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EFFECT OF NON-THERMAL PLASMA ON MOLECULAR SPECIES FORMED IN WATER BASED SOLUTION

BY

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Abstract. This paper presents the experimental results for the nitrates and hydrogen peroxide production in one and more point to point NTP (Non-Thermal Plasma) reactors connected in series, from hydrodynamic and electric point of view, in water. The experimental set up has a modular structure with identical NTP electrical discharge reactors. A NTP reactor consists of two stainless steel tubes, as electrodes, placed in a glass tube, which generates a surface discharge to obtain non-thermal plasma. This approach allowed successive treatment of the same sample of water through one, two or three identical columns of NTP electrical discharge. The hydrogen peroxide concentration, nitrates concentration have been determined and the pH of treated water has been measured. In all configurations, the efficiency of the nitrates and hydrogen peroxide production in treated water in the NTP reactor(s) has been also calculated.

Key words: nitrates synthesis; hydrogen peroxide; cold plasma; surface discharges.

1. Introduction

The NTP technology has been used in order to produce molecular compounds in water or to remove organic pollutants from aqueous solutions (Burlica *et al.*, 2006).

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The reactive species generated by NTP discharges have been investigated as a potential treatment technology for gas phase pollution treatment, water pollution treatment, biological disinfection or gas reformation.

There are numerous advanced technologies, which use electrical discharges to induce electrochemical reactions in water, such as DC corona discharge, pulse corona discharge, gliding arc discharges (Burlica *et al.*, 2004, 2011).

Recently, the electrical discharge process, obtained between two electrodes placed face to face (point to point), has also been demonstrated to be effective for production of electrochemical active species in water. The electrical discharge reactor uses a high voltage pulse power supply, to produce an electrical gas phase discharge over a thin layer of water (Abdelmalek *et al.*, 2006).

Classical non-thermal plasma reactors used cylindrical vessels with two stainless steel electrodes placed in a narrow chamber where the water or liquid solution is treated.

The present study uses a similar system of surface discharge reactors (SDR). The non-thermal plasma reactor for environmental applications has a limited water flow rate treatment capacity.

Due to this fact, in order to obtain significant results for treated water, it was necessary to increase the number of the reactors working simultaneously. The non-thermal plasma reactors can work in series or in parallel. The goal of this paper is to emphasize the effects of serial configuration of NTP reactors on nitrates and hydrogen peroxide concentrations in surface discharge reactor (SDR).

The effects of the water flow rate and the number of one up three similar reactors connected in series on nitrates and hydrogen peroxide formation in water have been studied.

This paper presents experimental results for the nitrates and hydrogen peroxide production, in one and more point to point NTP reactors placed in series, from hydrodynamic and electric point of view in water, in the presence of a surface discharge that generates non-thermal plasma.

2. SDR Reactor's Experimental Set-Up

The experimental SDR reactors assembly it is a serial interconnection of three SDR modules (also called mini-reactors). A mini-reactor has two tubular electrodes (E1, E2) placed into a cylindrical glass vessel. In Fig. 1 is illustrated the SDR reactors assembly.

The tubular electrodes are connected to a power supply, so that may be obtaining different configurations for the SDR reactors (one, two or three reactors). The experimental set up is equipped with an injection nozzle with one port for the gas and one port for the liquid, so that the solution which was treated was sprayed directly into the non-thermal plasma zone, formed in the

gap between electrodes. The injection nozzle enhances the yield efficiency of production active species in the liquid sample. Spraying allows a larger contact area between the plasma column and treated solution, so the production of active species molecules, is more effective.

The three serial reactors with spray permit continuous treatment of the solution, a longer solution exposure to the action of plasma. The water flows from the first reactor R1 passing through reactors R2 and R3 to the outlet of the reactor.

The power supply was a pulse high voltage HVPS, which consist of a fly-back pulse generator that uses a high voltage transformer similar with a car ignition coil (automotive type), suited to produce electrical discharges from 50 Hz up to 500 Hz.

