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Determination of Arsenic in the Process of its Drinking Water Removal

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Abstract. Inorganic arsenic is a multi-site human carcinogen getting into the body by drinking water route. The technology of As adsorption onto iron oxyhydroxide granules in the fluid bed reactor was applied to efficient arsenic removal from polluted drinking water below to accepted Slovak Standard. The technology was used in the middle Slovakia region. The As concentration decreased in Jasenie from value 0.041mg/L (0.033-0.048mg/L) and in Pohronský Bukovec from value 0.089mg/L (0.062-0.104mg/L) respectively, both to value less then limit of determination (<0.006 mg/L-ETA AAS method, <0.0016 mg/L-FI HG AAS method).

The addition of 5 – 6mg/L $FeSO_4.7H_2O$ is adequate for As removal at the level of pH in the water 6.5-6.7. A liquid retention time by 15 minutes is needed for the process. The consumption of O_2 during the reaction is approximately 2mg/L. The concentration of Fe does not exceed value 0.2mg/L (according to the Decree 29/2002 by the Ministry of Health) by treatment of water if all technological rules are kept.

The concentration of observed arsenic was measured by AAS method. The accuracy of analytical data was continuously secured by the system of analytical quality assurance and the principles of good laboratory practice.

The other water quality parameters in the treated water correspond to the requirements according to the Slovak Standard for drinking water.

The waste product is a compact iron granulate with high density (approx. 3kg/L) and a low water content (approx.10-20%).

Key words: arsenic, removal, fluid bed reactor, AAS

Introduction

Arsenic is an element that occurs naturally in rocks, soil, water, air, plants, and animals. There are numerous natural sources as well as human activities that may bring arsenic into drinking water. Inorganic arsenic can exert toxic effects after acute (short-term) or chronic (long-term) exposure. The World Health Organisation guidelines the amount of arsenic in drinking water to 10 μg/l as the maximum contaminant level (MCL). The limit was based on the re-evaluation of the uncertainties in arsenic risk assessment due to recent epidemiological evidence when the risk of cancer is considered (Okoji et al., 1999).

The MCL for arsenic in drinking water was defined in a Slovak Standard STN 75 7111 mandatory in the Slovak Republic (July 1998) and next in the Decree by the Ministry of Health 29/2002 about drinking water requirements and quality control (9th January 2002), as 0.01 mg/L.

The arsenic distribution in Slovak groundwater shows that higher concentrations of this element occur rarely most analyses was below the detection limit of the analytical method (1 μg/l), (Rapant et al., 1996). Higher contents have two sources: 1 sulphide deposits (Malé Karpaty, Nízke Tatry and Slovenské Rudohorie Mts.) and 2. Human-caused contamination sporadically distributed throughout Slovak territory, sometimes reaching concentrations of 50-250 μg/L (Šikulová, 2001).

Arsenic removal

The choice of a suitable treatment option for a specific water supply will depend on a number of factors, including the mandated arsenic concentration limit, the existing treatment system and the extent to which it can be modified to optimise arsenic removal, and other water quality parameters that must be met along with the arsenic standard. Different methods for arsenic removal are known, such as nanofiltration, reverse osmosis and flocculation/precipitation.

Materials and method

Chemical composition of groundwater reflects the underlying geology of the region. The groundwater in the Low Tatras infiltrates through granite and a Mesozoic belt, accumulates and rises from the huge layers of limestone-dolomite complexes. It spends a significant time in contact with subsurface rock and this results in the dissolution of minerals. The arsenopyrite FeAsS is the accompanying mineral in the wide range of rocks owing to increase the arsenic distribution in groundwater of the study region (Rapant et al., 1996). Therefore the higher concentration of As in drinking water is undesirable and has to be removed. Long-term values of arsenic concentration in the study region are given in the Table 1.

Table 1. Long-term values of arsenic concentration in the study region

Source	**Supplied village (Number of inhabitants)**	**Spring discharge (L/s)**	**As concentration (mg/L)**
Rastová	Jasenie, Predajná, Nemecká, (approx. 5000)	36.0	0.040-0.050
Seče 1-4	Pohronský Bukovec, (approx. 100)	0.5-1.0	0.070-0.120
Vyvieračka	Brusno, (approx. 2000)	5.0	0.050-0.060
Kráľ Matyáš	Lopej, Podbrezová, (approx. 5000)	30.0	0.012-0.020

Chemical principles of applied technology (Nielsen, Christensen)

