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Selected Sorption Materials for Removal of Heavy Metals from Water

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Abstract. Increased pollution of water resources leads to deterioration of surface water and ground water quality and it initiates application of various methods for water treatment. Passing the Decree of the Ministry of Health of the Slovak Republic No. 247/20174 on requirements for drinking water and monitoring of drinking water quality have determined the limit of heavy metal concentrations in drinking water. Based on this fact some water resources in Slovakia became unsuitable for further use and they require appropriate treatment. The present research related to removal of heavy metals is focused on introduction of natural materials as well as industrial and agricultural waste that can be used as cost-effective sorption materials.

Arsenic and antimony are present in the aquatic environment as result of rock weathering reactions, biological activity, geochemical reactions, volcanic emissions, mining operations and anthropogenic activities. The objective of this work was to verify the sorption properties of granular filter materials READ-As (hydrous cerium dioxide adsorbent) in removal of heavy metals from water. This material was developed in Japan for removal of arsenic from water. One part of experiments was carried out in ground water source Dúbrava, where a high concentration of antimony in water is caused from mining activities as well as from rain falling on antimony-rich waste rock piles and a sludge-settling pond has led to higher concentrations of antimony in the relevant water resources. At the other part of article there are presented results with the same material READ-As for removal of arsenic from ground water source in Jasenie. The values of the bed volume and the adsorption capacity for this sorption material when reaching the limit concentration of antimony and arsenic were determined. READ-As material has shown to be more efficient in antimony removal from water in Dúbrava locality than GEH, for average antimony concentrations of antimony in a raw water 27.73 µg/L, filtration rate 5.58 m/h reached the antimony concentration of 5 µg/L in the outflow from the adsorption column of high level 48 cm, V/V_0 (bed volume) 3967 and adsorption capacity of a value 128.4 µg/g. Limit concentration of antimony 5 µg/L was exceeded after 336 hours of operation of the model equipment. Lower efficiency of the GEH material in Sb removal from the water was observed in consideration with currently published results. By pilot plant tests in Jasenie locality was determined adsorption capacity 354 µg/g and ration V/V_0 (bed volume) 5130 µg/g for water with arsenic content of 55-60 µg/L and filtration rate 5.35 m/h, two steps filtration with READ-As material. These values were determined when the limit concentration of arsenic in water outflowing the columns (10 µg/L) was reached. Mentioned values are significantly higher than it was in a case of antimony.



1. Introduction

Since 1998, an intensive attention has been paid to the presence of heavy metals in the water, when technical standard STN 75 7111 Drinking Water was introduced into the Slovak legislation. By transposition of European Directive 98/83/EC and WHO recommendation [1,2] 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 metals 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 metals occurrence presents the same risks as the risks of industrial or agricultural contaminants. Some of them, such as Arsenic, Cadmium or Lead are carcinogenic. The knowledge about the health aspects of heavy metals presence in drinking water are included in the paper Water Quality and Treatment, A Handbook of Community Water Suppliers [3].

In case, when ensuring the drinking water for the customer in accordance with current legislation is not possible (the Decree of the Ministry of Health of the Slovak Republic No. 247/20174 on Drinking Water), it is necessary to ensure the substitutional water source or treating the water eventually. Solving this problem has to be considered also in economic point of view. Transporting the water from the other regions or using the various treatment methods represents advantages but the disadvantages at the same time.

Technological process of removing the heavy metals from a large water sources (surface water especially) consists of coagulation and filtration (single stage water treatment), resp. coagulation, sedimentation and filtration (two stage water treatment). It is being used for coagulation by dosing the coagulant agent while the removal level of heavy metals from water depends on sort of used coagulant, the amount of coagulant dosage pH value during the coagulation and initial value of heavy metals in the water that is going to be treated.

