

THE REDUCTION OF THE NITRATES FROM THE DRINKABLE WATER BY ELECTROCHEMICAL METHODS. CASE STUDY

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ABSTRACT. The paper presents the electrochemical pre-treatment step followed by pre-aeration step, implemented within the flow of drinkable water treatment, from the potable water unit in the village Romuli, Bistrița-Nasaud county. The purpose of introducing electrochemical pre-treatment step, in the flow of a standard units of drinkable water is to increase the degree of water safety by removing different pollutants occurring accidentally in the water and to decrease the doses of reagents used in the chemical treatment step. Among the observed effects of electrochemical treatment by medium frequency pulsed currents in the water are getting active species (hydroxyl radicals, active oxygen, chloride ions, etc.), removing nitrate and chemical oxygen demand (COD), the appearance of an ultrasonic field between electrode which clean the system and mixt treated water. In addition, the electrochemical pretreatment step, favors coagulation, flocculation and precipitation in the chemical treatment step.

In the paper are presented the water parameter in water treatment process and electrical model of electrochemical step using MATLAB software and SIMULINK Module.

Key words: *electrochemical treatment, EAOP, multiple oxidants, nitrate, drink water*

FOREWORD

Attempts of cleaning or disinfecting water by direct electrolysis were reported before the 19th century (Chisholm, 1858). There was a speculation that the electrical elements (the so-called Baghdad batteries) discovered in 1936 in the ruins of the Parthian town (inhabited between 300 BC and 300 AD) near Baghdad, Iraq, had been used for the electrochemical disinfection of water (König, 1940). Ever since the end of the 19th century there have been many attempts to electrochemically disinfect water (Burgess, 1916; Salles, 1927; Juda and McRae, 1956; Reis et al., 1980). None of them has succeeded so far, at least not for a practical utilisation on the long run.

In order to describe this water treatment process or the water obtained by this process one has used various terms, such as 'electrolytic disinfection', 'electrochemical disinfection', 'anodic oxidation', 'functional water' or 'electro-chemically activated water' etc. There are three reasons why the electrochemical treatment of water has reached technical maturity only recently, more than 2000 years since its discovery:

a) It is only these past 40 years that enough stable and efficient materials used for making electrodes for electrochemically disinfecting water have been developed and improved. We talk about titanium electrodes covered with various mixed oxides based on iridium and/or ruthenium oxide (Hayfield, 1998a,b,c) and diamond-doped electrodes (Kraft, 2007).

b) Only recently has the functional inconsistency between the concentration of the chlorides from the water, the current, the current density, the electrode material, the water quality, the electrochemical production of free chlorine and water disinfection been investigated in detail (Kraft et al., 1999a,b; Kraft et al., 2003; Nakajima, 2004; Bergmann and Koparal, 2005).

c) The works for electrochemically disinfecting water were often initiated by amateurs in chemistry and this holds true to some extent even nowadays. There were but a few electrochemists that were interested in this topic, usually for a short period of their career, which led to mistakes in dimensioning the devices and to non-scientific explanations for the functioning mechanism of the process.

In comparison with other disinfection chemical processes, the advantages of the water disinfection electrochemical process are obvious: there is no need for carrying, storing and dosing the disinfectants. The process of disinfection can be adjusted on site, subject to necessities. The electrochemical disinfection process displays the 'reservoir' flaw, is often more economical and calls for less maintenance than other methods.

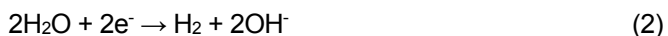
PRESENTATION OF THE PROCESSES WITHIN THE ELECTRO-CHEMICAL PRE-TREATMENT STAGE (Electrochemical Processes Description)

The electrochemical processes are usually simple and easy to develop in various environments and at various sizes. Pollutants can be actually removed either by oxidation, electrochemical reduction, electrochemical coagulation or floating.

In the water treatment electrochemical process, the electrodes (at least one cathode and an anode) are immersed either directly in the amount of water that needs treating or in a bypass pipe. A continuous or pulsating current is applied between the electrodes, leading to water electrolysis. At the anode the main product is oxygen (equation 1):



accompanied by water acidification near the anode. The cathode sees the formation of hydrogen (eq. 2):



and the water near the cathode becomes alkaline. Since the generated hydrogen is in general unwanted, it should be separated from the water flow. Since small amounts get formed in case of a normal current (approx. 0.4 l of hydrogen is produced per ampere/hour), in most cases this is achievable with no great efforts. In most practical applications, the simplest undivided electrochemical reactor needs plate-parallel electrodes and the mono-polar electrode pile is inserted in the reactor pipe. The electrode plates can be configured either as punched or non-punched plates or as an expanded metal.

