REMOVAL OF ANTIMONY FROM WATER BY COAGULATION

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Abstract: *Increased pollution of water resources leads to a deterioration of surface water and groundwater quality, and it initiates the application of various methods for water treatment. The enactment of the Slovak Technical Standard 75 7111 for Drinking Water in 1998 resulted in a reduction in heavy metal concentrations and, for the first time, defined the limit concentrations for some heavy metals (As, Sb), respectively. Based on this fact some water resources in Slovakia became unsuitable for further use and require appropriate treatment.*
The aim of this work was to investigate the effectiveness of coagulation to remove antimony from the surface water of Bukovec water tank and groundwater source of Dúbrava, determine the optimum dose of coagulant and optimize the coagulation process. Ferric sulphate was used (Prefloc) as coagulation reagent.
The results showed that the dose of 11 $mg.l^{-1}$ of Fe^{3+} into the surface water of Bukovec is sufficient to reduce the antimony below the limit value of 5 $\mu g.l^{-1}$. To the groundwater from the site Dúbrava be added more than 30 $mg.l^{-1}$ of Fe^{3+} to reach the limit for drinking water.

Keywords: *Water treatment, removal of antimony, coagulation, ferric sulphate, water analysis*

1. Introduction

Antimony (Sb), atomic number 51, molecular weight 121.75 is a brittle silver-white metal that is found in the earth's crust as the chemically bound state and minerals.

Antimony is released into the environment from natural sources and from industry, while the anthropogenic emission into the atmosphere exceeds the natural resources emission. Antimony is a standard component of coal and oil. Industrial plants, emissions from car exhausts and the burning of fossil fuels are the main sources of antimony in the air. The emissions are getting into the atmosphere also from factories by melting the ore and by incineration of the municipal waste. Then they are transported from the air into the soil, lakes, rivers and bottom sediments. Major part of antimony ends up in the soil where the antimony is strongly bounded to particles containing iron, manganese or aluminum. From the soil is released into the food chain. At lower concentration, antimony could be found in some lakes and rivers, and even in drinking water.

At the present time, it is very difficult to distinguish the anthropogenic pollution of the waters from the natural background.

Antimony is a toxic heavy metal with effects similar to arsenic and lead. The Intoxication by antimony is not as much severe as it is 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 of accumulation in the bodies of organisms is low. Findings on health aspects related to the occurrence of some

heavy metals in drinking water are summarized in publication [1,2].

Till now, 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 $\mu g.l^{-1}$ [3]. This limit value is in accordance with the WHO Recommendations [4] and the EU Directive [5].

Antimony is presented 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). The organic form of antimony is very rare, especially in drinking water [6,7].

Concentrations in natural waters not polluted by anthropogenic activity are in a range from tens of $ng.l^{-1}$ up to $1\mu g.l^{-1}$. The threshold limit value (Sb = 5 $\mu g.l^{-1}$) has been exceeded in Slovakia (Figure 1), for instance, in the locality of Košice and its surroundings (Zlatá Idka, the Bukovec water reservoir), the Low Tatras in the locality of Dúbrava (Liptovský Mikuláš), Spišsko-Gemerské rudohorie (Čučma, Poproč) and in the Little Carpathians (Pernek).

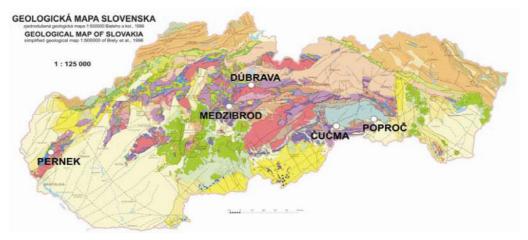Today, it is very difficult to distinguish between anthropogenic and natural pollution caused by antimony.

Figure 1 Areas of antimony in Slovakia

There are several technological methods of heavy metals removal, which are used in water treatment: precipitation (clarification), ion exchange, membrane technologies, adsorption, electrochemical processes and recently also biological methods [8-20].

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 (iron and aluminum salt, lime, sodium carbonate, sodium hydroxide and sulphates) to obtain the optimum pH value of the 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 certain effects that are reducing 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 effective 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.

In comparison with the other metal removal methods the advantage of precipitation is its relatively low cost. 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 the 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 the ion exchange due to the high competitiveness of some ions (selenium, fluorine, nitrates and sulphates) 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 are 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, activated carbon or new adsorption materials such as granular hydroxide or ferric hydroxide (GFH, CFH12, CFH18, Bayoxide E33) etc., for removing heavy metals. Both filtration sand and zeolite modified by higher manganese oxides (MnO_2), whether in a reactor with a fluidized bed or filter, have significant adsorption properties for the removal of antimony and arsenic.