As shown in Fig. 1, the voltage has been measured using a high voltage probe (divider R_{d1}-R_{d2}) and the values of the current have been taken from a shunt resistor R_{sh}.

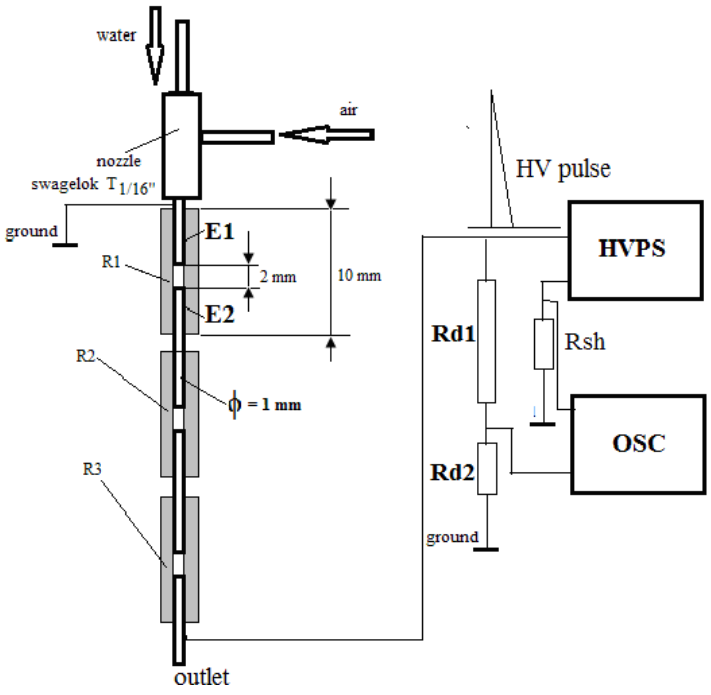

Fig. 1 − The SDR reactors assembly.

The voltage and the current waveforms have been analyzed using a digital oscilloscope (OSC) from LeCroy. The power of the discharge has been calculated by multiplying the voltage and the current waveforms of the discharge (Mededovic *et al.*, 2009).

The voltage and current waveforms are presented in Fig. 2, and have a 240 Hz frequency.

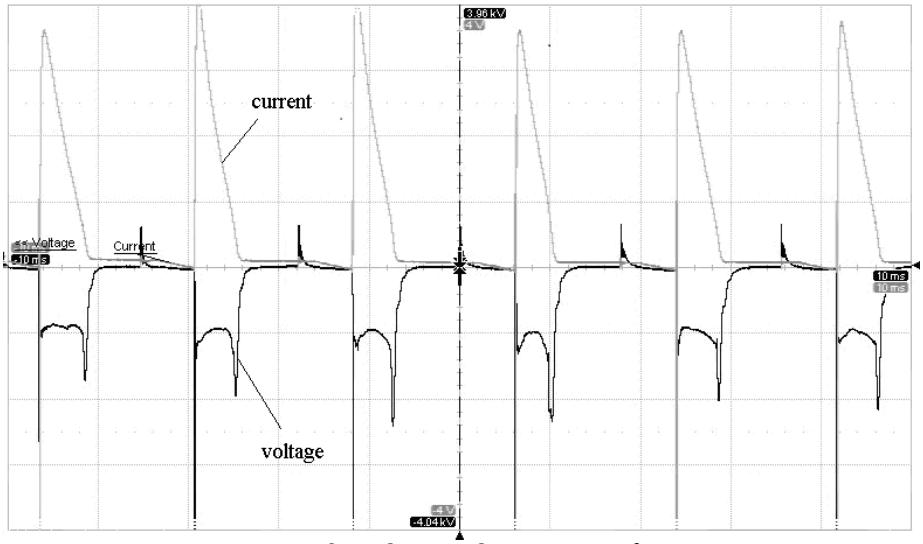

Fig. 2 − The voltage and current waveforms.

The discharge power was considered approximately 6W. The effects of the solution flow rates influence on the energy efficiency of active species generation were determined.