If the electrochemical treatment stage is applied to the water containing salts, especially chlorides, hypochlorite is obtained in the water. The disinfectant, the hypochlorous acid / the hypochlorite is produced at the anode by a reaction that hinders the formation of oxygen. Please find below a simplified reaction mechanism. First of all, the chlorine from the chloride ions dissolved in water is obtained electrochemically (equation (3)):



The chlorine hydrolyses in the water, giving rise to the hypochlorous acid (HClO) – equation (4):



The hypochlorous acid and the hypochlorite anion form a pH-dependant balance – equation (5):



In the nomenclature, for the water disinfection process, the sum of the concentrates of hypochlorous acid and hypochlorite is usually called 'free chlorine' or 'active chlorine'. The effect of disinfection of the free chlorine is based on the production of oxygen (the oxygen release), according to equations (6) and (7):



Where there is a small concentration of chlorides, in the water that has to be treated (like in case of the drinkable water), the efficiency of the electrode (the material out of which it is made) to produce current is crucial, as this efficiency has to be as high as possible. Big differences were noticed when free chlorine was obtained, depending on the type of material out of which the electrode is made at small concentrations of chlorides (Kraft et al., 1999a,b; Kraft et al., 2003; Bergmann and Koparal, 2005).

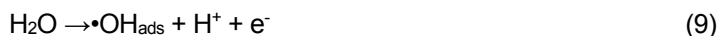
The electrolysis reactions in a water lacking impurities lead to the production of ozone in the water. The utilisation of anodes with a great oxygen over-tension, a high density of current and a low water temperature can lead to the generation of ozone directly from the water, according to equation (8):



The electrochemical production of ozone has been known since the 19th century (Wünsche et al., 2005). Electrolysis was the very first method used to produce ozone (Rubin, 2001), but nowadays for most applications ozone is produced by corona discharge.

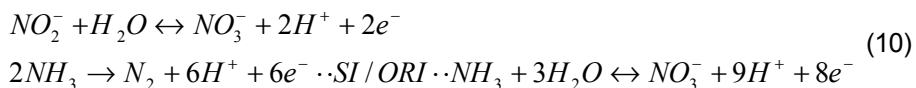
Some other effects specified in the literature regarding the electrochemical treatment of water include the disinfection with hydrogen peroxide obtained in the cathode area, ammonium and nitrates reduction and the diminishment of the chemical oxygen demand (the oxidability). The mitigation of the water oxidability as a result of the electrochemical treatment is normal, as during the process there appear active chemical species that unselectively oxidise the substances dissolved in the water till their mineralization (carbon dioxide and gaseous nitrogen).

Electrochemical oxidation is an efficient electrochemical technique, which is used to oxidise various types of compounds in the waters. Thanks to the electrochemical oxidation, many organic substances (such as phenols), the ammonium and also the pathogenic agents and the bacteria from the drinkable waters were successfully oxidised and inactivated. This technique is also environmentally friendly, because no chemical reacting agents are used. The classical anodic oxidation is the most common electrochemical method for the treatment of the toxic compounds from the water – both organic and inorganic (ammonium, nitrates, nitrites). This technique uses an anode that generates high over-tension O_2^- from Pt, PbO_2 and BDD in order to favour the process of generating the $OH\cdot$ radicals absorbed at its surface from the water oxidation process – equation (9). The generated hydroxyl radical is a very strong non-selective oxidation agent, which rapidly reacts with the organic compounds by the hydroxylation reaction, by adding the hydroxyl group to an unsaturated bond or by the reaction of dehydrogenation with the loss of an atom of hydrogen, according to a radical-related mechanism till the total mineralization of the compounds, namely the transformation of the initial pollutants into carbon dioxide, water and inorganic ions. The anodic oxidation can be used either alone or associated to other processes.



Electrochemical coagulation is a technique for the purification of the promising waters, being used in certain applications as well. The already known Fe-Al electrodes (Fe and Al) are used to release the Al^{3+} and Fe^{2+} ions that will coagulate the organic and inorganic substances from the water.