Efficiency of heavy metal removal by adsorption material depends on the pH of the water, oxidation-reduction potential of a given metal in the water, concentration of substances in the 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, 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.

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.

The most of the water treatment processes described in terms of removal of the antimony are only in the experimental stage, and the antimony removal possibilities of some of these technologies has not been proved sufficiently.

The literature relating to water treatment deals more often with the arsenic removal, which presence is relatively more frequent in the water.

By water treatment processes effectiveness evaluation it has been documented that the conventional technological water treatment processes such as coagulation, iron and manganese removal or water softening to elimination of dissolved arsenic As^{5+} could be very effective [19]. In the case of coagulation the removal efficiency of arsenic is particularly influenced by pH value, while the pH decrease from 7,4 to 6,8 increased the arsenic removal efficiency from 30% to 70%. Throughout the coagulation by ferric coagulants there was reached a higher arsenic removal efficiency than it was reached by aluminous coagulants. In technologies focused on iron and manganese oxidation the removal efficiency of the dissolved forms of arsenic was particularly depending on the $Fe(OH)_3$ coagulum formation and in the case of the optimal conditions was the arsenic removal efficiency higher than 75%. By the water treatment aimed at the water softening the

striking reduction of dissolved arsenic was not detected and the high efficiencies (from 60% to 95%) were reached by $Mn(OH)_2$ coagulation what is related to the As adsorption on the hydroxide particles.

The aim of this work was to investigate the effectiveness of coagulation of antimony removal from the surface water from Bukovec water tank and groundwater source from Dúbrava, determine the optimum dose of coagulant and optimize the coagulation process. As coagulation reagent was used ferric sulphate (Prefloc).

2. Experimental

2.1 Chemical analysis of raw water

Table 1 shows the quality comparison of monitored natural waters, the concentration of antimony in surface water ranged from 23 to 29 $\mu g.l^{-1}$, and groundwater range was 58 to 67 $\mu g.l^{-1}$.

Table 1
Quality comparison of monitored natural waters

parameter	unit	Bukovec	Dúbrava
pH		7.34	7.10
conductivity	mS/m	9.7	21.8
color	mg/l	6	3
turbidity	FTU	1	1
$ANC_{4.5}$	mmol/l	0.943	3.122
$BNC_{8.3}$	mmol/l	0.094	0.378
Cl^-	mg/l	6.82	5.94
NO_3^-	mg/l	8.83	6.67
SO_4^{2-}	mg/l	19.23	24.89
F^-	mg/l	0.14	0.09
PO_4^{3-}	mg/l	0.03	0.01
Mn	mg/l	0.026	0.001
Fe	mg/l	0.05	0.01
Ca^{2+}	mg/l	16.59	38.47
Mg^{2+}	mg/l	5.30	15.62
COD_{Mn}	mg/l	0.61	0.48
TOC	mg/l	1.7	1.2
solutes	mg/l	225	160
Ca+Mg	mmol/l	0.632	1.602

Table 1 shows the difference in some parameters, for example in pH, $ANC_{4,5}$ (alkalinity), $BNC_{8,3}$ (acidity), in the contents of Ca+Mg, in the concentration of solute, conductivity, etc. These parameters significantly affect the coagulation process.

2.2 Coagulation test

The coagulation test is a common laboratory procedure used to determine the optimum operating conditions for water treatment procedure. A jar test simulates the coagulation and flocculation processes. Coagulation is the process by which colloidal particles and very fine solid suspensions initially presented in the water are combined into larger agglomerates that can be separated via sedimentation, floccula-tion, filtration, centrifugation or other separation methods. Coagulation is commonly achieved by adding different types of chemicals (coagulants) to the wastewater to promote destabilization of the colloid dispersion and consequently to agglomerate the resulting individual colloidal particles [20].

For coagulation test the device with five mixers adjustable for slow and fast mixing was used (Figure 2).
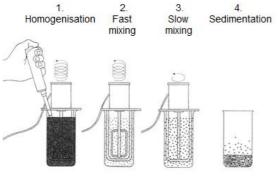

Figure 2 Scheme of laboratory coagulation device

One liter of natural water was added into 5 beakers. After the addition of coagulation agent (1% solution Prefloc) followed 3 minutes of fast mixing (180rpm) and 10 minutes of slow stirring (40 rpm). After

sedimentation (1 hour) and filtration using filter paper, the sample was analyzed. pH, $ANC_{4,5}$ and the concentration of iron and antimony was determined.

