THE ELECTROCOAGULATION/ADVANCED OXIDATION TREATMENT OF THE WELL WATER FROM ŽUPANJA

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The work was development and application of the purification system suitable for the treatment of groundwater used for human consumption as well as watering of the plants in the system for the hydroponic cultivation of tomatoes. For that purpose the well water from the 60 m deep water layer situated near the city of Županja (Eastern Croatia) was processed. Most of the measured parameters exceeded upper permissible limit (UPL) for drinking water. The concentrations of the parameters color, turbidity, iron, manganese, arsenic, phosphates, chemical oxygen demand and ammonia were as follows 292±20 mg/PtCo, 21±5 NTU, 1.72±0.34 mg/L, 0.075±0.014 mg/L, 0.074±0.011 mg/L, 10.4±1.7 mg/L, 37±1 mg/L and 1.2±0.1 mg/L, respectively. Due to the complex composition of the treated water, the purification system required the combination of electrochemical treatment, using iron and aluminum electrode plates with simultaneous ozonation followed by post treatment with hydrogen peroxide and ozone. The electrocoagulation/ozonation approach was used for the removal of heavy metals, color, turbidity, phosphates and partially organic matter while the rest of the organic contaminants and ammonia were removed by the treatment with hydrogen peroxide and ozone. Following the combined electrochemical treatment and post treatment with hydrogen peroxide and ozone all measured parameters in the treated water were in agreement with regulated values. The combined treatment resulted in total removal of arsenic, color, turbidity, ammonia and organic contaminants while the removal of other parameters of interest was up to 97.98%.

Keywords: Heavy metals, arsenic, ammonia, electrocoagulation, ozonation, iron anode, aluminum anode, hydrogen peroxide

INTRODUCTION

Groundwater of the Pannonian basin which covers the parts of Hungary, Romania, Croatia, Serbia and Slovakia represents the complex system with elevated to high values of heavy metals and arsenic, color, turbidity, suspended solids, ammonia, and other nutrients as well as natural organic matter (1-10).

When considering the human health risk, among the mentioned contaminants, arsenic is of the highest importance. Its values ranged from 1.3 to $611.8 \ \mu$ g/L in the Croatian part of the basin (1-4).

Deterioration of the water quality can be attributed with various natural and anthropogenic factors. The elevated heavy metal and total arsenic concentrations can be probably associated with the dissolution of oxohydroxides of iron, manganese, and aluminum under reducing conditions, and desorption of arsenic and heavy metals from these minerals (4). The mayor source of ammonia in the groundwater is microbial degradation of the natural organic matter under reducing condition (4). Anthropogenic sources lead to inorganic, microbiological and organic contamination of groundwater.

The aim of this research was the development of an effective system for the treatment of groundwater used for human consumption and watering of the plants in the system for the hydroponic cultivation of the tomatoes in order to reduce operational problems (formation of deposits in the pipes and nozzle system with significant reduction of the system efficiency) as well as human health risk (due to the consummation of the contaminated water). The system must guarantee high quality of the treated water as regards to all measured parameters. Due to exellent results obtained in our previous research (11-13) both on laboratory and pilot plant scale we decided to apply electrocoagulation as the main treatment and post-treatment with hydrogen peroxide and ozone.

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MATERIALS AND METHODS

Groundwater was collected from the 60 m deep well situated near the city of Županja (Eastern Croatia) into five acid pre-cleaned polyethylene containers (60 L each). Prior to the purification experiments water samples were homogenized for 10 minutes and 50 L of water was subjected to electrocoagulation using iron electrode plates (I = 50A, U = 10 V) for 5 minutes and aluminum electrode set (I = 28 A, U = 12 V) for additional 10 minutes with simultaneous ozonation. Each electrode set contained of 10 quadratic, one millimeter thick plates (75 x 250 mm) in the parallel arrangement, separated by an electro insulator. The distance between plates was 10 mm. Each even plate was connected to + pole of DC power supply and represented sacrificial anode, while odd plates connected to the – pole of DC served as the cathodes. Either Fe or Al electrode set was placed at the bottom of the reaction vessel perpendicular to the vessel bottom. In the end of electrochemical treatment the suspension was re-circulated in strong electromagnetic field for 10 minutes and subjected to slow mixing for another 15 minutes while the settlement time was 30 minutes (11, 12). After the settlement clear water was decanted and post-treated with ozone in the presence of hydrogen peroxide (30% H₂O₂; volume of H₂O₂ = 5 mL) for 10 minutes in order to remove ammonia. Ozone was generated by ozone generator model OzoneMax 1668 (500 mg/h).