Another effect of the electrochemical treatment for water is the action upon the nitrates. After the electrochemical treatment, the ammonium is reduced to gaseous nitrogen if chlorine ions are dissolved in the water and, in their absence, they turn into nitrites and then into nitrates.



Reverse reactions: departing from the nitrate, one arrives to nitrite, in the presence of the chlorine ion the final product is gaseous nitrogen and the absence of the chlorine ion leads to ammonium, nitrites and gaseous nitrogen (see figure 1).

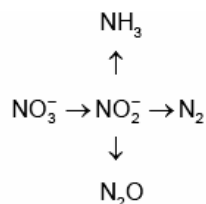


Fig. 1. *The routes of the electrochemical denitrification reaction*

As a theoretical conclusion, the reaction below, which describes the variation of the concentration of the substance subjected to the electrochemical treatment, can be put down for a certain chemical compound:

$$\Delta C = \eta_{\text{REACTION}} \cdot \frac{I_{\text{med}} \cdot A_{\text{MOLAR}} \cdot 1h}{Q_{\text{TREATED}} \cdot z_{\text{VALENCY}} \cdot F} \quad (11)$$

where - $\eta_{R/C}$ – the efficiency of the reaction in the cell configuration;

- I_{MED} – the medium current through the treating cell;
- A_{MOL} – the molar weight of the treated substance;
- 1h – the one hour time;
- Q_{TREATED} – the hourly water flow rate subjected to the treatment;
- Z_{VALENCY} – the number of valency electrons involved in the reaction;
- F – the Faraday constant, equalling 96.485 C/mol.

PRESENTATION OF THE ELECTROCHEMICAL PRE-TREATMENT STAGE WITHIN THE POTABILISATION STATION

The electrochemical treatment stage, as implemented within the drinkable water station that supplies the Romuli township (Figure 2), is composed of a reaction chamber made of stainless steel, where a system of electrodes supplied by medium frequency voltage pulsations is installed (Figure 3), followed by a water aeration chamber, where the air is introduced into the water by a lubrication-free (dry) air compressor. This treatment stage is part of the water treatment flow after the cake of alum injection point.

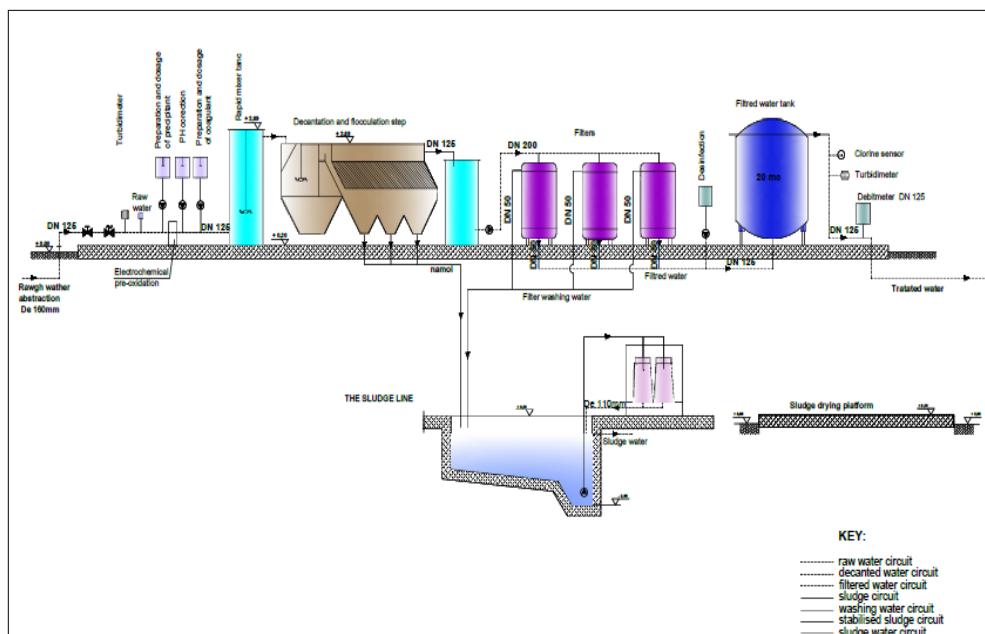


Fig. 2. The scheme of the water treatment flow in the water potabilisation station