In case of small water resources, the use of advanced technological configurations is not proper. Adsorption on a suitable adsorption material is among the most frequently used methods in water treatment. In terms of plant operation, two stage filtration process represents a simple, effective and economical friendly method of heavy metals removal namely for the possibility of using a large scale of substances with a sorption ability – sorbents. Oxides, oxyhydroxides containing iron, activated alumina, a sand covered by some hydroxide containing iron, activated carbon, media with the TiO_2 or MnO_2 surface layer etc. [4,5] are among the most frequently used sorbents of the heavy metals. The quality of the treated water (pH, silica, phosphorus, fluorides, sulphates, chlorides, vanadium, total mineralisation, iron and manganese), redox conditions and the valency has the impacts on heavy metal removing efficiency [6,7].

For example, arsenic may be presented in the water in a form of the As (III) or As(V). Arsenic in a form of arsenite (III) (H_3AsO_3) as the prevailing form of his presence occurs in the drinking water with pH 6-9 whereas in a form of arsenate is represented by H_2AsO_4^- and HAsO_4^{2-} . Removing the arsenite (III) with no charge from the water is more difficult than removing the arsenate due to the difference of the arsenate and arsenite (III) charge in a pH between 6-9. For this it is necessary to transform arsenite (III) into the arsenate by oxidation and its removal from the water perform after this transformation [8].

2. Material and Methods

Experimental part of this work is divided into two parts to what extent of the work was to verify the sorption characteristics of ceric oxide (READ-As) in removal of the arsenic from the water in the locality of Jasenie and to compare the efficiency of READ-As materials and GEH in removal of the antimony from the water of locality Dúbrava.

READ-As was provided by the company Global Water KFT. Material, the granulated ceric oxide has been developed by Company Nihin Kaisui Co Ltd in Japan. READ-As is a material produced for removal of the arsenic from water in a large scale of conditions and it is sorbing efficiently both the arsenate and arsenite. The oxidation of arsenite (III) to arsenate is not needed. Nor adjusting the pH of

the water before and after the sorption is needed. It is possible to regenerate this material by the addition of sodium hydroxide, sodium hypochlorite after it and by washing with water at the end. Regenerated material needs to be neutralized by hydrochloric acid and needs to be washed with water before the next use. In dependence on the amount of the sorbent and a chemical composition of the water the regeneration should be performed after 4-12 months [9].

Material GEH was obtained from GEH Wasserchemie Company, Germany. It is a sorption material which was developed in order to be able to remove arsenic from water at the Chair of Water Quality Control at the Technical University of Berlin. It consists of ferric hydroxide and oxyhydroxide FeOOH with the dry matter content of 57% ($\pm 10\%$). The iron content is 610 g/kg ($\pm 10\%$) at the dry state [10,11]. Physical and chemical properties of these materials are listed in the Table 1.

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

Parameter	READ-As	GEH
Matrix/ Active agent	$\text{CeO}_2 > 98\%$	$\text{Fe}(\text{OH})_3 + 52\text{-}57\% \beta\text{-Fe OOH}$
Physical form	moist granular	moist granular
Color	yellow	dark brown
Bulk density [g/cm]	0.76	1.22-1.29
Grain size [mm]	0.3-1.0	0.32-2.0
Grain porosity [%]	-	72-80

2.1. Water source Jasenie

Water treatment Plant Jasenie treats the spring water with the yield of 15 l/s. Water contains arsenic at the concentration of approx. 0.060 mg/L. In connection with the hydrological conditions the values are used to be higher in certain seasons.

The pilot-plant equipment in which the treated water is flowing through the sorbent READ-As in a regime of two stage filtration was used for verifying the efficiency of arsenic elimination from water while the total volume of the sorbent was approx. 50 litres and the equipment capacity was 250 l/h. Used filter was of one of the closed type filters and was plastic with the inner diameter of column 24.4 cm, surface of 467.6 cm^2 , column depth 1m and filling depth 53.4 cm. Water flowed through filtration equipment from the top to the bottom direction.

2.2. Water source Dúbrava

The yield of water source Dúbrava is approx. 40 l/s and it consists of three springs (Brdáre, Močidlo, Škripen). Spring Škripen is currently the sole spring that is used for supplying the drinking water for inhabitants. This water spring water contains no antimony. Other springs are contaminated by antimony. A deposit of antimony ore is considered to be the main cause of the increased antimony concentrations in the wells of Močidlo and Brdáre. Furthermore, a high concentration of antimony in water from mining activities as well as from rain falling on antimony-rich waste rock piles and a sludge-settling pond has led to higher concentrations of antimony in the relevant water resources.