Measurements were conducted for one reactor or two and three reactors working in series as shown in Fig. 1, for different water flow rates and different powers of the discharge, with air as the working gas.

The most important reactive species formed in the SDR reactors in water are the hydrogen peroxide (H_2O_2), and the nitrates.

The concentration of hydrogen peroxide has been determined by a spectroscopic method using a titanium sulfate acid solution that leads to a yellow coloration of the water containing H_2O_2 with maximum absorbance at 410 nm.

For measurement of nitrates concentration, it has been used a NO_3 kit for environmental purposes. The brown colorization of the solution has been also measured using a Shimadzu UV-VIS spectrophotometer.

The Fig. 3 shows the evolution of the hydrogen peroxide concentration produced in water, in the SDR reactors assembly for air as working gas, with 1 l/min flow rate.

With air as carrier gas, nitrogen oxides form in the plasma, in gas phase. Nitrogen oxides can form nitrites in liquid phase which react with hydrogen peroxide to form nitrate (7). The nitrates affect the conductivity and pH through the formation of acids and ions in water and reduce the formation of hydrogen in gas phase and hydrogen peroxide in water droplets, reactions (5),…,(9). Ionization by electron/ion impact may occur by the reactions:

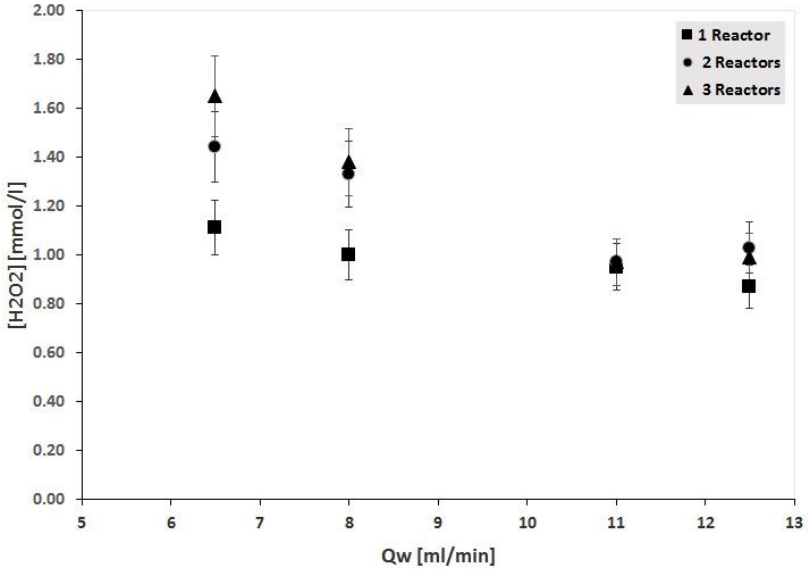

Fig. 3 − The evolution of the hydrogen peroxide concentration produced in water in the SDR reactors with air as working gas.

$$H_2O + e^- \rightarrow H^+ + OH^* + 2e^- \quad (1)$$

$$2H_2O + e^- \rightarrow H_3O^+ + OH^- + e^- \quad (2)$$

H_2O_2 may also form through an overall reaction such as:

$$2H_2O \rightarrow H_2O_2 + H_2 \quad (3)$$

H_2 and O_2 respectively, may also form through an overall reaction such as:

$$H_2O \rightarrow H_2 + ½\ O_2 \quad (4)$$

In the case of air and nitrogen as carrier gas the formation of NO_X occur by reactions:

$$N_2 + e^- \rightarrow 2N + e^- \quad (5)$$

$$O_2 + e^- \rightarrow 2O + e^- \quad (6)$$

$$N + O \rightarrow NO \quad (7)$$

$$NO + O \rightarrow NO_2 \quad (8)$$

The nitrogen oxides affect the pH and the conductivity of the water through the formation of ions and acids described by reactions (8):

$$NO_2 + OH \rightarrow HNO_3 \quad (9)$$

The highest concentration of (H_2O_2) has been obtained when all three reactors were working in series followed by the other two cases (see Fig. 3) and in all cases, for high water flow rates, the H_2O_2 concentration tends to a constant level.