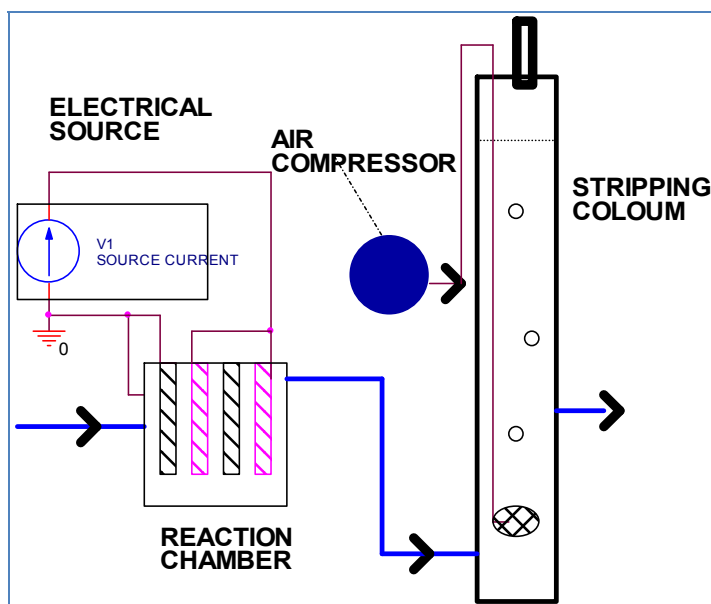


Fig. 3. The theoretical scheme of the electrochemical treatment stage

The positive electrodes (the anodes) are 11 titanium bars of 8 mm in diameter and 500 mm in length; they are mounted in front of the negative electrode (the cathode), which is a sieve made of stainless steel. The surface of the positive electrode is 0.124 m² and the average distance between the two systems of electrodes is 10 mm, the impedance of the reaction chamber depending on the water conductivity. Figure 4 sets out the simplified electrical template of the electrochemical treatment stage.

Great energies are generated in small amounts in the water by the pulsating discharge, because the phenomena take place especially at the surface of the electrodes, where there appear the condition of plasma induced by the electric field (electro-plasma in the water) and the electrical field of the electrodes gets screened due to the presence of the other electric charges. From the electrical viewpoint (the circuit element), the water behaves like a one resistance series condenser, at low frequencies and weak electric fields. The condenser appears at the liquid-solid interface because of the charge accumulations on the surface of that solid. In this area there appears a twofold electric layer, a condenser in fact (Jones and Wang, 2004). The capacity of the twofold electric layer depends on the characteristics of the liquid and of the solid from the interface. In the absence of the exterior electric field, neither the electric charges nor the chemical ions can go through this potential barrier. When the voltage between the electrodes rises, the twofold electric layer is exceeded by the electric charges, so that the electrochemical cell is represented in the template by a resistance with two diodes in antiparallel and one condenser at each end.