3. Results of coagulation experiments with water from WT Bukovec

The results obtained by WT Bukovec sample analysis are shown in Table 2. Concentration of antimony in the raw water (RW) before coagulation test was 29.4 µg.l^{-1}.

Coagulation using ferric sulphate (Prefloc) is a sufficient method for removing the antimony from the water what results from the measurements. The dose of 40 mg.l^{-1} of 1 % $Fe_2(SO_4)_3$ which represents 11,2 mg.l^{-1} Fe^{3+} is already sufficient amount for antimony content decrease below the limiting value 5 µg.l^{-1}, which is set up by Slovakian drinking water legislation no. 496/2010 (Collection of Laws). Because of pH decreasing by impact of ferric sulphate the pH adjustment after the coagulation is needed, e.g. by lime addition.

4. Results of coagulation experiments with groundwater from water source Dúbrava

The second group of laboratory tests were performed with groundwater from the locality of Dúbrava. The concentration of antimony in water before coagulation tests was 66.8 µg.l^{-1}. The Table 3 shows the results of coagulation tests with 1% solution of ferric sulphate (Prefloc).

According the results mentioned in Table 3 it is obvious that by this coagulation test was achieved reduction of antimony to the desired value of 5 µg.l^{-1} as much as about 150 mg.l^{-1} of 1% $Fe_2(SO_4)_3$, which is the equivalent around 42 mg.l^{-1} of Fe^{3+}. The disadvantage of this process is the increased Fe content in the treated water and low pH, which requires additional water treatment.

Table 2

The results of coagulation tests removing Sb from surface water Bukovec

Bukovec 1 % Prefloc [mg/L]	Coagulant dose [mg Fe^{3+}/L]	pH	$ANC_{4,5}$ [mmol/L]	Fe [mg/L]	Sb [µg/L]
SV	0	6.91	0.825	0.05	29.4
32.2	9	5.98	0.340	0.03	7.9
35.8	10	5.72	0.204	0.03	5.4
39.4	11	5.48	0.131	0.03	5.0
42.9	12	5.12	0.079	0.04	3.8
46.5	13	4.67	0.038	0.06	2.2

Table 3

The results of coagulation tests removing Sb from groundwater in Dúbrava

Dúbrava 1 % Prefloc [mg/l]	Coagulant dose [mg Fe^{3+}/L]	pH	$ANC_{4,5}$ [mmol/l]	Fe [mg/l]	Sb [µg/l]
SV	0	7,40	3.088	0.01	66.8
71.6	20.0	6.41	1.716	0.04	25.3
107.4	30.0	5.90	0.926	0.08	10.2
143.2	40.0	5.52	0.515	0.11	6.5
179.0	50.0	4.10	0	0.24	3.9
214.8	60.0	3.20	0	1.32	0.67

In order to optimize coagulation and effort to reduce the amount of coagulant, which would also reduce the operating costs of the treated water the effect of slow mixing times, respectively rotational speed of slow mixing to produce a flakes was investigated.

These experiments have shown that a 15 minute slow mixing (at 40 rpm), respecttively 10-minute slow mixing at 20 rpm are the most effective in removing antimony from the water by coagulation. Not by the dose of 30 mg/L Fe^{3+}, nor by the time of mixing adjusting or nor by changing the speed of slow stirring the value 5 µgl^{-1} was attained, which represents the limit for antimony in drinking water.

By adjusting the pH of water with addition lime (calcium hydroxide dosing in the range 10 to 40 mg/L) prior to dosing coagulant has not been achieved more effective coagulation to remove antimony from water. Therefore, pH adjustment and coagulant dosing should be done together, respectively after coagulation.

The new coagulation tests of groundwater from the site Dúbrava have been performed, whereby the additional parameters were monitored (turbidity and color). Obtained results are shown in the Table 4.

The result shown in Table 9 indicates the change in water quality led to the optimum coagulant dosing reduce. Already the dose 107 mg/L of 1% of $Fe_2(SO_4)_3$, which is the equivalent of 30 mg/L Fe^{3+} suffice to reduce the antimony below the limit value of 5 µg/L, which is given by the Slovak Government Regulation 496/2010 for drinking water. The disadvantage of this process is the increased Fe content in the treated water and the low pH, which require additional water treatment.