The treatment process operates by continuous addition of ferrous ions and an oxidation agent (O_2, H_2O_2, Cl_2) to the polluted raw water. Addition and mixing take place in a fluid bed reactor containing a carrier material. By controlling the process conditions, the oxidation of ferrous ions will take place heterogeneously after they have been adsorbed to the carrier material. An adsorptive granulate of oxyhydroxide will then be generated as a coating reddish-brown layer on the surface of the carrier material. Hence, the adsorptive surface is renewed permanently and the added iron is removed. Iron oxyhydroxide has significant adsorptive properties towards inorganic micopollutants, which are easily adsorbed onto surface of the carrier material. At the pH<7.8 it is capable to adsorb the ions and therefore to create the surface complexes, as follows:

$$FeOOH + HAsO_4^{2-} \rightarrow FeO(HAsO_4)^- + OH^-$$

$$-FeOOH(s) + Fe^{2+} + 1/4O_2 + 2OH^- \rightarrow -FeOOH-FeOOH(s) + \tfrac{1}{2} H_2O$$

In comparison to conventional chemical treatment with sludge production, no wash water is necessary; no sludge is created, waste product has the superb handling properties; the density of granulate is approx. 3kg/L. The waste stream is reduced; the water content is 10-20%. The operating and personnel ability costs are minimal.

Description of fluid reactor

The main part of equipment is the fluid reactor. It is a cylinder made of polypropylene, in dimensions according to the treated water output. It is filled with the quartz sand. The scheme of reactor is given in the Figure 1. The reactor is divided into four parts:

In *inflow part,* water is pumped through a jet system located at the bottom of the reactor. Water is divided to flow permanently with controlled speed. It provides the creation of sand fluid bed. Two jets add the chemicals.

Reaction part is filled by fine quartz sand. The sorption of formatted complexes is done on the surface of carrier material covered by iron oxyhydroxide.

The greater diameter of *calming part,* according to the reaction part, slows down the speed of flowing water and the separation of turbulating sand covered with the absorbing layer from the treated water occurs.

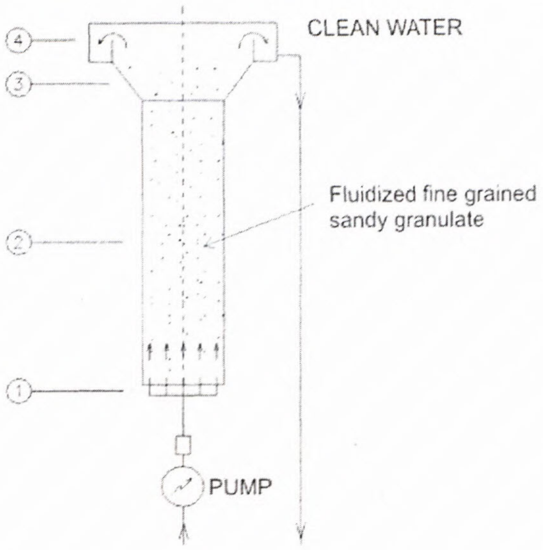

Figure 1. Scheme of fluid reactor: 1 - inflow part, 2 - reaction part, 3 - calming part, 4 - outflow part.

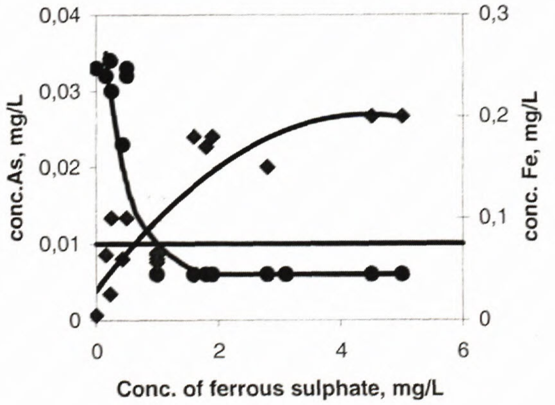

Figure 2.The observed As and Fe concentration in the treated water as a function of added $FeSO_4.7H_2O$

In *outflow part,* the treated water flows out gravitationally from the top of the reactor into accumulating tank and the sand returns back to the reaction part.

Test result

The recommended technology was applied in groundwater sources Jasenie and Pohronský Bukovec. Operating parameters: amount of $FeSO_4.7H_2O$ added, the volume of treated water and aeration was investigated. The observed As and Fe concentration in the treated water as a function of added $FeSO_4.7H_2O$ is given in Figure 2.

