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REMOVAL OF ANTIMONY FROM WATER BY SORPTION MATERIALS

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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 enactment 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 has 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) from selected water resources and compare their effectiveness.

KEY WORDS

- *Treatment of drinking water,*
- *Antimony adsorption and filtration*
- *Sorption materials (GEH, Bayoxide E33),*
- *Removal of antimony from water*
- *Water analysis*

1. INTRODUCTION

The chemistry of antimony and its natural occurrence in some water resources combine to create a potent, widespread human health risk, requiring management and removal from drinking water.
The chemical behaviour of antimony is as complex as that of arsenic, its neighbour 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 mainly bound to extractable iron and aluminium [1].
There are two forms of antimony in water: Sb(III), which occurs as $Sb(OH)_3$. This form is generally considered the most toxic, but it is stable only under anaerobic conditions. Sb(V), which occurs as anion $Sb(OH)_6^-$ (antimonate) is generally the most commonly occurring form of antimony in water.
The toxicity of antimony is a function of the solubility of water and the oxidation state of the antimony species under consideration. In general, Sb(III) is more toxic (ten times higher) than Sb(V), and inorganic compounds are more toxic than organic compounds, with stibin (SbH_3), a lipophilic, being the most toxic (through inhalation).
Concentrations of antimony in groundwater and surface water normally range from 0.1 to 0.2 μg/litre. Antimony is not likely to occur at significantly higher concentrations in natural waters, except in those areas affected by acid mine drainage. Domestic wastewater is practically free of antimony in contrast to wastewater from glass or metal processing enterprises [1].
Traditional treatment technologies used to reach the 0.05 mg/l As level in treated water include co-precipitation and adsorption onto coagulated floc, lime softening, sulfide precipitation, ion exchange, adsorption onto activated carbon or activated alumina, and membrane processes.

SLOVAK JOURNAL OF CIVIL ENGINEERING

2008/2 PAGES 1 – 6

2. GEH AND BAYOXIDE E33 – SORPTION MATERIAL PROPERTIES

The present research which is related to the removal of heavy metals, is focused on the introduction of natural materials as well as industrial and agricultural waste that can be used as cost-effective sorption materials [2]. The most frequently tested sorbents of heavy metals are: zeolite, carbonates, clay, peat, iron oxides and oxihydroxides (natural, synthetic on the surface of coal, wood, lignite and coconut shells), activated alumina, etc.

Today, adsorption by iron oxides and oxihydroxides represents an efficient and cost-effective method for the removal of heavy metals from water. A number of experiments and model studies on heavy metal adsorption is described in publications [3 – 14].

The objective of the study was to verify the sorption properties of some new sorption materials for the removal of antimony from (Bayoxide E33, GEH) selected water resources and compare their efficiency. These materials are very efficient in the removal of arsenic from water. Their basic physical and chemical properties are listed in Table 1.

Bayoxide E33 is a granulated medium based on ferric oxides. It was developed by the SEVERN TRENT Company in cooperation with BAYER AG for the removal of arsenic and other contaminants from water. The system of arsenic adsorption is called SORB 33.

Granulated ferric hydroxide (GEH) is a new material which has only recently been developed at the Department of Water Quality Monitoring of the Berlin University. The treatment technology consists of contaminant adsorption to ferric hydroxide (GEH-sorbent) placed in a column, through which treated water flows.

Tab 1. *Physical and chemical properties of sorption materials*

Parameter	Bayoxide E33	GEH
Matrix/Active agent	Iron oxide composite (>70% Fe_2O_3 and 90,1% α-FeOOH)	52-57% $Fe(OH)_3$ and β-FeOOH
Physical Form	Dry granular media	Moist granular media
Color	Amber	Dark brown
Bulk Density [$g.cm^{-3}$]	0.45	1.12-1.19
Specific Surface Area [$m^2.g^{-1}$]	120-200	250-300
Grain Size Distribution [mm]	0.5-2	0.32-2
Moisture Content [%]	< 15	43-48
Grain Porosity [%]	85	75-80
Operating pH Range	6.0 to 8.0	5.5 to 9.0
Regenerability	No	No

2.1 Factors Affecting the Efficiency of GEH and BAYOXIDE

The effectiveness of antimony removal using these materials depends on the following:

1) pH of the water (a lower pH results in increased sorption capacity as well as the increased life of the filter medium). Figure 1 shows the effect of pH on antimony removal using GEH adsorption material in the locality of Dúbrava [15],
2) redox speciation of Sb (i.e. Sb(III)/Sb(V) ratio),
3) concentration of aqueous species that will interfere with the adsorption of antimony by competing for adsorption sites or modifying adsorptive media surface charges,
4) concentration of aqueous and colloidal species that interfere with the uptake of arsenic by physically blocking the access of arsenic to the interior of the particles or grains of adsorptive media,
5) surface area and pore size distribution of the adsorptive media, and
6) hydraulic properties of the filtration media during treatment.