Table 4
The results of coagulation tests removing Sb

Dúbrava 1 % Prefloc [mg/L]	Coagulant dose [mg Fe^{3+}/L]	pH	Turbidity [FTU]	Color [mg/L Pt]	ANC$_{4,.5}$ [mmol/L]	Fe [mg/L]	Sb [µg/L]
-	0	7.62	2	10	3.432	0.08	62.0
71.6	20.0	6.08	1	8	1.052	0.09	9.2
89.5	25.0	5.56	1	9	0.396	0.17	5.3
107.4	30.0	4.83	1	10	0.172	0.22	< 3.0
125.3	35.0	3.48	1	12	0	0.44	< 3.0
143.2	40.0	3.02	2	13	0	1.76	< 3.0

Note : < 3.0 = under the detection limit

The increased value of pH and ANC$_{4,5}$, respectively lower amount of antimony in the raw water had a significant influence on the coagulation results (to decrease the dose of coagulant).

By determining the optimal coagulant dosage is necessary to take into account not only the electric charge of dispersed particles and coagulant, but also their morphology (the shape and size) and dynamic properties. When the coagulant is overdosed, it leads to a significant reduction in its effectiveness. It is therefore necessary to achieve such a state that the water was indented as little flakes whose size is less than 125 microns. Just this negative phenomenon was observed during our experiments, a maximum indentation micro-flakes in water after adding 50 - 60 mg Fe^{3+} to 1 liter of water.

At the optimal course of coagulation there are mostly elongated heavier mainly extended flakes in the sediment. The most accurate reproduction (representation) of the flakes was in the sediment, which was obtained at a coagulant dose 60 mg/L of Fe^{3+} (Figure 3). The decline of these flakes onto the sediment depends primarily on the size of precipitated dispersed particles. In the Table 5 and 6 there is shown the size, shape and the total number of flakes obtained by coagulation.
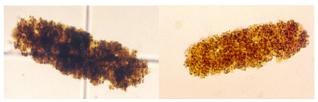

Figure 3 Elongated shape of flakes in the sediment

Table 5
Number and shape of flakes in the indented water

Dúbrava 1 % Prefloc [mg/L]	Coagulant dose [mg Fe^{3+}/L]	The shape of flakes					Number of flakes
		round	elongated	<125 µm	125 – 250 µm	>250 µm	
SV	-	0	0	0	0	0	0
107.4	30.0	35	65	155	40	85	380
143.2	40.0	22	50	165	35	92	364
161.1	45.0	25	60	195	110	90	480
179.0	50.0	5	18	350	140	70	583
214.8	60.0	3	3	425	46	8	485

Table 6
Number and shape of flakes in the sediment

Dúbrava 1 % Prefloc [mg/L]	Coagulant dose [mg Fe^{3+}/L]	The shape of flakes					Number of flakes
		round	elongated	<125 μm	125 – 250 μm	>250 μm	
SV	-	0	0	0	0	0	0
107.4	30.0	25	75	200	96	80	576
143.2	40.0	15	45	250	140	70	520
161.1	45.0	15	148	200	185	163	711
179.0	50.0	49	200	236	198	146	829
214.8	60.0	94	355	126	105	300	980

The inorganic particles have penetrated into the filtered water (the dominant were bright and dark crystal formations) which were a bit fewer presented there than they were presented in the raw water. (Fig. 4).
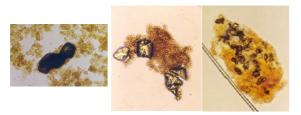

Figure 4 Non-coagulated the bright and dark crystal formations in flaked

5. Conclusion

Performed laboratory tests of surface water from water tank Bukovec and also the tests of groundwater originated in the spring Dúbrava have shown that the antimony content could be decreased at the values limited by Slovak Government Regulation No. 496/2010 for drinking water throughout the application of ferric sulphate. The disadvantage of this method usage is the high coagulant dose requirement. This disadvantage is particularly and significantly being shown in the Water Treatment Stations in which only the antimony value does not match the legislation. This disadvantage is not so striking in antimony removal from surface water where the coagulant addition is needed for the increased turbidity removal, oxidability and insoluble substances removal. According to the coagulation test results the single-stage water treatment is sufficient for the decreasing the antimony content, i.e. dosing of ferric sulphate, 10 minutes of slow mixing, 40 rpm.

Optimal dose of coagulant is important. We have evaluated that the dose 11 mg.l^{-1} of Fe^{3+} is sufficient for antimony content decrease below the limit value at 5 μg.l^{-1} from the surface water Bukovec. For the achievement of the limit value there must be added more than a 30 mg.l^{-1} of Fe^{3+} to the Dúbrava undeground water.

6. Acknowledgement

7. References

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