Two adsorption columns filled with READ-As and GEH sorption material were used for examining of the elimination efficiency of antimony. Adsorption column was made from the glass, column diameter was 5.0 cm, column depth 80 cm, filling depth 48 cm in case of READ-As material and 49 cm in case of GEH. Raw water flowed through the filtration equipment from top to bottom.

3. Results and discussions

Following scheme represents the used process of water treatment:

Raw water $\rightarrow$ filtration and adsorption (without regeneration and washing the filters)

Raw water without any pre-treatment flowed through the filtration equipment while the arsenic and antimony concentration were monitored in a raw water and in a treated water outflowing from particular

filtration columns. The flow of the water at the discharge from each column and the amount of filtered water were monitored also.

3.1. Experiment 1 – Arsenic removal

Arsenic concentration in a raw water were about 55-60 $\mu\text{g/L}$ during the pilot plant experiments at WTP Jasenie (average 58.71 $\mu\text{g/L}$), filtration velocity 5.35 m/h, detention period of the water in column (EBCT) 5.99 min. Filtration conditions are shown in a Table 2.

Table 2. Filtration conditions

Parameter	READ-As
Grain size [mm]	0.3 – 1.0
Medium height [cm]	53.4
Volume of adsorption column [cm³]	24.97
Mass of sorption material [g]	18980
Average flow through column [l/h]	250
Average filtration rate [m/h]	5.35
Empty Bed Contact Time (EBCT) [min]	5.99

Figure 1 shows the arsenic concentration progress in dependence on ratio V/V_0 (so-called bed volume) for two stages filtration as well as the calculated values of READ-As adsorption capacity (in $\mu\text{g/g}$) and outflowing the column bed volume from column no. 1 and at the end of two stage filtration (columns 1 and 2 together, joined one by one in series) for concentration of arsenic 10 $\mu\text{g/L}$ is also shown in Figure 1. Summarized results of arsenic removal from the water at Jasenie WTP are listed in Table 3.

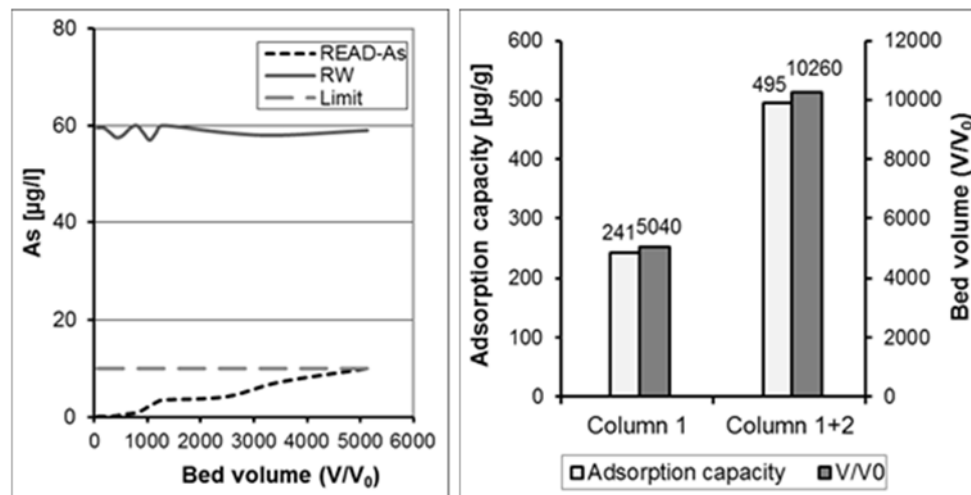


Figure 1. The concentration of antimony ($\mu\text{g/L}$) at the outlets of adsorption media in relation with V/V_0 (left) and the values of V/V_0 ratio and adsorption capacity ($\mu\text{g/g}$) for each sorption material (right) when was reaching the limit concentration of arsenic (10 $\mu\text{g/L}$)