The first four of the above factors are linked by chemical equilibria between the various aqueous species in the water entering, the

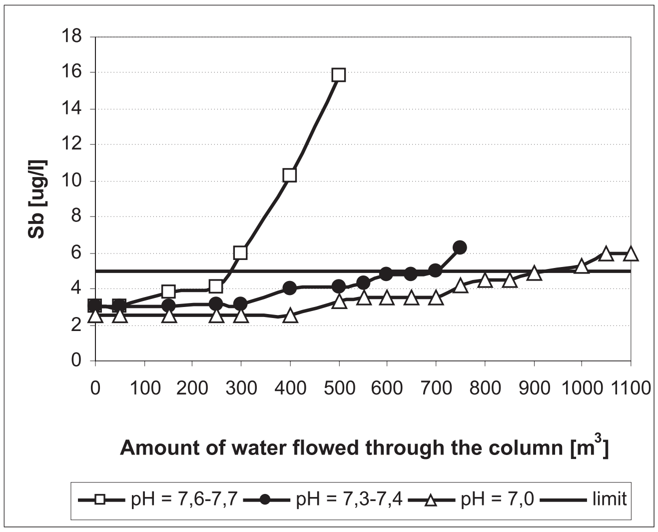

Figure 1: *Influence of pH in the removal of antimony with the GEH sorption material*

SLOVAK JOURNAL OF CIVIL ENGINEERING

2008/2 PAGES 1 – 6

treatment media; the fourth and last two factors are affected primarily by physical mass transfer processes and media properties as discussed below.

Antimony sorption can be influenced by substances such as heavy metals, iron, manganese, silicates, hydrogen-carbonates, phosphates, fluorides, etc. The disadvantage of these materials is the cost associated with their purchase, regeneration or disposal. Therefore, it is important to compare this treatment process using available methods.

3. EXPERIMENTAL PART

Technological tests were carried out at the facility of the Slovak Water Company, Liptovský Mikuláš Branch Company, in the locality of Dúbrava (former chlorine plant) with a well capacity of approximately 40 l/s.

3.1 Model equipment

In order to verify the effectiveness of the antimony elimination process, two adsorption columns filled with the sorption material (Bayoxide E33 and GEH) were used. The adsorption column was made of plastic material with a diameter of 6.0 cm and medium height of 20.0 cm. The adsorption column with a volume of 565.4 cm^3 covered an area of 28.27 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 5 m/h. 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 2.

3.2 Raw water chemical analysis

Based on the groundwater analyses carried out during these tests (2006, May 16 – 23), the antimony concentrations in the raw water ranged from 62.50 to 65.10 µg/l. No other heavy metals were present in the water.

Other parameters in the raw water potentially affecting the sorption properties of the filtration materials were as follows: pH value (the pH value ranged from 6.8 to 6.9 during the test), acid neutralization capacity, base neutralization capacity, aggressive CO_2, water hardness, water temperature, etc.

Table 2 *Filtration conditions*

Parameter	Bayoxide E33	GEH
Grain Size [mm]	< 2.0	< 2.0
Mass of sorption material [g]	608	495
Average flow through column [ml/min]	246	251
Average filtration rate [m/hod]	5.22	5.32
Total filtration time [hod]	164	164
Total amount of water passed through filtration column [m^3]	2.43	2.44
Multiple of water amount passed through filtration column	4298	4315

4. RESULTS AND DISCUSSION

Based on the results of the tests with the Bayoxide E33 and GEH sorption materials, the following water treatment process was applied using the model equipment:

raw water → filtration/adsorption

These tests were aimed at the initial verification of the possibility of using the abovementioned sorption materials in the process of water treatment – antimony removal.

The model equipment was developed for the designed technological procedure until the exhaustion of the sorption capacity of the medium (without any regeneration).

The results of the technological process are shown in Figure 2, there is demonstrated relationship between antimony concentration and bed volumes treated (volume of the water passed through filtration column to volume of the adsorption column). The effectiveness of the monitored sorption materials in the antimony removal process can be seen.