Table 2. Review of the analytical quality assurance

Test sample	Certified value μg/L	Observed value μg/L	Number, *n*	Method used
MT-ŠAA-5/2000[a)]	14.0±2.1[b)]	14.50±0.44	24	FI-HG-AAS
MT-SAA-9/2001[a)]	9.90±1.98[b)]	10.32±0.26	3	FI-HG-AAS
SRM 1643d	56.02±0.73	55.96±1.20	10	ETA AAS

a) Internal standard materials - samples obtained from the Slovak Water Management in the inter-laboratory test

b) values are based on the inter-laboratory tests

Table 3. Results of inter-laboratory tests

Test samples	Certified value μg/L	Accepted value μg/L	Observed value μg/L	*z*-score
MT-ŠAA-5/2000[a)]	14	11.9-16.1	13.7	<-2, +2>
MPS-ŠAA-9/2002[a)]	8	6.40-9.60	7.72	<-2, +2>
IMEP 12[b)]	9.07	8.17-9.96	10.53±1.67	

a) The inter-laboratory tests of Slovak Water Management

b) The International Measurement Evaluation Programme (IMEP) was organised by the Institute for Reference Material and Measurements (IRMM), Geel, Belgium

Table 4. Spiked samples recovery

Test sample	As, added μg/L	Recovery %	Number, *n*	Method used
Randomly selected sample	10	101,0±6,3	16	FI-HG-AAS
	10	108,6±4,4	18	ETA AAS

The As concentration decreased in Jasenie from value 0.041mg/L (0.033-0.048 mg/L) and in Pohronský Bukovec from value 0.089mg/L (0.062-0.104 mg/L) respectively, both to value less then limit of determination (<0.006mg/L-ETA AAS method, <0.0016 mg/L-FI HG AAS method).

The optimal amount of added iron depends on the original concentration of As in the water, the temperature of the water, the amount of O_2, the time of the reaction and the amount of water to be treated. For monitored sources the addition 5 – 6mg/L $FeSO_4.7H_2O$ is adequate for removal of As and it also decreases the level of pH in the water to the acceptable norm 6.5-6.7. The greater amount of Fe does not cause an increased effectiveness of the treatment, but it decreases pH under the level of 6.5. What is more, the concentration of Fe in outflow water is increased, what is undesirable. The interruption of dosing $FeSO_4$ and the interruption of aeration causes the suspension of the technology, it follows that the activated sand is not able to catch As.

The concentration of Fe does not exceed value 0.2mg/L (according to the Decree 29/2002 by the Ministry of Health) by treatment of water if all technological rules are kept. A liquid retention time by 15 minutes is needed for the process.

Water, that will be used, needs to be oxidised. The lowest necessary concentration of O_2 is 5mg/L. The shortage of O_2 does not influence removal of As, but it decreases the ability of creating and catching iron oxyhydroxide, that causes the increasing concentration of iron at the output of the reactor. The consumption of O_2 during the reaction is approximately 2mg/L.

The monitored parameters (pH, the amount of O_2, conductivity, temperature of water) in the treated water correspond to the requirements according to the Slovak Standard for drinking water.

Determination of As by AAS method

The arsenic concentration was measured by AAS method for the whole period. The Perkin-Elmer 4100ZL atomic absorption spectrometer with the Zeeman background correction, THGA furnace and the pyrolytic graphite platform tubes with end caps were used to all measurements. The lamp current 350 mA and the resonance line of 193,7 nm of arsenic electrodeless discharge lamp was set. The addition of 5μL Pd/Mg matrix modifier to 20μL sample aliquots was applied to avoid losses of arsenic during the ashing stage. The optimal furnace conditions - ashing temperature 1300°C and atomisation temperature 2200°C were found.

Nevertheless, the limit of determination (0.006mg/L) is not sufficient with respect to the 10% of MCL criteria for limit of detection defined in Decree 29/2002 by the Ministry of Health.

Therefore, a flow injection hydride generation AAS method was used to achieve high sensitivity and more reduction of matrix interference in the drinking water (LOD, 0.0005mg/L). Volatile arsine was generated in flow injection system FIAS 100 and transported to a quartz cell heated to 900°C, where the arsine was converted to gaseous metal atoms and then absorb the light from the EDL As lamp.

Arsine is more easily formed from As^{3+}. Samples to be analysed for As should be prereduced by the KI and ascorbic acid prior to analysis.

The accuracy of analytical data was continuously assured by the system of analytical quality assurance and the principles of good laboratory practice. The checks of analytical quality assurance comprised inter-laboratory analyses of water samples, spiked samples (matrix spike – standard addition of 10μg/L As is spiked to the randomly selected sample in the batch of samples), certified reference materials, parallel samples. The review of the items accomplished within analytical measurements is given in Tables 2-4.

Conclusion

Presented results show efficient applying of arsenic removal from polluted drinking water below to accepted Slovak Standard value by adsorption onto iron oxyhydroxide granules in the middle Slovakia region. The technology was operated in the fluid bed reactor. The concentration of observed arsenic was measured by AAS method. The other water quality parameters in the treated water correspond to the requirements according to the Slovak Standard for drinking water. The waste product is a compact iron granulate with high density (approx. 3kg/L) and a low water content (approx.10-20%).

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