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PILOT PLANT FOR TREATMENT OF RAW DRINKING WATER WITH HIGH CONTENT OF ARSENIC USING FERRATE (VI)

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Abstract: The paper presents the results of treatment of raw drinking water, loaded with organic substances (COD = 94.68 mg / l) and high concentration of As (up to 38.66 mg / l). The treatment of raw water was carried out by *in situ* electrochemically synthesized ferrate(VI) in a pilot plant with a flow-through electrochemical cell. For the treatment of water the pilot plant batch type with three reaction columns was formed. The developed method was applied to the treatment of raw water from four different sources. The results showed the removal of up to 97% As, and permanganate index close to the statutory limit value (12 mg / l of $KMnO_4$).

Keywords: Arsenic, ferrate(VI), electrochemical synthesis, oxidation, coagulation, pilot plant

INTRODUCTION

Preparation of drinking water is a very complex area in which is engaged a significant part of scientific and technical potentials in the world. Increasing demands in terms of quality and quantity of drinking water and, on the other side, increasingly polluted water resources result in intensive researches in this area.

Very serious difficulties in the process of preparing high-quality drinking water is the increased amount of natural organic matter in water resources, or the formation of a large number of by-products of disinfection and coagulation. In addition to organic matter in water resources a large number of inorganic pollutants, including arsenic, as one of the most widespread, can be found. Based on the UN Synthesis Report arsenic poisoning is the second major health risk related to drinking water [1]. The World Health Organization in 2001 estimated that about 130 million people are exposed to a concentration of 50 μg / l of arsenic in drinking water. The European Directive has defined maximum allowable concentration of arsenic in drinking water of 10 μg / l [2]. Arsenic in drinking water has never been a subject of interest in most European countries because the maximum allowable concentration of 10 μg / l of arsenic in drinking water have been rarely exceeded. However, in countries such as Hungary, Serbia, Croatia, Greece, Italy and Spain elevated arsenic content in drinking water was confirmed and additional efforts are needed in the treatment of raw water with the aim of achieving the maximum allowable As concentration of 10 μg / l [3,4].

Groundwater in the territory of the Republic of Serbia is the basic resource of water supply system and in the territory of AP Vojvodina water supply is exclusively oriented to groundwater. Much of the groundwater contains unacceptably high levels of arsenic. According to the Regulation on hygienic quality of drinking water [5] maximum allowable concentration of arsenic in drinking water is 10 μg / l. More than 40% of the population of AP Vojvodina is supplied with water containing a higher concentration of arsenic than allowed [1]. In most cases, the concentration of arsenic in drinking water ranges from 50 to 100 μg / l, but there are also municipalities, such as Zrenjanin, where the concentration of arsenic in drinking water ranges from 150 to 250 μg / l [6]. Content of the natural organic matters in these waters expressed through the consumption of potassium permanganate is from 20 to 150 mg / l, and in extreme cases up to 200 mg / l [1]. There are many harmful effects of arsenic on human health - cardiovascular diseases, diseases of the respiratory system, nervous system, various skin lesions, and cancer [7]. Most of the water supply systems in Vojvodina, except the system in Subotica do not own the technology for arsenic removal from groundwater. Efficient removal of organic matter

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and arsenic from drinking water resources is still one of the greatest challenges in modern production of safe drinking water. A number of different techniques for reducing the content of organic substances in water are being applied, of which the most applied are conventional physic-chemical methods, such as coagulation-flocculation processes or improved treatment of coagulation. This is a multiphase technique that requires a considerable area of land, continuous supply of chemicals, and generates a significant amount of sludge. Literature indicates that cost-friendly treatment of wastewater and drinking water resources with minimal use of chemicals, which allows the sustainable management of water resources, is necessary. One alternative could be a potential treatment of raw water by ferrate(VI), which at the same time oxidizes the organic material and converts arsenic(III) is to As(V), which is far more mobile and removes from the solution as a slurry in the process of coagulation by generated $Fe(OH)_3$.

MATERIAL AND METHODS

The Na_2FeO_4 solution, concentration of 3,5 g/l used for the treatment was synthesized electrochemically. The process of electrochemical synthesis of the alkaline solution of ferrate(VI) was carried out in a laboratory facility, Figure 1, for electrochemical synthesis of ferrate(VI) composed of a two-part flow-through electrochemical cell and based on the transpassive anodic dissolution of iron alloys in a 10 M NaOH solution, in accordance with previous studies [8,9]. The concentration of synthesized ferrate(VI) was controlled by the titrimetric chromite method at a temperature of 25 °C. Freshly synthesized ferrate(VI) was used for the treatment of the solution.