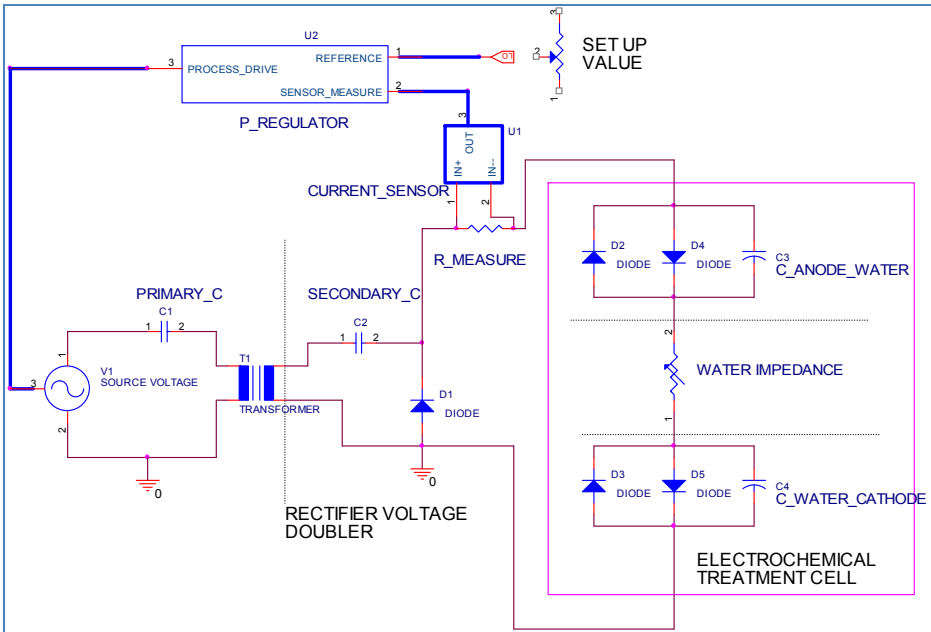


Fig. 4. The simplified electrical scheme of the electrochemical treatment stage

The parameters at which the electrochemical treatment stage took place:

- The water flow rate = 24 m³/h;
- The power absorbed from the electrical network by the electrical source of the treatment stage = 704 W;
- The average voltage between the anode and the cathode = 47 V;
- The average current through the electrochemical treatment cell = 11.08 A;
- The frequency of the applied current pulsations = 15 kHz;
- The source yield (the power applied on the electrochemical cell / the power absorbed from the electrical network = 74 %;
- The air flow rate used for airing the water = 3 Nm³/h.



Fig. 5. *The electrochemical pre-treatment stage within the water potabilisation station of Romuli township - Bistrița-Năsăud county*

$$R_{ANODE-CATHODE} = \frac{U_{MED}}{D_{ELEC_CHARGE_DOSE} \cdot Q_{WATER}} \quad (12)$$

$$R_{ANODE-CATHODE} = \frac{1}{\chi_{WATER_COND}} \cdot \frac{D_{ANODE-CATHODE_DIS}}{S_{T-ANODES}}$$

where:

- $D_{ELECTRIC_CHARGE_DOSE}$ – the dose of charge applied to the water;
- χ_{WATER_COND} – water conductivity;
- $D_{ANODE-CATHODE_DIST}$ – the distance between the electrodes;
- $S_{T-ANODES}$ – the anode surface.

Relation (12) shows that the anode surface (the anode and the cathode being of the sandwich type) is provided by relation (13):

$$S_{T-ANODES} = \frac{D_{ELECTRIC_CHARGE_DOSE} \cdot Q_{WATER} \cdot D_{ANODE-CATHODE_DIS}}{\chi_{WATER_COND} \cdot U_{MED}} \quad (13)$$

These parameters are used to calculate the value of the concentration of the substance reduced as a result of the electrochemical treatment, which is a value expressed by the following relation:

$$\Delta C = \eta_{REACTION} \cdot \frac{I_{med} \cdot A_{MOLAR} \cdot 1h}{Q_{TREATED} \cdot z_{VALENCY} \cdot F} \quad (14)$$

where

- $\eta_{R/C}$ – the efficiency of the reaction in the cell configuration;
- I_{MED} – the average current through the treatment cell;
- A_{MOL} – the molar weight of the treated substance;
- 1h – the one hour time;
- $Q_{TREATED}$ – the hourly water flow rate subjected to the treatment;
- $Z_{VALENCY}$ – the number of valency electrons involved in the reaction;
- F – the Faraday constant, equalling 96.485 C/mol.

THEORETICAL RESULTS OBTAINED BY THE TEMPLATE DEVELOPMENT

The introduction of the measured parameters, namely voltage and current, on the treatment electrochemical cell leads to the cell toughness and to the optimal surface of the anode, that is the necessary number of electrodes in its composition. Another theoretical result is the efficiency of the reaction calculated on the basis of relation (14) from the paper. Figure 7 presents the calculated concentration for the nitrates reduction according to the aforesaid relation, at such efficiencies of 1, 5, 10, 15, 20 and 25, meaning the average number of nitrate molecules that react till gaseous nitrogen in case of each electron pulled from the cathode that reaches the anode.