The H_2O_2 is formed in water due to the electric impact by the reactions (Benstaali *et al*., 2002; Benstaali *et al*., 1998; Burlica *et al*., 2010). For the same energy of the electrons, the increasing, of water flow rate leads to a saturation of the reactive species formed in water, therefore a decreasing of H_2O_2 concentration (Wandell *et al*., 2014). The insignificant differences in the concentration of H_2O_2, for high water flow rates, can be explained by a higher dilution of the product.

Contrary to the evolution of hydrogen peroxide, the highest concentration of nitrates (NO_3) has been obtained for a single reactor, followed by the configurations with two or three reactors in series (see Fig. 4).

Similar with the case of H_2O_2 formation in water treated by non-thermal plasma, the concentration evolutions of nitrates have been determined and are showed in the Fig. 4.

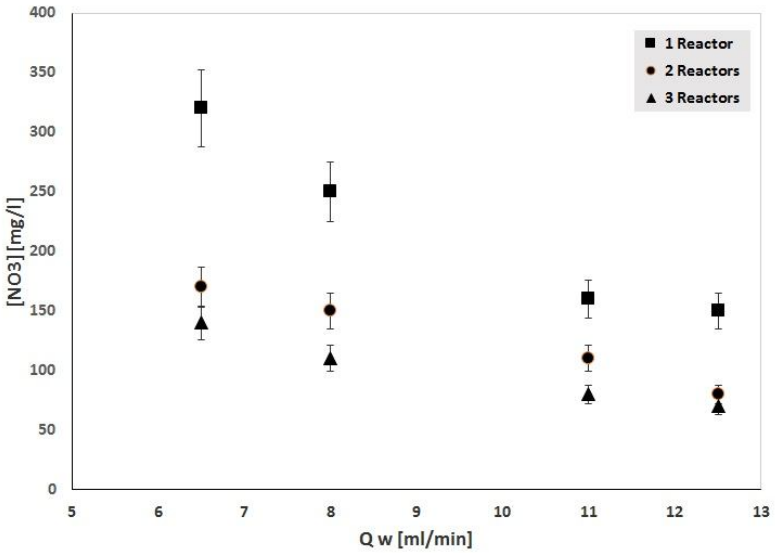

Fig. 4 − The evolution of the NO_3 concentration produced in water in the SDR reactors with water flow rate for air as working gas.

This can be explained by that the nitrates are the result of reaction between NO_2 and OH (Benstaali *et al*., 2002). The oxidation of N to NO_2 it is directly related with the oxygen in the air, the carrier gas, and in the water, so that the nitrogen reactive species concentration depends on the gas flow rate which it is constant in this case (Q_g = 1 l/ min), and the treated water flow rate (Kirkpatrick *et al*., 2005; Locke *et al*., 2009).

There was made some comparisons between the reactive species concentrations, for the relevant configuration one or three serial SDR (Fig. 5 and Fig. 6 respectively).

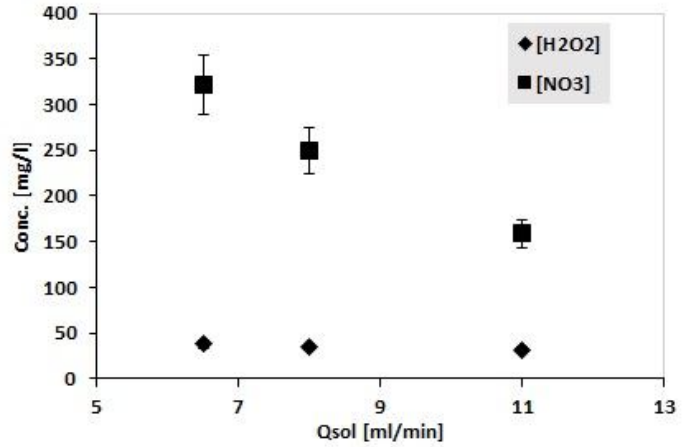

Fig. 5 – Reactive species concentrations level for one reactor SDR configuration with water flow rate for air as working gas.