In case of column no. 1, the arsenic concentration value 10 $\mu\text{g/L}$ in treated water after 507 hours of filtration equipment operation was exceeded. Water amount which flowed through this equipment at this time period represents 126 m^3 , i.e. 5040 times of filling volume. Because of the limit value 10 $\mu\text{g/L}$ of arsenic concentration in treated water in two stage filtration process was not exceeded, even not after 700 hours of operation at the end of the experiments, reaching the limit value time as well as bed volume, amount of through the filter flowed water and the amount of caught arsenic were calculated by extrapolation (in Table 3 marked *).

Table 3. Results of arsenic removal from water with sorption materials READ-As

Parameter	Column 1	Column 1+2
Total filtration time [hour]	700	700
Filtration time [hour] after exceeding 10 µg/L	507	1020*
Total amount of water passed through filtration column [m³]	174	174
The amount of water overflow [m³] to the limit	126	255*
The ratio of the volume of water overflow and column medium (V/V₀) to the limit – bed volume	5040	5130*

At the current operational conditions (average As concentration in a raw water 58.71 µg/L, filtration rate 5.35 m/h) the As amount of 6.51 g was adsorbed in a column no.1 by READ-As material (18.98 kg). By performing two-step filtration with the filling mass of 37.96 kg, 13.4 g of Arsenic was adsorbed while the amounts of absorbed arsenic are calculated for value 10 µg/L of arsenic at outflow of the filtration columns. According to these results the adsorption capacity of the READ-As was 343 µg/g when was used column no.1 and 354 µg/g when was used both columns joined in a series (Figure 1).

3.2. Experiment 2 – Antimony removal

Within the range model experiments the antimony concentration in a raw water were in a range of 21.5-31.8 µg/L (average 27.73 µg/L). In case of column with READ-As material usage the filtration rates were in a range of 5.44-5.68 m/h, in a column with GEH material the filtration rates were 5.44-5.81 m/h, water retention time in a column (EBCT) 5.16 min for READ-As and 5.29 min for GEH. Filtration conditions are listed in the Table 4.

Table 4. Filtration conditions

Parameter	READ-As	GEH
Grain size [mm]	0.3 – 1.0	0.32 – 2.0
Medium height [cm]	48	49
Volume of adsorption column [cm³]	942.48	962.12
Mass of sorption material [g]	717.5	1204.8
Average flow through column [ml/min]	182.57	181.86
Average filtration rate [m/h]	5.579	5.557
Empty Bed Contact Time (EBCT) [min]	5.163	5.292

In the Figure 2 there is shown the progress of the antimony concentrations depending on V/V₀ ratio (so-called bed volume), as well as the calculated values of adsorption capacity (in µg/g) and bed volume of used materials (READ-As and GEH) for antimony concentration of the outflow of 5 adsorption fillings (µg/L) are shown in the Figure 2. Antimony removal from the water results are presented in the Table 5.