For the analysis of heavy metals and arsenic 100 mL of the original or purified water was adjusted to pH 0.1, 3 and 11 by addition of hydrochloric acid and ammonium hydroxide, preconcentrated by ammonium pyrrolidine-dithiocarbamate (APDC), filtered through a Millipore HAWP filter (pore size 0.45 mm; diameter 25 mm) using a Millipore micro filtration system) and analyzed by energy dispersive X-ray spectrometry (EDXRF) (11, 12).

Spectral data were collected by Genie-2000 software (Canberra) while for spectrum deconvolution and quantitative analysis WinAxil software package (Canberra) was used. In order to obtain a good counting statistic, collecting time was measured 10000 s. Calibration model for the qualitative and quantitative analyses was created on the basis of the measurements of the standard solutions (Merck) having the concentration range from 10 to 200 μ g/L, prepared and measured in the same way as unknown samples. Minimum detection limit for heavy metals and arsenic was 1 μ g/L. Relative standard deviation based on five consecutive measurements of the target containing 100 μ g/L of Fe, Mn and As prepared from the Merck standard solution was < 3% for all three elements.

pH value, electrical conductivity (EC) and total dissolved solids (TDS) were determined by PHT-027 - water quality multiparameter monitor (Kelilong Electron) (11, 12). Minimum detection limit for the parameters pH, EC and TDS were 0.01, 0.01 mS/cm, and 10 mg/L, respectively.

Color, turbidity, calcium, phosphates, fluorides, COD and ammonia were determined using HACH DR890 colorimeter (Hach Company, Loveland, Colorado, USA) (11, 12). Minimum detection limit for the above mentioned parameters were 1 PtCo, 1 NTU, 10 mg/L, 0.02 mg/L, 0.05 mg/L, 1 mg/L and 0.02 mg/L, respectively.

RESULTS AND DISCUSSION

Table 1 presents the values of the parameters measured in the groundwater used for human consumption as well as watering of the plants prior/after the combined treatment and upper permissible limit (UPL) of each parameters for drinking water.

Most of the measured parameters in untreated water exceeded upper permissible limit (UPL) for drinking water. The highest increase over UPL was found for the parameters phosphates (34.7 times), color (14.6 times), iron (8.6 times), arsenic (7.4 times), COD_{Mn} (7.4 times), turbidity (5.3 times), ammonia (2.4 times) and manganese (1.5 times). The presence of the soluble Fe (II) in the concentration of 1.72 ± 0.34 mg/L caused yellowish coloration of the water. Addition of the nitric acid as a strong oxidizing agent in order to achieve optimum pH value of the water resulted in the oxidation of Fe (II) to Fe (III) and consequently, creation of poorly soluble oxyhydroxides. Elevated values of manganese were also found which in the combination with trivalent iron creates hardly soluble Fe-Mn oxy-hydroxides. Besides, the presence of the phosphates in the concentration of 10.4 ± 1.7 mg/L, calcium 100 ± 10 mg/L, and traces of fluorides resulted in the formation of hardly soluble compounds like apatite (Ca₅(PO₄)₃), hydroxyl-apatite (Ca₅(PO₄)₃(OH)) and fluorapatite (Ca₅(PO₄)₃F) in the pipes and nozzles system with significant reduction of the system efficiency. From the toxicological point of view arsenic in the concentration of 0.074 ± 0.011 mg/L was determined as a mayor contaminant. Besides, additive and synergistic effect of arsenic with heavy metals, must be also considered.