Figure 1. Pilot plant for the electrochemical synthesis of ferrate(VI)

Within these activities the laboratory pilot device for the removal of As(III) from raw drinking water loaded with organic substances is formed.

Pilot plant for the treatment of raw drinking water by ferrate (VI) is composed of three reaction columns:

- Reaction column for the treatment of water by ferrate(VI),
- Reaction column for coagulation,
- Filtration column.

Between the reaction column are: transport pump for fluids, compressor for aeration, receiving tank, sedimentation tank, dozers for ferrate(VI) and $AlCl_3$, tanks for acid and hydroxide and tank for treated water.

Figure 2. Pilot plant for the treatment of raw drinking water by ferrate(VI) ferrate(VI)

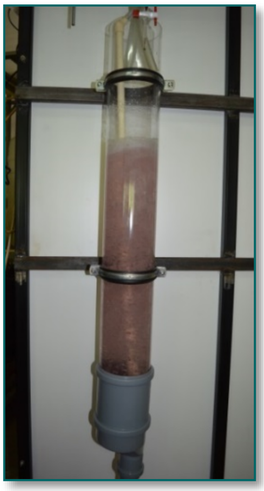

Figure 3. Reaction column for the treatment of raw water by ferrate(VI) with aeration

Formed pilot plant is a batch-type with capacity of 10 liters and batch exchanges on every 30 minutes. In the formed pilot plant for the treatment of raw drinking water with high content of As, Figure 2, raw water from four different sources is treated. The procedure consist of: the treatment of raw water in the first reaction column by ferrate(VI) added from the doser, with aeration by air compressor, Figure 3, wherein the oxidation of As(III) to As(V) and the partial coagulation occur. After pH adjustment to the value pH = 6 by H_2SO_4, the treated water is transported by pumps and system of pipes and control valves, to the reaction column for coagulation, Figure 4.

Figure 4. The reaction column for coagulation

Figure 5. Sedimentation tank

Figure 6. Filtration column with filtration sand of different granulite

In second reaction column is carried out the process of coagulation by some of the common coagulants ($AlCl_3$, $FeCl_3$, $Al(OH)_3$) at pH = 8, with pH adjustment by NaOH. From the second reaction column the treated water is discharged into the sedimentation tank, Figure 5. From the sedimentation tank clear solution is transported by pump into the filtration column, Figure 6, with pH adjustment to neutral value of pH = 6 - 7 by H_2SO_4.

Filtration column contains sand filters with various granulation after which the purified water in the receiving tank has satisfactory characteristics, necessary for drinking water.

RESULTS AND DISCUSSION

Pilot plant is applied for the treatment of raw drinking water from 4 different locations from the theritory of Banat (locations known to the authors) with initial characteristics given in Table 1.

Table 1. Initial content of As and permanganate index of raw drinking water from various locations

Location 1		Location 2	
As, mg/l	$KMnO_4$, mg/l	As, mg/l	$KMnO_4$, mg/l
38,66	94,82	1,62	13,91
Location 3		**Location 4**	
As, mg/l	$KMnO_4$, mg/l	As, mg/l	$KMnO_4$, mg/l
1,1	38,56	3,57	16,44

The samples of raw water from all locations were treated with two different concentration of ferrate(VI) of 71 µM and 142 µM in the ratio (As : Fe(VI)) = 1 : 5 and 1 : 10. After ferrate(VI) treatment, in each sample was added a coagulant, $AlCl_3$ in a molar ratio ($AlCl_3$: Fe(VI)) = 1 : 1. After filtration and pH adjustment to 6-7 As concentration and the presence of organic matter (permanganate consumption) are analyzed.

Table 2. As content in untreated drinking water from the territory of Banat after treatment by ferrate(VI)

Location 1		Location 2	
Reduction of As,%		Reduction of As,%	
71 µM, Fe(VI)	142 µM Fe(VI)	71 µM Fe(VI)	142 µM Fe(VI)
		93	97
Location 3		**Location 4**	
Reduction of As,%		Reduction of As,%	
71 µM Fe(VI)	142 µM Fe(VI)	71 µM Fe(VI)	142 µM Fe(VI)
84,5	96,4	90	95

Table 3. Percentage of reduction of permanganate index in raw drinking water from the territory of Banat after treatment by ferrate(VI)

Location 1		Location 2	
Reduction of permanganate index		Reduction of permanganate index	
71 µM, Fe(VI)	142 µM Fe(VI)	71 µM Fe(VI)	142 µM Fe(VI)
		30,4	47
Location 3		**Location 4**	
Reduction of permanganate index		Reduction of permanganate index	
71 µM Fe(VI)	142 µM Fe(VI)	71 µM Fe(VI)	142 µM Fe(VI)
41	50,5	39	51

Results of the treatment and analysis of As and permanganate index are shown in Tables 2 and 3, in percentage of reduction compared to initial values.