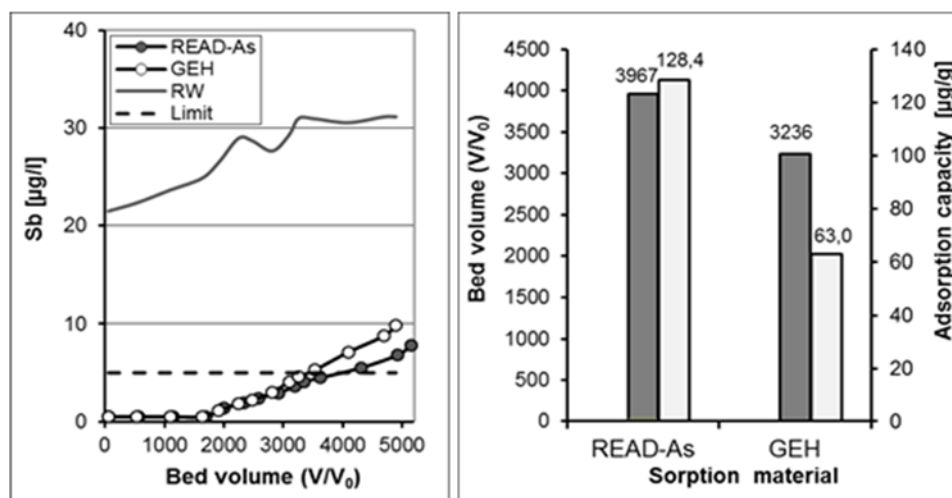


Figure 2. The progress of antimony removal from water (on the left) by using the sorption materials READ-As and GEH depending on V/V_0 ratio (bed volume) and bed volume values, resp. adsorption capacity of these materials for antimony concentration - 5 µg/L at the outflow from adsorption columns (on the right side).

By using the sorption material READ-As the limit value for antimony concentration 5 µg/L was exceeded after 336 hours of operation (285.5 hours for GEH) and the water amount which flowed through the filtration equipment was 3.74 m³ which represents 3967 multiple of filtration media volume for this period of time (3236 multiple in case of using the GEH). Capacity of the adsorption material was not exhausted completely even after that flowed 4.85 m³ of water through the column (5146 multiple of filter media volume).

Table 5. Results of antimony removal from water

Parameter	READ-As	GEH
Total filtration time [hour]	433	433
Filtration time [hour] after exceeding the limit of 5 µg/L	336.3	285.5
Total amount of water passed through filtration column [m³]	4.85	4.74
The amount of water [m³] to the limit 5 µg/L	3.74	3.11
The ratio of flowed through water to the volume of column media to the limit 5 µg/L – bed volume	3967	3236

At the current operating conditions (antimony concentration in a raw water 27.73 µg/L, filtration rate 5.58 m/h in a column with READ-As material, resp. 5.56 m/h with GEH material) the amount of antimony adsorbed by READ-As (717.5 g) was 92165 g and 75945 g of antimony was adsorbed by GEH (1204.9 g). As the obtained results show the adsorption capacity of READ-As was 128.4 µg/g and GEH adsorption capacity was 63.0 µg/g (Figure 2).

4. Conclusions

Performed technological experiments with the groundwater of springs in locality Dúbrava and Jasenie shown that it is possible to decrease the antimony and arsenic content in the water down to the values which are limited by the Decree of the Ministry of Health of the Slovak Republic No. 247/20174 on requirements for drinking water and monitoring of drinking water quality with the tested selected sorption materials.

READ-As was tested for the first time in Slovakia with the testing sight to remove the heavy metals (As, Sb) from the water. It is a new material which is being made in Japan (ceric oxide) and which was supplied by Hungarian company Global Water Filter. This material may be regenerated which means an advantage of this material. According to the data provided by Hungarian company the total costs attributable to treatment of 1000 m³ of water per day (arsenic concentration 20 µg/L) represents 0,0975 €/m³ (operating, investment, waste disposal).

READ-As material has shown to be more efficient in antimony removal from water in Dúbrava locality than GEH, for average antimony concentrations of antimony in a raw water 27.73 µg/L, filtration rate 5.579 m/h reached the antimony concentration of 5 µg/L in the outflow from the adsorption column of high level 48 cm, V/V₀ (bed volume) 3967 and adsorption capacity of a value 128.4 µg/g. Limit concentration of antimony 5 µg/L was exceeded after 336 hours of operation of the model equipment while the amount of the water that flowed through the equipment was 3,74 m³. Lower efficiency of the GEH material in Sb removal from the water was observed in consideration with currently published results (by an impact of pH change of the raw water).

By pilot plant tests in Jasenie locality was determined adsorption capacity 354 µg/g and ration V/V₀ (bed volume) 5130 µg/g (Table 3) for water with arsenic content of 55-60 µg/L and filtration rate 5.35 m/h, two steps filtration with READ-As material. These values were determined when the limit concentration of arsenic in water outflowing the columns (10 µg/L) was reached. Mentioned values are significantly higher than as it was in a case of antimony.

Acknowledgment(s)

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