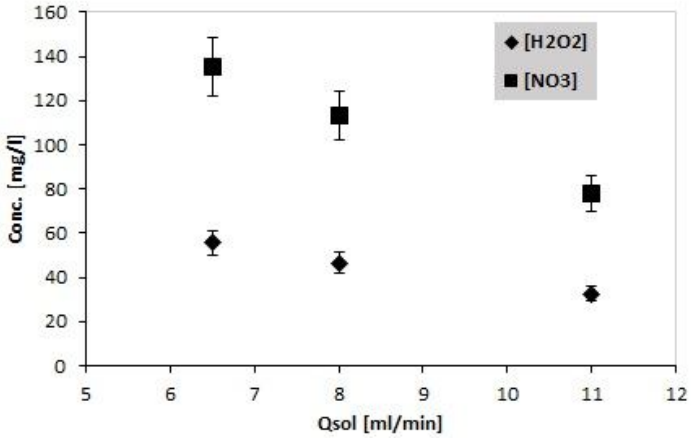

Fig. 6 – Reactive species concentrations level for three reactor SDR configuration with water flow rate for air as working gas.

It reveals a nitrates concentration 7 times higher than the peroxide concentration, for one reactor SDR configuration, respectively 2.5 times higher in the case with three serial SDR reactors.

Evolution of treated water pH in SDR reactors, shown in Fig. 7, fits with the evolution of the nitrates concentration. Since it is know that the pH is in close relation with the nitrates concentration the treated water in SDR reactors, the pH rises with the decreasing of NO_3 concentration.

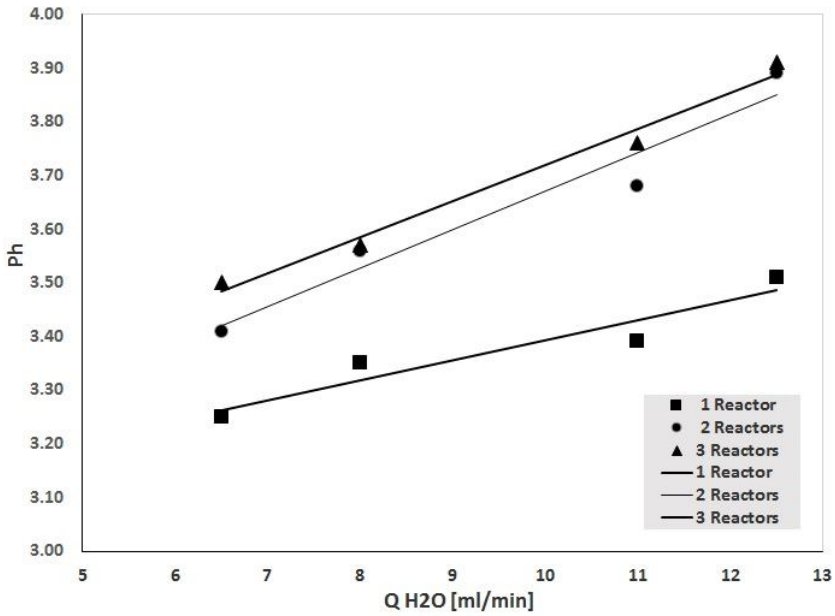

Fig.7 − The evolution of the pH in SDR reactors assembly.

To evaluate the reactor's efficiency for hydrogen peroxide production, were calculated the specific energy yields, EEf (g/kWh), for all reactor configurations with the relation:

$$\mathrm{EEf} = k\frac{[\mathrm{H_2O_2}]\mathrm{M_{H_2O_2}}\mathrm{Q_w}}{\mathrm{PV}} \times 60, \tag{10}$$

where: EEf is the specific energy, [g/kWh]; $[H_2O_2]$ – hydrogen peroxide concentration, [mM]; $M_{H_2O_2}$ – the molecular mass of hydrogen peroxide, [g]; Q_w – the water flow rate, [ml/min]; P – the power of the discharge, [W]; V – the volume of water treated in the reactor, [ml]; K – a constant that takes into account the volume of water treated (k = 0.8).