CONCLUSIONS

Aim of the work to define the procedure for As removal from the raw drinking water by ferrate(VI) is reached. As removal is up to 97%, while permanganate index is close to the statutory limit values (12 mg / l $KMnO_4$) [5]. Further optimization of the process would reach the concentration of total As below 10 µg / l which is, according to the Regulations on Hygienic Quality of Drinking Water of the Republic of Serbia, the limit value of arsenic concentration in drinking water.

The application of ferrate(VI) in the treatment of raw drinking water is possible and desirable, due to the high environmental performances of ferrate(VI) in comparison to the oxidants based on oxygen, ozone or hydrogen peroxide and aluminum-based and chlorine-based coagulants. Alternative or pre-treatment to conventional methods, can potentially be the treatment of raw water by ferrate(VI), which at the same time oxidizes the organic material, and As(III) to As(V), which is far more mobile than As(III) and can be removed from the solution by coagulation and flocculation with the resultant $Fe(OH)_3$ as a slurry.

The created pilot plant for the purification of raw drinking water has proved very effective application of ferrate(VI) in both, primary and secondary treatment process for raw drinking water. However, the treatment of fresh drinking water need to be specifically optimized depending on the initial values of As and permanganate index. In the presented pilot plant the treatment of raw drinking water by some other oxidizing and coagulation agents is also possible.

Note

This paper is based on the paper presented at The Vth International Conference Industrial Engineering and Environmental Protection 2015 – IIZS 2015, University of Novi Sad, Technical Faculty „Mihajlo Pupin”, Zrenjanin, SERBIA, October 15-16th, 2015, referred here as[10].

REFERENCES

[1] Mohora E., Mogućnost primene i efikasnost elektrokoagulacione tehnike u preradi podzemne vode sa visokim sadržajem prirodnih organskih materija - doktorska disertacija, 2012.
[2] WHO, Guidelines for Drinking-Water Quality, Vol.4. World Health Organisation, Geneva, pp. 315–318, 2011.
[3] Milenković Lj., Koščal M., Mijatović M., Geomorphological Map of Serbia 1:500,000, Geozavod-Gemini and Magic Map, Belgrade, 2003.
[4] IPA, Arsenic Platform, HUSRB/1002/121/075, 2012.
[5] Pravilnik o higijenskoj ispravnosti vode za piće ("Sl. list SRJ", br. 42/98 i 44/99)
[6] Ćuk M., Todorović M., Stojković J., Arsenic in groundwater for water supply in Vojvodina, XIV Srpski Simpozijum o Hidrogeologiji, Zlatibor, pp. 611-615, 2012.
[7] Kongkea P., Sthiannopkao S., Kim K.W., Wong M.H., Sao V., Hashim J.H., Yasin M., Salleh M., Syed Mohamed A., Health risk assessment of inorganic arsenic intake of Cambodia residents through groundwater drinking pathway, Water Research, Vol.44, pp. 5777–5788, 2010.
[8] Wood R.H., The heat, free energy, and entropy of the ferrate(VI) ion, Journal of American Chemical Society Vol.80, pp. 2038-2041, 1958.
[9] Čekerevac M.I., Nikolić-Bujanović Lj.N., Jokić A., Simičić M.V., Investigation of electrochemical synthesis of ferrate Part II: Optimization of the process parameters, Hemijska industrija, Vol.64(2), pp. 111-119, 2010.
[10] Ljiljana Nikolić Bujanović, Milan Čekerevac, Milena Tomić, Mladen Zdravković, Marijana Stamenković Đoković, Pilot plant for treatment of raw drinking water with high content of arsenic using ferrate (VI), The Vth International Conference Industrial Engineering and Environmental Protection 2015 – IIZS 2015, University of Novi Sad, Technical Faculty „Mihajlo Pupin”, Zrenjanin, SERBIA, October 15-16th, 2015

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