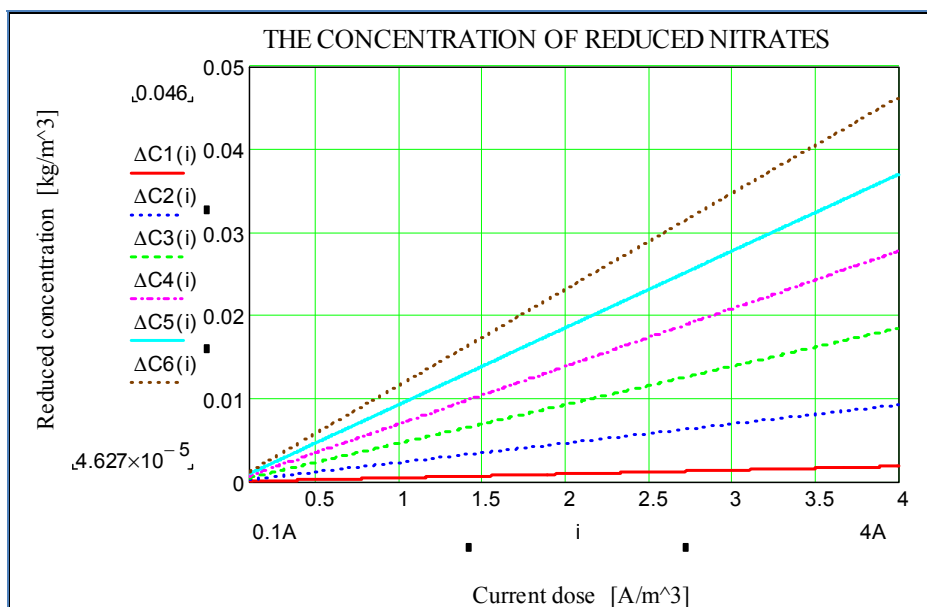


Fig. 7. The concentration of reduced nitrites subject to the current dose used

RESULTS

As follows are presented the experimental results concerning the nitrates reduction process and the chemical oxygen demand (the oxidability) by using electrochemical pre-treatment (EAOP).

The parameters of the water station were monitored between July 2012 and October 2013, at an average time frame of 45 days. The source of water used to obtain drinkable water is the surface water taken from the Repedea brook that flows nearby. The quality of the water (turbidity, pH, nitrates, ammonium, organic carbon etc.) from this source depends on the season and on the recent hydrological history. The aim for the introduction of the electrochemical pre-treatment stage in the flow of a water potabilisation station is to enhance the degree of safety of the water parameters obtained, by the fact that various pollutants that accidentally appear in the entrance water are removed, the other aim being to mitigate the necessary doses of reacting agents needed in the chemical treatment stage, notably when there are high floods on the source of water, when the water potabilisation station should normally be stopped. The water potabilisation station runs in the automated working mode, subject to the water consumption of that human settlement, by measuring the level of the drinkable water in the storing tank, which means that the water potabilisation station runs at constant parameters (flow rate, electrical power in the electrochemical pre-treatment stage, aeration rate, filtered water flow rate) till the maximum level pre-set is reached in the storing tank, after which it stops till the minimum level pre-set in the tank, when it resumes functioning. The parameters aimed at were turbidity, the chemical oxygen

demand (oxidability), pH, hardness, ammonium, nitrates, chlorides and (free and total) chlorine. All these parameters from the distribution network have to be according to the effective norms, but we deem two of them to be most important:

1. The concentration of the nitrates from the drinkable water should be less than 10 mg/l, so that it may be consumed risk-free by the entire population (the legal norm – Act 458/2002 – allows a 50 mg/l maximum value permitted for the nitrates, whereas for the children less than 3 years old the recommendation for the water used is not to exceed 10 mg/l).
2. The chemical oxygen demand (COD) (Oxidability) should be as little as possible, for the water to be biologically stable in the distribution network and not to call for large doses of biocide.

Table 1. *The reduction of the nitrates and of the oxidability obtained as a result of the electrochemical pre-treatment within the water potabilisation station of Romuli township, Bistrița-Năsăud county*

No.	NO ₃ concentration upon admission (mg/l)	NO ₃ concentration after electro-chemistry (mg/l)	COD-Mn concentration upon admission (mg/l O ₂)	COD-Mn concentration after electro-chemistry (mg/ O ₂)	ΔCA	ΔCCCO Mn	ΔCA / CAin	ΔCCCOMn/ CCCOMnin
1	6.12	2.9	2.49	0.35	3.22	2.14	0.53	0.86
2	10.19	5.08	1.12	1.12	5.11	0	0.50	0
3	13.73	10.85	2.2	1.56	2.88	0.64	0.21	0.29
4	12.5	9.6	4	2.56	2.9	1.44	0.23	0.36
5	8.6	4.26	2.1	0.5	4.34	1.6	0.50	0.761
6	9.85	5.4	1.7	0.72	4.45	0.98	0.45	0.58
7	11.07	7.73	2.8	1.1	3.34	1.7	0.30	0.61
8	12.53	8.69	2.5	1.4	3.84	1.1	0.31	0.44
9	10.82	6.15	2.9	1.6	4.67	1.3	0.43	0.45
10	11.23	5.52	3.2	1.9	5.71	1.3	0.51	0.41

