

Removal of arsenic from drinking water

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ABSTRACT:

The drinking water well in Slovenska Bistrica, Slovenia, contains arsenic in concentration around 50 $\mu\text{g/L}$. Therefore it is necessary to implement a technological treatment to make the water suitable for drinking. In order to do so the following technologies were suggested: activated alumina, green sand, granular ferric hydroxide and special goethite media. They were all carried out on a laboratory scale. We managed to remove arsenic below 1 $\mu\text{g/L}$. Arsenic is usually found as an anion with acid characteristics in the trivalent (III) and pentavalent (V) forms. Chemical analyses of our drinking water showed that arsenic is present in pentavalent form. This means that the water is less toxic as it would be if it contained arsenic in the trivalent form.

On the other hand, all the important physical chemical parameters of water remained practically unchanged after the treatment. The hygienic water quality obtained was not an issue.

Finally, in addition to capability of arsenic removal, a comprehensive economic analysis of selected technologies is provided.

KEY WORDS:

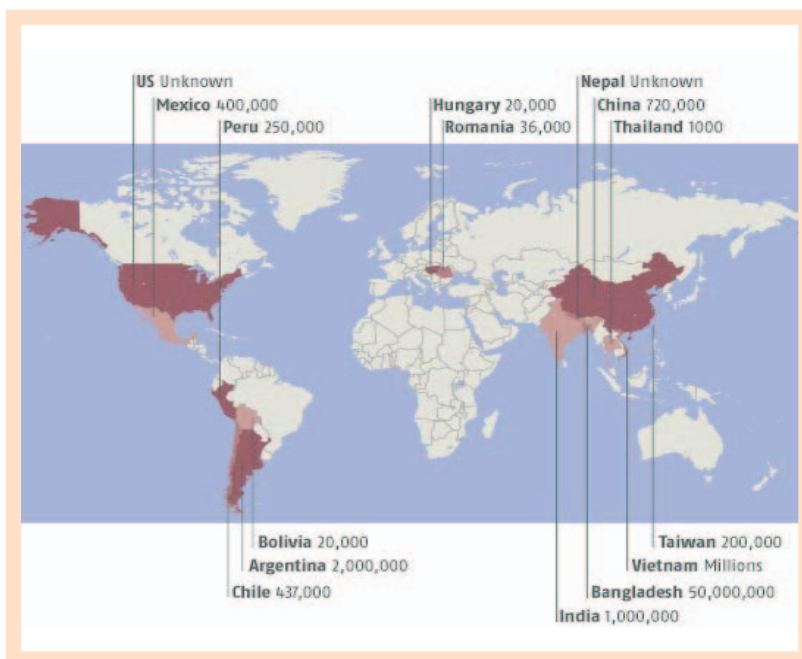
Drinking water, Arsenic, Activated alumina (AA), Goethite (TA)

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INTRODUCTION

The drinking water spring is not a new one, but physical-chemical research of this water has been ongoing during the last 10 years. Throughout this period the water stability remained unchanged. Even the concentration of arsenic did not change through the years. Water was suitable for drinking till 2004, when arsenic became to be regarded as a highly toxic substance by WHO and European Union with maximum level of contamination MCL lowered from 50 $\mu\text{g/L}$ to 10 $\mu\text{g/L}$ [1]. It was confirmed that arsenic causes skin, liver, lung, and kidney cancer. The water contains just below 50 $\mu\text{g/L}$ of arsenic in pentavalent form. Arsenic also occurs in oxidation states -III, 0, and III yielding a variety of compounds. Inorganic arsenic is more toxic than organic (monomethyl arsenic acid and dimethyl arsenic acid). According to recent studies [2] arsenic is more worldwide spread than imagined. People's lives from 17 countries around the world are seriously jeopardized, like those in China, Bangladesh, Vietnam, Argentina, Chile and USA. It is seen from Figure 1.

Figure 1:
Arsenic threat around the globe
(number of people in danger) [2].



UV rays and ozone were introduced for arsenic removal by Kuhlmeier and Sherwood in 1996.

