QUALITY OF GROUNDWATER IN EASTERN CROATIA. THE PROBLEM OF ARSENIC POLLUTION

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EXTENDED ABSTRACT

Ground waters are the main source of drinking water in the area of eastern Croatia. It has been found that they contain high concentrations of iron, manganese, ammonia, organic substances and arsenic. The appearance of inorganic arsenic in ground waters is caused by arsenic from natural geological sources, as well as anthropogenic activities. Since the ground waters are the main source of drinking water in this area, the population of 200.000 people are daily exposed to arsenic contamination in concentrations ranging from 10 and 600 ppb.

In two towns of this region (Osijek and Vinkovci) ground waters are processed by coagulation-filtration method, which does not effectively remove arsenic, so the final arsenic content exceeds current European legislation for maximum arsenic level in drinking water of 10 ppb. In the year 2004 this maximum arsenic level was adopted by Croatian legislation.

Different studies show that chronic arsenic poisoning can occur after long-term exposure to arsenic through drinking water. According to US National Research Council even the small amounts of arsenic in drinking water can cause carcinogenic and cardiovascular diseases. Based on observation of population that consumes arsenic-contaminated drinking water, the concentration associated with an excess lifetime skin cancer risk was calculated to be 2 ppb. The hair arsenic concentration can be used as biomarker of overall arsenic exposure. The relationship between the high amount of arsenic in drinking water and hair arsenic concentration was investigated in several towns and villages in eastern Croatia. Analyses were preformed using hydride generation atomic absorption spectrometry.

In order to remove arsenic from water, different adsorbents were used in this study and then compared. Following modified adsorbents were used: clinoptilolite, manganese greensand, and cationic exchange resin. Adsorbents were chemically modified and saturated with Fe^{3+} -ions, while the arsenic solutions were prepared with processed groundwater (pH 7.4 and water hardness of 260 µgL⁻¹. CaCO₃).

Key words: arsenic removal, adsorption, clinoptilolite, manganese greensand, cationic exchange resin, hair arsenic concentration, Croatia

1. INTRODUCTION

Arsenic (As) is a chemical element present in inorganic and organic forms in the atmosphere, soil, rocks, natural water and organisms. As a result of anthropological activities and reduction conditions, natural ground waters may contain high concentrations of inorganic arsenic species (arsenite (As(III) and arsenate (As(V)). The average arsenic levels in groundwater are <1 ppb, however in the areas with volcanic rocks and soils which contain large amounts of sulphide minerals, arsenic concentrations can exceed much higher levels. The highest arsenic concentration level in natural water was reported in the Western USA (48.000 ppb) [1]. The high amount of arsenic in groundwater was also reported in southeastern Asia (Bangladesh, India, China, Taiwan, Philippines), North and South America, and some parts of Europe (Hungary, Romania, Serbia and Monte Negro) [1,2].

Preliminary analysis of drinking water from waterworks of several towns and villages in the eastern Croatia region showed that population of 200.000 people are daily consuming water with arsenic concentrations between 10 and 610 ppb [3,4]. In the late nineteeneighties analysis of groundwater from water-wells of town Osijek were conducted, and arsenic concentration higher than 200 ppb were registered. Monitoring of these waterwells during the following years showed the increase of arsenic concentrations up to 330 ppb (see Figure 1).



Figure 1: Arsenic concentrations (μ g/L) in ground-water resources of Osijek.

2. ARSENIC IN HAIR

Arsenic hair concentration is a biomarker of overall exposure of an organism to arsenic compounds, and it correlates well with the amount of arsenic in drinking water [6]. For the purpose of this study, hair samples were taken from non-smoking adults, whose hair was not chemically treated. The collected samples of hair were analysed for arsenic. In the same time, drinking water samples were taken directly from the kitchen tap in the homes of subjects. The samples were take in the control area (town of Nasice) with arsenic concentrations < 0.1 ppm, and in the exposed area (Osijek, Cepin and Andrijasevci). The samples of hair, as well as the samples of drinking water were analysed using hydride generation atomic absorption spectrometry (Perkin-Elmer 2380, MHS Type 10).