Following the combined electrochemical treatment and advanced oxidation using ozone and H_2O_2 , the treated water was clear and colorless with the values of all measured parameters (Table 1) in accordance with the limit values of the Ordinance on the health quality of drinking water (14) and the recommendations of the World Health Organization (15).

The combined treatment resulted with 100% removal efficiency of color, turbidity, total arsenic, COD and ammonia (Table 1). The high removal degree was also determined for the total iron (97.91%), total manganese (77.33%), total phosphates (97.98%) and fluorides (80%).

In the last ten years, the research on the application of electrochemical methods for the treatment of drinking water and wastewaters was intensified. Orescanin et al. (11) by using electrocoagulation with iron, and aluminum electrode sets were able to achieve a 100% removal of total arsenic from the drinking water from the area of the former uranium mines (Cameron, Tuba City, Arizona) with the initial arsenic values ranged from 21-52 μ g/L. Application of the same method in the combination with ozone and UV irradiation resulted in 100% removal of total arsenic from the groundwater used for the supply of pig farms in Eastern Slavonia (12). Laboratory and pilot plant study using electrochemical methods and advance oxidation processes also resulted with 100% removal of arsenic from the water supplying Temerin and Zrenjanin towns (13). The removal mechanism in all cases is based on the oxidation of As(III) to As(V) using ozone, and its removal by coagulation/flocculation using electrochemically generated cations of iron and aluminum, and/or co-precipitation with iron and aluminum hydroxides. Higher degree of the removal is achieved by applying iron electrodes due to the high affinity of arsenic to the iron species. Kumar et al. (16) used the iron, aluminum and titanium set of the electrodes for the removal of As(III) and As(V) from the synthetic water containing 200 μ g/L. The best results are achieved using iron sets of electrodes (removal efficiency higher than 99%; final value less than 10 μ g/L). The removal efficiency was 37% in the case of aluminum electrode sets, and 58% when titanium electrodes were used. Koby et al. (17) under optimum experimental conditions removed 94.1% of the total arsenic using iron electrodes, and 93.5% using aluminum electrodes from drinking water containing 150 μ g/L of arsenic. Parga et al. (18) reached 99% removal of arsenic from drinking water after 90 seconds of the electrocoagulation using electroces made of carbon steel in the combination with oxidation by air.

Parameter	Before purification	After purification	Removal efficiency (%)	UPL _{HR}	UPL _{WHO}
Color (mg/PtCo)	292±20	n.d.*	100.00	20	-
Turbidity (NTU)	21±5	n.d.	100.00	4	5
pН	7.52±0.31	7.59±0.56	-	6.5-9.5	6.5-8
EC (mS/cm)	0.73±0.03	0.59±0.01	19.18	2.5	-
TDS (mg/L)	510±20	410±5	19.61	-	600
Fe (mg/L)	1.72±0.34	0.036±0.006	97.91	0.2	0.3
Mn (mg/L)	0.075±0.014	0.017±0.004	77.33	0.05	0.4
As (mg/L)	0.074±0.011	n.d.	100.00	0.01	0.01
Ca (mg/L)	100±10	60±4	40.00	-	-
F ⁻ (mg/L)	0.25±0.02	0.05±0.003	80.00	-	1.5
PO₄ ³⁻ (mg/L)	10.4±1.7	0.21±0.03	97.98	250	250
COD _{Mn} (mg/L)	37±1	n.d.	100.00	5	-
NH_4^+ (mg/L)	1.2±0.1	n.d.	100.00	0.5	1.5

Table 1. Physico-chemical parameters and standard deviations based on five replicas determined in untreated/treated well water, mean value of the removal efficiency for each parameter and upper permissible limit prescribed by Croatian (UPLHR) and World health organization (UPLWHO) regulatory body

* not detected

It could be concluded that our results on the removal of arsenic were in agreement or better compared to the available literature data. Excellent results were also achieved for the removal of organic matter, which was partially removed by coagulation/flocculation with electrochemically generated flocs of iron and aluminum and oxidation by ozone. The main mechanism of the removal was oxidation with reactive oxidative species formed in the reaction of ozone and H_2O_2 . The removal efficiency of COD following the combined treatment was 100%. These results were in agreement with previous research. The electrocoagulation using aluminum electrode set resulted in 97.8% removal of the humic acids from the groundwater (19). The similar removal efficiencies were obtained by Yildiz et al. (20) for the aluminum based electrocoagulation. In the presence of Na₂SO₄ and NaCl electrolytes, 96.84% and 99.64% of humic acid was removed, respectively. The application of aluminum electrode set in either mono-polar or bipolar arrangement resulted in up to 67.5% removal of DOC and up to 89% removal of color from the river water (21).