In 1978 Sorg and Logsdon [3] first started to study the arsenic removal technologies, like coagulation, lime softening, ion exchange, adsorption, reverse osmosis and electrodialysis. Jekel [4] continues their work by testing oxidation processes and activated alumina. Kartinen and Martin [5] found good results on arsenic removal by using green sand and they also systematically arrange different treatment technologies into categories. UV rays and ozone were introduced for arsenic removal by Kuhlmeier and Sherwood in 1996 [5]. Rott and Friedle [5] demonstrated in 1999 how to remove arsenic by adsorption onto fresh $\text{Fe}(\text{OH})_3$ precipitation if the water contains iron and manganese. There are a number of technologies used for removing arsenic [6]. It is very important to establish the form in which arsenic is present in water, because the

pentavalent form is easier to remove than trivalent form. Some literature data exist [7,8] that favor catalytic coated materials like granular (black) iron reducing material (BIRM) and green sand. Further some research was done on synthetic zeolites [9], which demands carefully preparation of the material and water to be treated.

Recent studies of arsenic removal by pressure-driven membrane processes were summarised by Shih [10], where there is among other explained the possible influence of some water parameter on removal efficiency.

The most authors agree that nanofiltration is the best choice among membrane processes for arsenic removal [11,12,13].

Following all the researches, some comparisons of conventional and new techniques for the removal of arsenic in full scale water treatment plants were done recently [14].

The aim of our research was therefore, to:

- a) test the quality of water by means of physical chemical and microbiological analyses,
- b) find the most adequate pilot-plant test for arsenic removal and
- c) provide an economic analysis of selected technologies.

MATERIALS AND METHODS

Activated alumina (AA) was obtained from Alcan Chemicals, Netherland, Greensand (GS) from Esot, Slovenia, and TehnoArz (TA) from Tehnobiuro, Slovenia; TA is a commercial name for α -FeOOH. As coagulant, iron chloride (p.a.) was used, purchased by Chemica, Croatia.

All chemical substances used were of a high degree of purity (pro-analysis).

Analyses of cations NH_4^+ , Fe^{2+} , Mn^{2+} , Al^{3+} and anions Cl^- , NO_2^- , NO_3^- , PO_4^{3-} , SO_4^{2-} were determined on spectrophotometer Cary based on the standard methods (DIN 38406, DIN 38405-D19) [15].

The concentrations of K^+ and Na^+ were measured by an atomic absorption spectrometer Perkin Elmer 1100 B using appropriate source of radiation (DIN 38406 E-13, E-14, E-15) [15].

Ca^{2+} , Mg^{2+} , HCO_3^- , CO_2 were determined titrimetrically, by standard methods (DIN 38 409 H6) [15].

pH was measured using pH meter MA 5740, after calibration with buffers of pH 4 and 7 (DIN 38404-C5).

The turbidity was measured with a turbidimeter Hanna, 2100P and the conductivity was measured using conductivity meter WTW, LF 537 (DIN 38404 C2) [15].

The absorbance was determined with a spectrophotometer at wavelengths of 436 nm and 254 nm (DIN 38404 C1, DIN 38404 C3) [15].

Dry residue was measured gravimetrically after evaporating the samples to dryness on a water bath and after drying at 180 °C (38409-H1) [15].

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Analyses of arsenic microbiological analyses were performed on ICP-MS Elan 6000. Microbiological analyses were performed following the APHA standard methods [16].

EXPERIMENTAL

We wanted to find out the stability of the water while considering water flow capacity, the temperature and pH value. In our case no effect of weather on enumerated parameters was noticed. As it is obvious from Table 1, they remained constant all over the 10 years period. Only a slight oscillation of the conductivity was observed. The water flow is 18 000 m³ per year.

Table 1:
Stability of water quality.

Parameter	Year		
	1995	2001	2005
Temperature / °C	13.0	13.0	13.0
Capacity / (L/s)	0.7	0.7	0.7
pH (at 20°C)	7.6	7.6	7.6
Conductivity (at 25°C) / (μS/cm)	530.0	550.0	550.0

The water samples were taken directly at the spring. Water is odorless, colorless and tasteless. All measured parameters are presented in Table 2. For all measurements three replicates were made and very good reproducibility was obtained. There is no iron, manganese, nitrite and phosphate in water as it is noted in Table 2. During the last ten years only the concentrations of chloride, nitrate and sulphate-ions have increased more than 10 years ago, although other ion-concentrations have remained the same throughout the period of measurements. According to the MCLs' the concentration of arsenic is too high. Thus it should be removed before the water is used for drinking.