The results of analysis revealed that arsenic concentrations in drinking water of Osijek (40 ppb), Cepin (170 ppb) and Andrijasevci (610 ppb) exceeded the maximum permissible level set by Croatian legislation over ten times [5]. Hair arsenic concentration in the control area was < 0.1 ppm. In the exposed area with 45 ppb of arsenic in drinking

water, hair concentration was 0.1 to 0.5 ppm, with 180 ppb from 1 to 2 ppm, and with 600 ppb from 1.5 to 5 ppm. The results showed positive correlation between the occurrence of hair arsenic concentrations and the arsenic concentrations in drinking water. There were significant differences between the arsenic concentrations in drinking water and hair arsenic concentrations of subjects [4,7]. Figure 2. shows statistic interpretation of hair arsenic concentrations analysis in towns and villages of eastern Croatia.



Figure 2: Statistic interpretation of hair arsenic concentration analysis in towns/villages of eastern Croatia.

3. ARSENIC REMOVAL

There are several technologies for arsenic removal from water and their efficiency is dependent on the valence of arsenic. Arsenic is most effectively removed or stabilized when it is present in the pentavalent arsenate form. Most of the technologies include the following processes: precipitation-coagulation, membrane separation, ion exchange and adsorption. Two water supply systems in the eastern Croatia (Osijek and Vinkovci) use precipitation-coagulation processes in the water treatment. By continuous optimisation of water treatment process in Osijek waterworks, using coagulation and filtration methods up to 85 % of total arsenic has been removed (from average 250 ppb to average 40 ppb) (Figure 3.) However, the obtained concentrations are still higher than the current maximum permissible concentration of arsenic in drinking water in Croatia [5].

The water supply system of Andrijasevci use rapid sand filtration for drinking water treatment, which results in high arsenic residuum. Thus, the population of 200.000 people from that area are daily consuming water with arsenic concentrations that highly exceed maximum permissible concentration (Andrijasevci, 600 ppb) [4].



Figure 3: Scheme of coagulation/ direct filtration plant of Osijek waterworks system (supplying about 150.000 people).

The aim of this study was to investigate and compare the sorption of inorganic arsenite and arsenate compounds from the water. Following modified adsorbents were investigated: zeolite - clinoptilolite (Donje Jesenje, Croatia), manganese greensand (New Jersey, USA) and cationic exchange resin (Dowex Marathon C). Stock solutions of trivalent and pentavalent arsenic were prepared by dissolving Na-arsenite (NaAsO₂, Kemika) and sodium arsenate heptahydrate (Na₂HasO₄ × 7H₂O, Carlo Erba) in processed water from Osijek water supply system. Characteristics of processed water are summarized in Table 1. The final concentrations of trivalent and pentavalent arsenic used in the experiments were 100, 200, 300, 400 and 500 μ gL⁻¹.

lon	Concentration (mgL ⁻¹)	 Parameter	Unit	Value
Cl	20.1 - 31.3	рН		7,25 - 7,74
SO4 ²⁻	1.7 - 15	Conductivity	mSm⁻¹	79 - 86
HCO ₃ ⁻	580 - 620	Hardness	mgL ⁻¹ CaCO₃	120 – 136
NO ₃ -N	0,01 - 1,35	Turbidity	NTU	0,25 - 0,46
F ⁻	< 0.02	TOC	mgL⁻¹	3,5 – 4
PO ₄ -P	0,009 - 0,08	[As]	mgL⁻¹	0.02 - 0.05
Mn	0.009 - 0.034	[Fe]	mgL ⁻¹	< 0,5

Table 1. Characteristics of processed water from Osijek waterworks system.

In the purpose of increasing efficiency, the adsorbents were chemically modified and converted into a protonised form using 0.1 M HCl, then into Na-form using 2M NaCl and finally into Fe-form using 0.1 M FeCl₃ in acetate buffer pH 3.6 during 24 hours at 70°C. After reaching balance, FeCl₃ solution was separated from the adsorbents. Finally, the adsorbents were washed with deionised water until the eluate washings became free from chloride ions and then dried on 100°C.