The results obtained have proved that the GEH material is more effective for the removal of antimony from the water compared to the Bayoxide E 33. The limit value for the antimony (5 µg/l) was

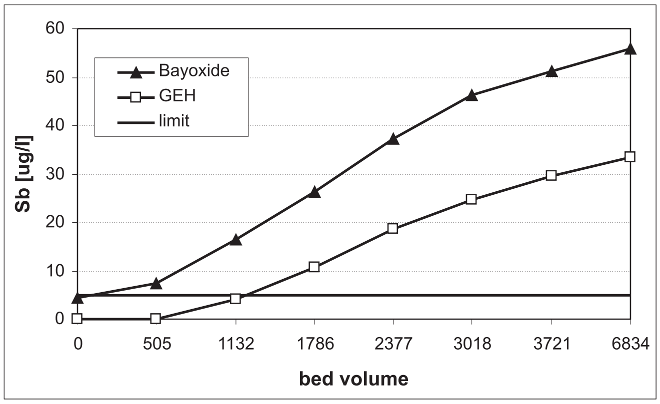

Figure 2: *Antimony removal from water by Bayoxide and GEH sorption materials*

SLOVAK JOURNAL OF CIVIL ENGINEERING

2008/2 PAGES 1 – 6

exceeded after 50.8 hours' operation of the filtration device filled with GEH. The water volume flowing through the filtration device amounted to 0.728 m^3 for the given time period, i.e., a 1.288-fold volume of the GEH. The adsorption capacity of the medium was not exhausted completely (the total amount of water flowing through the GEH filtration material during all the experiments was 2.44 m^3, i.e., a 4.315-fold volume of the GEH).

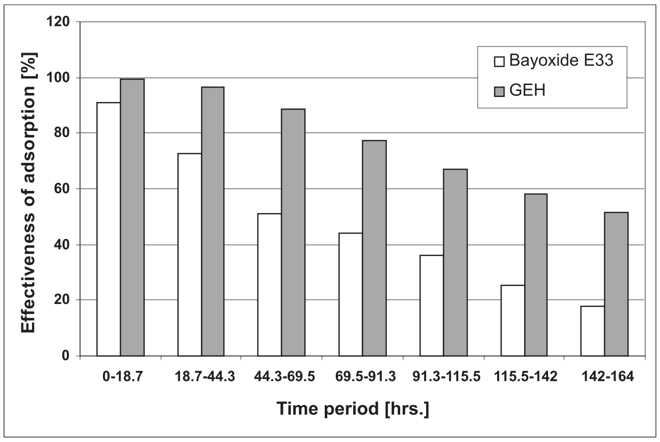

Figure 3: *Comparison of Sb removal efficiency using sorbents Bayoxide and GEH*

The Bayoxide material showed higher values of antimony at the outlet of the adsorption column just after the start of the experiment, i.e., it had an insufficient effect on the given type of water. The limit value for antimony (5 μg/l) in drinking water (under the Slovak Government Regulation No. 354/2006) was exceeded after 6.5 hours operation of this filtration material. The water volume flowing through the filtration device was 0.100 m^3, i.e., a 176-fold volume of Bayoxide (the total amount of water flowing through the Bayoxide filtration material during all the experiments was 2.43 m^3, i.e., a 4.298-fold of the Bayoxide volume).

Figure 3 includes a comparison of the effectiveness of the antimony removal using sorbents (in %) during the model experiments (for the individual time periods).

According to the equation:

$$m_A = (c_S - c_U) \,.\, Q \,.\, t \qquad (1)$$

where m_A is the amount of antimony adsorbed in the filtration medium in the individual time intervals; c_S is the mean antimony concentration at the filter inlet in the individual time intervals; c_U is the mean antimony concentration at the filter outlet in the individual time intervals; Q is the water discharge; and it is the time interval evaluated.

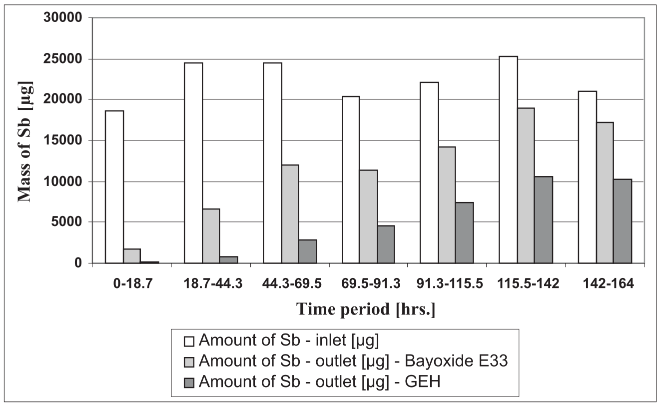

Figure 4: *Comparison of amount of Antimony at filter outlet*

The equation was applied to calculate the amount of antimony at the filter outlet (Figure 4) and the amount of antimony adsorbed in the filter medium during the individual time intervals (sampling).