Table 2:
Physical chemical parameters of water through 10 years period.

Parameters	1995	2001	2005
pH	7.6	7.6	7.6
γ(As) / (ug/L)	47	47	50
γ(Na ⁺) / (mg/L)	4	4	4
γ(K ⁺) / (mg/L)	1.9	1.5	1.5
γ(Ca ²⁺) / (mg/L)	59	52	53
γ(Mg ²⁺) / (mg/L)	40	48	44
γ(Fe ²⁺) / (mg/L)	<0.05	<0.05	<0.05
γ(Mn ²⁺) / (mg/L)	<0.005	<0.005	<0.005
γ(Cl ⁻) / (mg/L)	6.2	13	13
γ(NO ₃ ⁻) / (mg/L)	1.4	15	12
γ(NO ₂ ⁻) / (mg/L)	<0.002	<0.002	<0.002
γ(SO ₄ ²⁻) / (mg/L)	9.3	23	22
γ(HPO ₄ ²⁻) / (mg/L)	<0.02	0.02	0.02
γ(HCO ₃ ⁻) / (mg/L)	354	320	320

RESULTS AND DISCUSSION

The obtained results are presented in Table 3 for each arsenic removal procedure. The same parameters were determined in original water sample and after the four chosen removal techniques: activated alumina, green sand, FeCl₃-C, and conventional coagulation using iron chloride. All experiments were done under the same (room) temperature and on the same original water sample.

We succeeded in removing arsenic from drinking water. As presented in Table 4, the pH value increased from 7.6 to 7.8 after AA and GS methods. The concentration of Na⁺ remained practically unchanged in all methods, except after adsorption on AA. Slight oscillations were observed by Ca and Mg-ion concentrations.

Arsenic ions were reduced under the MCL's in all methods used, except in case of GS: concentration was just at the 10 µg/L limit value. The experiments were repeated several times and were always the same as presented in Table 3. Bacteria were not present even in the original sample.

Table 3:

Physical chemical parameters of water after treatment procedures.

Parameters	Water	AA	GS	TA	FeCl ₃ -C
pH	7.6	7.8	7.8	7.6	7.6
γ(As) / (µg/L)	50	6	10	0,2	3
γ(Na ⁺) / (mg/L)	4.5	11	4.6	4.5	4.5
γ(K ⁺) / (mg/L)	1.5	1.5	1.5	1.5	1.5
γ(Ca ²⁺) / (mg/L)	53	50	53	55	53
γ(Mg ²⁺) / (mg/L)	44	40	44	43	44
γ(Cl ⁻) / (mg/L)	6	6	6	6	6
γ(NO ₃ ⁻) / (mg/L)	15	15	15	15	15
γ(SO ₄ ²⁻) / (mg/L)	22	23	22	20	22
γ(HCO ₃ ⁻) / (mg/L)	330	330	330	330	330

It is clear that water purified in this way agrees with the standards for drinking waters.

Due to very high concentrations it was expected that adsorption media could become blocked very quickly. We did some tests on AA, GS, and TA. It was found that the AA and TA filtration efficiency is quite high unlike GS.

If q is the mass absorbed (mg/g), ρ_{AA} is the density of AA, γ_o is influent concentration and γ_1 effluent concentration, the bed life Y , the volume of water that can be treated per unit volume of AA, can be calculated:

$$Y = \frac{q \cdot \rho_{media}}{\gamma_0 - \gamma_1}$$

- q – adsorption capacity on media (mg/g)
 ρ_{media} – density (g/L)
 γ_0 – influent concentration (mg/L)
 γ_1 – effluent concentration (mg/L)
 Y – bed life

If we calculate Y for each media, results obtained shows Table 4.

Table 4:

Bed life calculations for AA, GS and TA.