The removal of ammonia during the electrocoagulation/ozonation was negligible due to the selectivity of ozone toward organic molecules compared to ammonia (11). So, complete removal of ammonia was achieved by the oxidation with the reactive oxidative species formed in the reaction of ozone and H_2O_2 (like HO2, °OH, O2, O°, O3).

CONCLUSION

From the presented results it could be concluded that the electrochemical methods combined with the advanced oxidation processes represent a suitable treatment approach for the removal of the complex mixture of contaminants found in the groundwater. Following the treatment, the concentrations of all selected contaminants were significantly lower compared to the Croatian and the WHO regulated values. Under the optimum treatment conditions, the removal efficiencies of color, turbidity, total arsenic, chemical oxygen demand and ammonia, were 100%. Contrary to the standard chemical coagulation, which increases the electrical conductivity and total dissolved solids in the purified water, the electrochemical methods in the combination with the advanced oxidation, resulted in the decrease of both parameters. The influence of the electrical and electromagnetic field on the treated water resulted in faster separation of the flocs, its higher stability, lower content of bound water and larger surfaces compared to the chemical flocs.

There was no need for the measurement and adjustment of pH by acids/basis during the treatment since pH changes through all the treatment phases were insignificant.

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PROČIŠĆAVANJE BUNARSKE VODE SA PODRUČJA ŽUPANJE ELEKTROKOAGULACIJOM / NAPREDNIM OKSIDACIJSKIM PROCESIMA

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Cilj ovog rada bio je razvoj i primjena sustava pogodnog za za pročišćavanje podzemne vode koja se koristi za ljudsku upotrebu, kao i za hidroponski uzgoj rajčice. U tu svrhu je korištena podzemna voda uzeta iz 60 metara dubokog bunara smještenog u neposrednoj blizini grada Županje (Istočna Hrvatska). Većina mjerenih parametara bila je viša od maksimalno dopustivih koncentracija (MDK) propisanih za vodu za piće. Srednje vrijednosti koncentracija i standardne devijacije parametara boja, mutnoća, željezo, mangan, arsen, fosfati, oksidativnost i amonijak su iznosile kako slijedi 292 \pm 20 PtCo, 21 \pm 5 NTU, 1.72 \pm 0.34 mg/L, 0,075 \pm 0,014 mg/L, 0,074 \pm 0,011 mg/L, 10,4 \pm 1,7 mg/L, 37 \pm 1 mg/L i 1.2 \pm 0.1 mg/L. Zbog kompleksnog sastava tretirane vode, sustav za pročišćavanje zahtijeva kombinaciju elektrokemijskih metoda, korištenjem željezovih i aluminijevih setova elektroda s istovremenim ozoniranjem te završnu obradu vodikovim peroksidom i ozonom. Kombinacija elektrokoagulacije i ozoniranja je korištena za uklanjanje teških metala, arsena, boje, mutnoće, fosfata i djelomično organske tvari, a ostatak organskih nečistoća i amonijak su uklonjeni obradom vodikovim peroksidom i ozonom. Nakon kombinirane elektrokemijske obrade te završne obrade vodikovim peroksidom i ozonom svi mjereni parametri u tretiranoj vodi su bili u skladu s MDK vrijednostima. Kombinirani sustav pročišćavanja je rezultirao potpunim uklanjanjem arsena, boje, mutnoće, amonijaka i organskog onečišćenja, a uklanjanje drugih parametara od interesa je dosezalo 97,98 %.

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