in pore size distribution of 80 and 47 Å for samples Bayoxide E33 and GEH, respectively (Figure 5(a)). Their total pore volumes are 0.447 and 0.295 cm^3/g.

Adsorption isotherm of sample CFH12 is completely different (Figure 4(b)). The isotherm lies at significantly

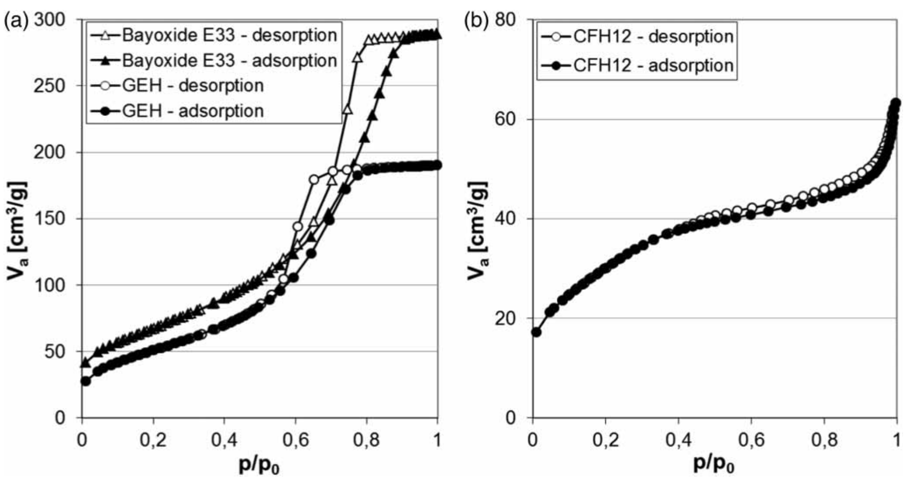

Figure 4 | Adsorption isotherms for sorption materials Bayoxide E33 and GEH (a) and CFH12 (b) used in the test.

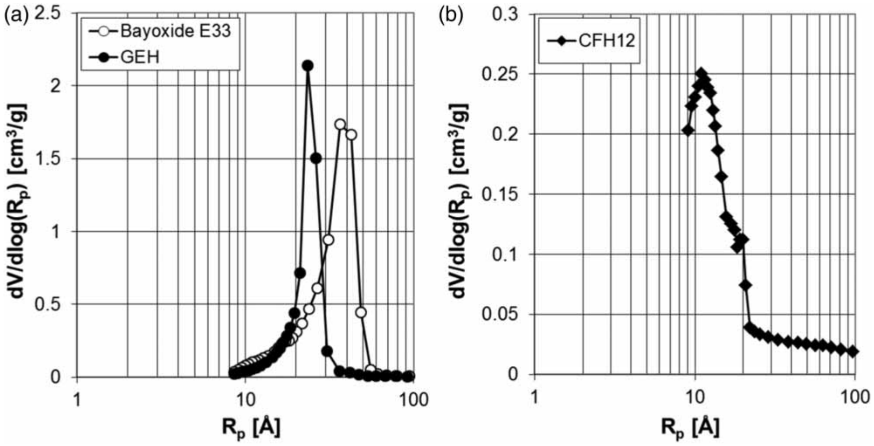

Figure 5 | Pore size distributions for sorption materials Bayoxide E33 and GEH (a) and CFH12 (b) used in the test.

lower adsorbed volume of nitrogen, and very narrow hysteresis loops of H4 type do not indicate strong mesoporous properties. The specific surface area $S_{BET} = 110\,m^2/g$ as well as total pore volume $V_a = 0.092$ are substantially lower than those of Bayoxide E33 and GEH. The pore volume of sample CFH12 is concentrated mainly in pores with diameter of about 22 Å (Figure 5(b)), that is on the lower boundry of the mesopore scale.

The model test was aimed at monitoring the effectiveness of the iron-based sorption materials GEH, CFH12 and Bayoxide E33 for the removal of antimony from water. The concentrations of antimony in the raw water ranged from 55 to 62 μg/L (an average of 58.3 μg/L); the media height was 50 cm, the volume of adsorption column was 982 cm^3, the filtration rates were 4.7–5.3 m/h for the GEH, 4.3–4.9 m/h for the Bayoxide E33 and 4.3–5.1 m/h for the CFH12, and the empty bed contact time (EBCT) was 6.0, 6.4 and 6.3 min, respectively.

Figure 6 shows the breakthrough curves of antimony as a function of water volumes treated in terms of bed volumes (the V/V_0 ratio, where 'V' is the volume of treated water flowing through at a given time and 'V_0' is the volume of the bed), and the values of the bed volume or the adsorption capacity for each sorption material when reaching the limit concentration of antimony (5 μg/L).