The amount of adsorbed antimony in the particular adsorbents was calculated partly for the whole model test period (Figure 5), but mainly for the periods during which the antimony concentrations at the filter outlets still met the requirements for drinking water quality ($c < 5$μg/l).

Based on the condition that the limit for antimony at the filter outlet was not exceeded, the adsorption capacity for the particular adsorbents was calculated using the following equation:

$$a_K(X) = m_A(t_B) \,/\, m(X) \qquad (2)$$

where $a_K(X)$ is the adsorption capacity of the sorption material X; $m_A(t_x)$ is the amount of the adsorbed antimony at time t_x; t_x is the

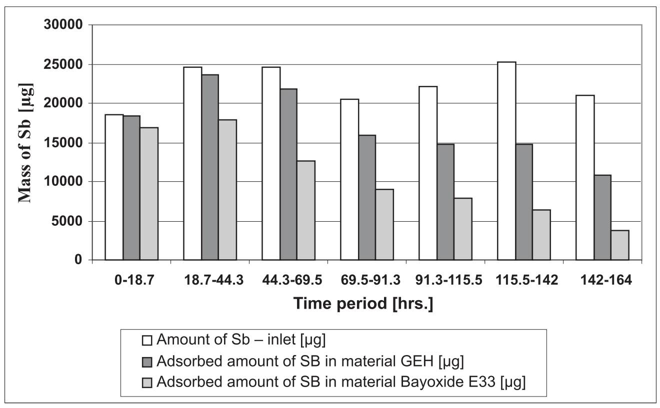

Figure 5: *Comparison of adsorbed amount of antimony in sorption materials*

SLOVAK JOURNAL OF CIVIL ENGINEERING

2008/2 PAGES 1 – 6

time at which the antimony concentration did not exceed the limit value (5 µg/l) at the filter outlet; and m(X) is the weight of the medium placed in the filter.

Under the given operational conditions (the antimony concentration in the raw water is 65 µg/l, the filtration rate is 5.3 m/h), the filter with the Bayoxide E33 with a weight of 608 g adsorbed 16.890 µg of the antimony, while the filter with the GEH with a weight of 495 g adsorbed 42.097 µg of the antimony. The results showed that the adsorption capacity of Bayoxide was 27.78 µg/g, and the adsorption capacity of GEH was 85.04 µg/g (Figure 6).

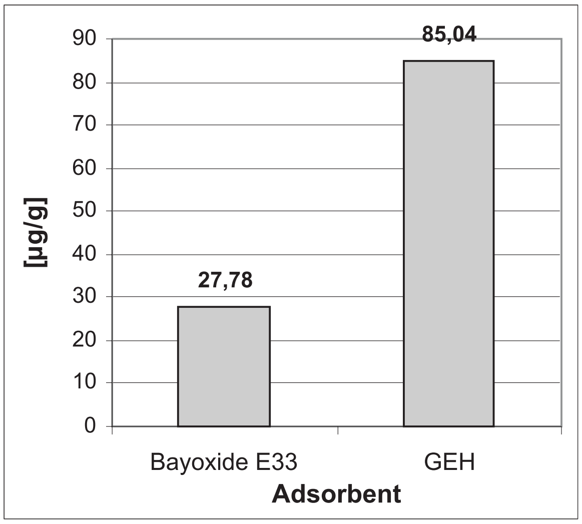

Figure 6: *Adsorption capacity of adsorbents used (v µg/g)*

5. CONCLUSION

The technological tests with groundwater from the Dúbrava well have proved that the new sorption materials can be used for reducing the antimony content in water to meet the values set under the Slovak Government Regulation No. 354/2006 on drinking water.

The results obtained support the published findings of foreign writers according to which these sorption materials are more effective for the removal of arsenic compared to antimony removal. Therefore, the results at this point have proved that both filtration (sorption) materials can also be used for antimony removal.

The effect of the pH on the economics of the operation creates some barriers for the use of these materials in water treatment processes. The disadvantages are the high costs of these materials (for example, GEH costs 220 SKK/l), the presence of salts and other heavy metals in the treated water, higher concentrations of metals, the presence of organic substances, the necessity for their disposal in hazardous waste landfills, etc.

This method of water treatment is especially suitable in localities where it is not possible to use coagulation, sedimentation and filtration for treatment processes or in emergency situations. Reliability, the filtration rate and the simplicity of the operation are among the major advantages of this technology.

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 these materials in water treatment processes.

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SLOVAK JOURNAL OF CIVIL ENGINEERING

2008/2 PAGES 1 – 6

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