The adsorption characteristics of the modified adsorbents were tested using Winkler vials with 0.25 g of modified adsorbent and 100 mL of arsenic solution in concentrations ranging from 0.1 to 0.5 mgL⁻¹ (C_o). The pH of 7,4 in each vial was adjusted using HCl and NaOH. Adsorption was conducted on constant temperature in temperature-controlled shaker at 25°C and the shaker speed of 120 rpm. The adsorption time was 180 min. After that time all the samples were filtrated and the residual concentration of arsenic (C_e) was determined using standard spectrophotometric method with silver diethyldithiocarbamate (ISO 6595-1982). The detection limit for this method is 1 ppb.

Adsorption characteristics were calculated and presented as constants of Freundlich and Langmuir isotherms. The Freundlich equation is an empirical equation that describes adsorption data. The exponential equation is of the form:

Exponential form

 $\frac{X}{M}$

$$= KC_e^{1/n} \qquad \log\left(\frac{X}{M}\right) = \log K + \frac{1}{n}\log C_e$$

Where:

X - mass of absorbed arsenic M - mass of adsorbent C_e – equilibrium concentration of arsenic in solution after adsorption K, n – constant The constant *K* is related primarily to the capacity of the adsorbent to adsorb arsenic. Larger values of *K* mean larger capacities of adsorption. The constant 1/n is a function of the strength of adsorption. Larger values of 1/n mean that the adsorption bond is weak because the value of X/M experiences large changes for small changes in C_{e} . Smaller values of 1/n mean the adsorption bond is strong.

The Langmuir equation is derived assuming that the area available for adsorption is limited, arsenic is adsorbed in a monomolecular layer, adsorption is reversible and equilibrium is achieved. The equation is of the form:

Exponential form	Linear form				
$\frac{X}{M} = \frac{x_m \ k \ C_e}{1 + k \ C_e}$	$\frac{M}{X} = \frac{1}{x_m} + \left(\frac{1}{x_m k}\right) \frac{1}{C_e}$				

Where:

M - mass of adsorbent

X - mass of adsorbed arsenic

 X_m – the limiting value for x (monolayer capacity)

K - constant relating to the energy of sorption

 C_e – residual concentration of arsenic in solution phase at equilibrium

The adsorption data were fitted with Freundlich and Langmuir isotherm equations and summarized in Table 2.

Table 2. Adsorption of As(III) and As(V) onto different adsorbents saturated with Fe³⁺ions: Freundlich and Langmuir isotherms (adsorbent dose: 2.5 gL⁻¹; pH: 7.4; temperature 25°C)

Adsorbents	Modified Manganese Greensand		Modified Cationic Exchange Resin		Modified Zeolite					
Freundlich isotherm										
	As(III)	As(V)	As(III)	As(V)	As(III)	As(V)				
K µg/L	0,619	0,325	4,863	1,556	5,379	4,183				
n	1,272	1,956	2,1368	1,020	2,5804	2,843				
R^2	0,982	0,817	0,841	0,942	0,968	0,734				
Langmuir isotherm										
	As(III)	As(V)	As(III)	As(V)	As(III)	As(V)				
Xm µg/g	228,830	8,699	77,580	42,463	55,309	36,350				
k	0,001	0,007	0,014	0,006	0,017	0,016				
K x m	0,2745	0,062	1,096	0,243	0,927	0,589				
R^2	0,944	0,797	0,844	0,975	0,931	0,785				

4. CONCLUSION

The results of this study indicate a strong relationship between the hair arsenic concentration and the arsenic concentration in drinking water in the area of eastern Croatia. Arsenic concentrations in some villages in this area exceed 600 ppb. The existing technologies for arsenic removal remove arsenic to significant level, but arsenic concentrations still exceed Croatian and EU maximum permissible level set at 10 ppb.

The results of investigation of adsorptions characteristic of Fe-complexes with zeolites and cationic resin can be used in order to increase the efficiency of arsenite and arsenate compounds removal from natural arsenic contaminated water. At the chosen pH value of 7.4, which represents the average pH value of natural waters, the modified zeolite exhibited the best adsorbent characteristics.

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