From the results presented in Figure 6, it can be concluded that GEH is the most suitable material for antimony removal compared to the other sorbents used in the test. The following bed volumes were measured for the antimony concentration (5 μg/L) at the outlet of the

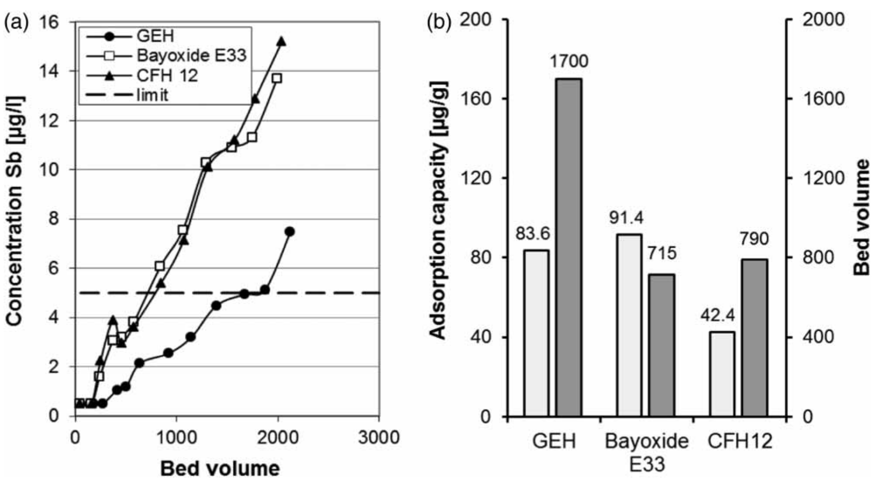

Figure 6 | Breakthrough curves of antimony (a) and the adsorption capacity and bed volumes achieved (b) at breakthrough concentration 5 μg Sb/L.

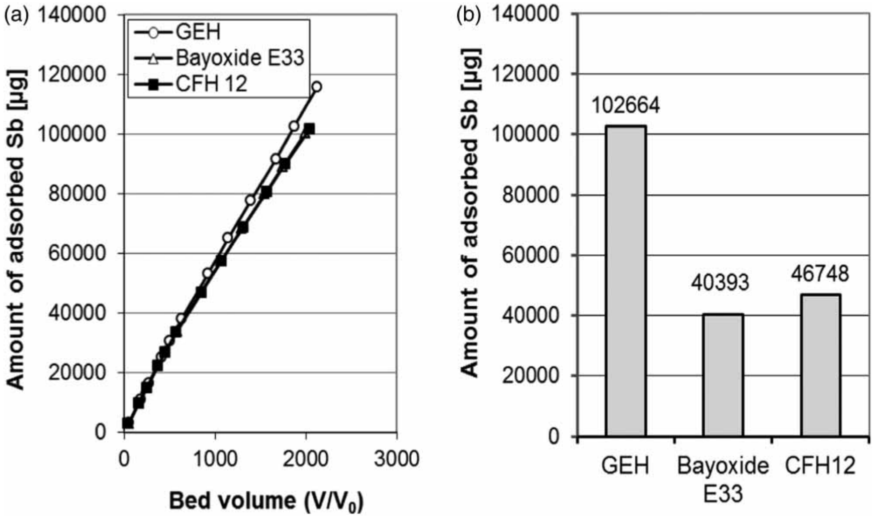

Figure 7 | Amount of adsorbed antimony in adsorption media depending on the V/V_0 ratio (a) and amount of adsorbed antimony in adsorption media when reaching the limit concentration 5 μg/L of Sb at the outlet of the media (b).

adsorbent media: bed volume 1,700 for GEH, 715 for Bayoxide E33 and 790 for CFH12. The adsorption capacities were as follows: GEH = 83.6 μg/g, Bayoxide E33 = 91.4 μg/g (a higher adsorption capacity of Bayoxide E33 is caused by the 2.5 times lower bulk density of this material) and CFH12 = 42.4 μg/g.

The values of adsorption capacity for the GEH and Bayoxide E33 media are in contrast to the development of the antimony concentration at the outlets of the GEH and Bayoxide E33 media, depending on the bed volume. A significantly higher effectiveness of the antimony removal from the water using GEH can be seen in Figure 6. Therefore, if sorbents with different bulk densities (Table 2) are used and compared, the effectiveness of sorption materials would be suitable to be expressed using the bed volume.

According to the material balance of antimony in these experiments, Figure 7 shows the amount of adsorbed antimony depending on the V/V_0 ratio, as well as the amount of adsorbed antimony in adsorption media when reaching the limit concentration Sb (5 μg/L) at the outlets of the media.

CONCLUSION

The technological tests performed on the ground water from the spring in the locality of 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.

The results obtained have proved that GEH material is more efficient for the removal of antimony from water compared to Bayoxide E 33 and CFH12. The limit value for antimony in drinking water (5 μg/L) was exceeded after a 172 hour operation of the filtration device filled with GEH, 80 hours for Bayoxide E33 and 87 hours for CFH12. For a given time period, water volume flowing through the filtration device amounted to 1.71 m^3 for GEH, 0.70 m^3 for Bayoxide E33 and 0.77 m^3 for CFH12. The adsorption capacity of the medium was not exhausted completely. For the antimony concentration (5 μg/L) at the outlet of the adsorbent media bed volume 1,700 for GEH, 715 for Bayoxide E33 and 790 for CFH12 and the adsorption capacities 83.6 μg/g for GEH, 91.4 μg/g for Bayoxide E33 and 42.4 μg/g for CFH12 were measured.

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

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

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