Parameter	AA	GS	TA
Adsorbed mass of As (mg/g)	2	0.1	32
Density (g/L)	657.7	433.1	425
Bed life Y (L/L) of water	32,885	1,082	422,618

For arsenic q is 2 mg/g of AA from the experiments we made, ρ_{AA} is 657.7 g/l, $\gamma_0 = 50 \cdot 10^{-6}$ g/L and γ_1 is $10 \cdot 10^{-6}$ g/L for a compound, after equation (1) the bed life Y for arsenic is 32.885 liters of water per liter of AA to regenerate. Greater volume of water can be treated by TA: water amount is around 390 times higher as by GS and almost 13-times higher as by AA, therefore TA is far the best option in order to remove arsenic regarding adsorption capacity (Table 4).

The strength of Fe-As bond in TA material was characterized by chemical analysis. It was determined that the powder composition expressed in mole fraction of FeOOH and As was 20:1.

First TA was stirred in water sample with 50 $\mu\text{g/L}$ As. After the equilibrium was reached it was dried and analysed. The same material was stirred with rain water for a week, and then for a month. As-concentrations were measured in water before and after stirring. As-ions were bond strongly to the TA and they did not re-dissolved into the water, because the concentration of arsenic in all samples did not changed. It

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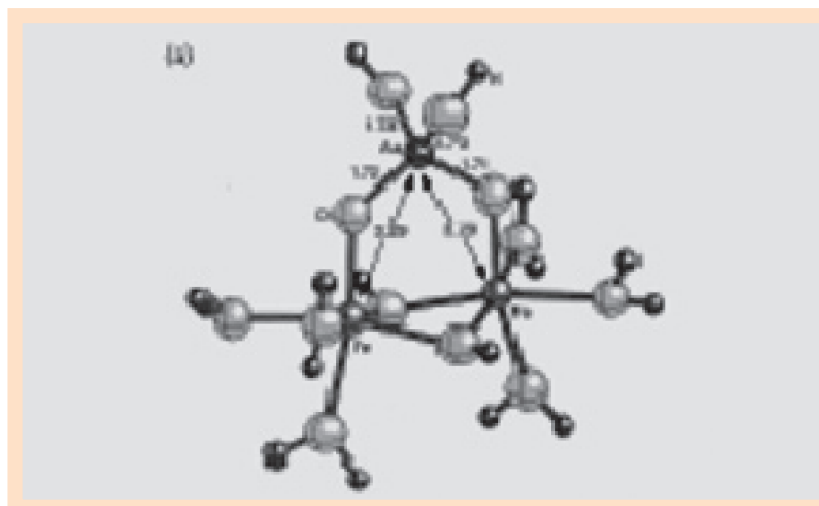


Figure 3:
Most probable geometry of $\text{Fe}_2(\text{OH})_2(\text{H}_2\text{O})_n\text{AsO}_4^+$ clusters [17].

was proved that spent material could be discharged to the landfill without the fear of As-leaking to the ground water sources.

Arsenic as AsO_4^{3-} forms a strong bond to $\alpha-Fe_2O_3$ and $\alpha-FeOOH$. The mechanism was not fully explained yet. As a result of bidentate corner sharing between AsO_4 and FeO_6 polyhedra (2C) clusters of $Fe_2(OH)_2(H_2O)_nAsO_2(OH)_2^{3+}$ and $Fe_2(OH)_2(H_2O)_nAsO_4^+$ are formed. Figure 3 shows most probable geometry of $Fe_2(OH)_2(H_2O)_nAsO_4^+$ and As-Fe distances (Å) [17].

Cost of different technologies for Arsenic removal

The comparison of the cost for different arsenic removal processes is provided in Table 5. Assumptions include 50 $\mu g/L$ total As influent and up to 6 $\mu g/L$ As effluent. Modifications may include the increased coagulant dosage or the reduction of the pH. No extra cost is assumed for waste disposal.

Table 5:
Costs for different arsenic removal processes.

Parameter (EUR)	AA	GS	TA	FeCl ₃ -C
Capital (EUR)	15,700	15,700	11,740	19,000
Operations and Maintenance (EUR)	13,400	46,600	11,730	16,200
Waste disposal (EUR)	105	105	105	1,050
Annual (EUR/m ³)	0.84	2.68	0.72	1.06

The best arsenic removal technology has been researched for small water system.