As set out, the water potabilisation station and the electrochemical treatment stage run at constant parameters. Theoretically speaking, the nitrate reduction rate (ΔC) should be constant, which stands valid within the limit of the fluctuations due to the modifications in the composition of the substances dissolved in the water. The average of the reduced nitrates concentration is 4.05 mg/l and for the chemical oxygen demand (the oxidability) the average is 1.22 mg/l. The nitrate reduction in the electrochemical treatment stage during monitoring is displayed in Figure 8 and the oxidability one in Figure 9.

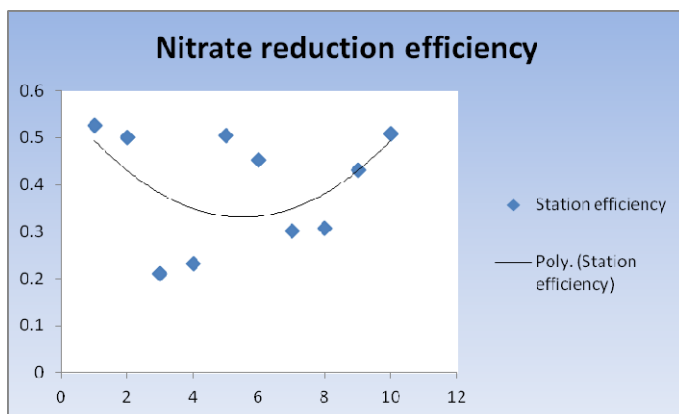


Fig. 8. Nitrate reduction in the electrochemical stage vs. their concentration upon admission

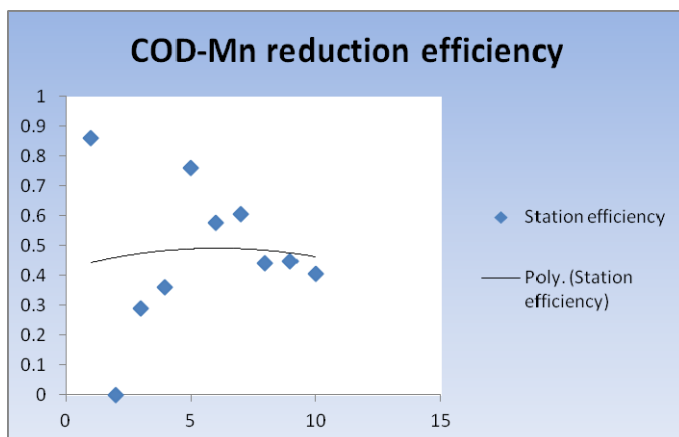


Fig. 9. Oxidability reduction in the electrochemical stage vs. its concentration upon admission

The nitrate reduction efficiency is calculated by means of the mean values (for nitrates), the resulting efficiency being 20 as an average (see previous section).

CONCLUSIONS

After monitoring the water treatment station, the results show that the electrochemical stage has got the following advantages:

- ▶ No chemical reacting agents are used in the treatment process, as they are generated on site. In addition, there are no toxic secondary reaction products.
- ▶ The stage is efficient in the potabilisation process by the fact that it largely contributes to the pollutant reduction.
- ▶ The energetic consumption vs. efficiency is low.

- ▶ The water will be chemically and biologically stable on account of the organic substances mitigation and of the reduction of the amount of biocide needed in the distribution system.

At the parameters measured within the experiment, that is nitrate reduction (g/m^3), water flow rate and medium current applied through the electrochemical cell, the measured concentration is 20 times higher than the one resulted from the template, even though a reaction yield of 1 (100 %) is calculated. This can be understood only if we accept that the reactions do not take place only at the surface of the electrodes (the anode and the cathode), but because of the high voltage between them (47 V) and of the voltage pulsations, an accelerated electron has got enough energy to participate in 20 successive reactions, as an average.

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