The economic analyses give annual costs per discussed drinking water spring for TA adsorption. When comparing these figures to other treatment technologies, it is apparent that TA adsorption is the most cost effective. The following comparisons consider implementation of new treatment plants. In the case of such small systems, TA is less expensive than all other technologies. In the case of large water system the situation might be very different, especially due to the high costs of adsorption media TA. Also it has to be emphasized that only As^{5+} removal was studied, not the arsenic organic compounds.

In comparison with the literature data [5,18] we can see that costs that were calculated are lower than reported. It is probably due to cheaper equipment available in Slovenia than in other EU countries and USA.

CONCLUSION

The best arsenic removal technology has been researched for small water system. The concentration of pentavalent arsenic was around 50 $\mu g/L$. The results showed that by adsorption on activated alumina, fresh $Fe(OH)_3$ or $\alpha-FeOOH$ arsenic was removed below MCL-value of 10 $\mu g/L$, while green sand allowed the removal of arsenic just around MCL. Economically the best solution for arsenic removal as well as the best technology option for small ground water systems is adsorption on $\alpha-FeOOH$ (TA).

REFERENCES

- [1] WHO Guidelines for Drinking Water Quality. Vol. 1. Recommendations. Geneva. 1996.
- [2] Arsenic's fatal legacy grows worldwide, http://www.scarab.se/arsenic/docs/arsenic_pearce.pdf (15.01.2007).
- [3] Sorg TJ. Longsdon GS. Treatment Technology to meet the Interim Primary drinking water Regulations for inorganics: Part II. *Journal of AWWA* 1978; 70 (7): 379-93.
- [4] Jekel MR. Removal of arsenic in drinking water treatment. In *Arsenic in the Environment Part I: Cycling and Characterisation*; Willey and Sons Inc New York 1994; Vol 26: 119-132.
- [5] Newcombe RL. Arsenic removal from drinking water: A dissertation. University of Idaho. College of Graduate Studies, 2003.
- [6] Corngold E. et al. *Desalination* 2001; 141: 81-84.
- [7] Clack Birm. Material safety data sheet, Enclosure to the fax message from Victrie Media on Dec 5th, 2002.
- [8] New Mexico State University. Arsenic Removal from Water Using Manganese Greensand: Laboratory Scale Batch and Column Studies. Contract No. 142596-FC-81-05016. June 1999.
- [9] Shevade S., Ford RG. Use of synthetic zeolites for arsenate removal from pollutant water. *Water Res* 2004; 38: 3197-3204.
- [10] Shih Ming-Cheng. An overview of arsenic removal by pressure-driven membrane processes. *Desalination* 2005; 172: 85-97.
- [11] Urase T., Oh J., Yamamoto K. Effect of pH of different species of arsenic by nano filtration. *Desalination* 1998; 117: 11-18.
- [12] Sato Y. et al, Performance of nanofiltration for arsenic removal. *Water Res* 2002; 36: 3371-3377.
- [13] Košutić K. et al. Removal of arsenic and pesticides from drinking water by nanofiltration membranes. *Sep Pur Technol* 2005; 42: 137-144.
- [14] Jekel M. and Seith R. Comparison of conventional and new techniques for the removal of arsenic in a full scale water treatment Plant. *Water Supply* 2000; 18 (1): 628-631.
- [15] Hütter L. *Wasser und Wasseruntersuchung*, III. Edition, Verlag Diesterweg-Sauerländer, 1988.
- [16] APHA. *Standard Methods for the Examination of Water and Wastewater*, Gordon A. Mc Feters (Ed). *Drinking Water Microbiology*, 1990.
- [17] Shermann D M., Randall S R. Surface complexation of arsenic(V) to iron(III) (hydr)oxides: Structural mechanism from ab initio molecular geometries and EXAFS spectroscopy. *Geochimica et Cosmochimica Acta* 2003; 67(22): 4223-4230.
- [18] Technologies and costs for removal of arsenic from drinking water, EPA 815-R-00-028. December 2000.