Also, to estimate the hydrogen peroxide production efficiency the electrical power has been measured for different values of the water flow rates. The results are presented in Fig. 8.

The measurements have revealed insignificant power variations with the water flow rates.

In Fig. 9 reflects the evolution of efficiency value for H_2O_2 production, for different water flow rates in SDR reactors assembly. It should be observed that similar with the evolution of H_2O_2 concentration, EEf shows the highest value for the case where all three reactors are working in series.

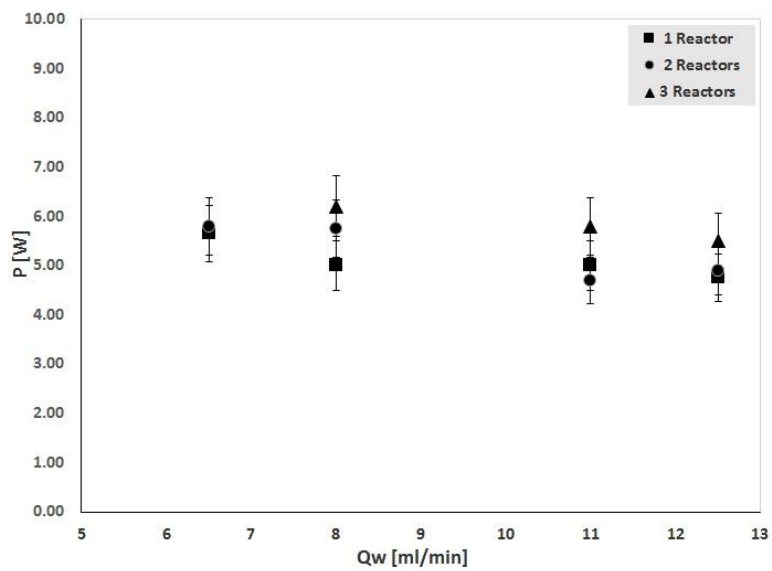

Fig. 8 − The evolution of the power for different water flow rates in SDR reactors assembly.

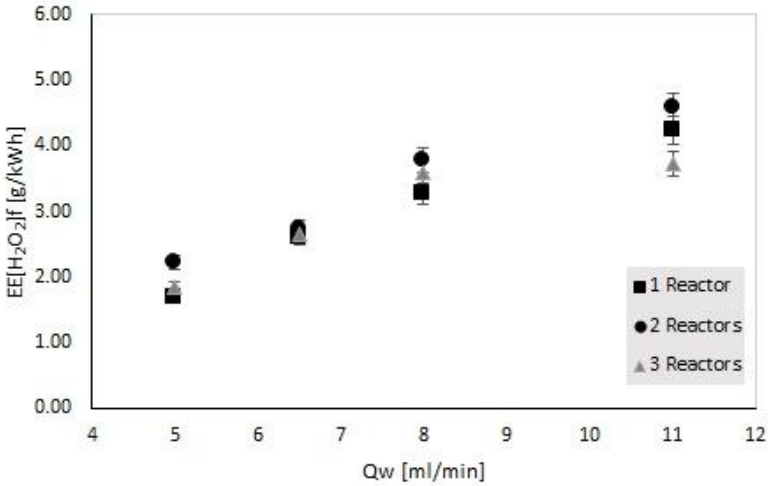

Fig. 9 − The evolution of the H_2O_2 efficiency production yield for different water flow rates in SDR reactors assembly.

The lowest values for H_2O_2 production efficiency were obtained for the case of one reactor operation. In all cases the production efficiency yield converges to 4 g/kWh for water flow rates higher than 11 ml/min. In the same way, have been calculated the NO_3 production yields, for different water flow rates, and the results are shown in Fig. 10.

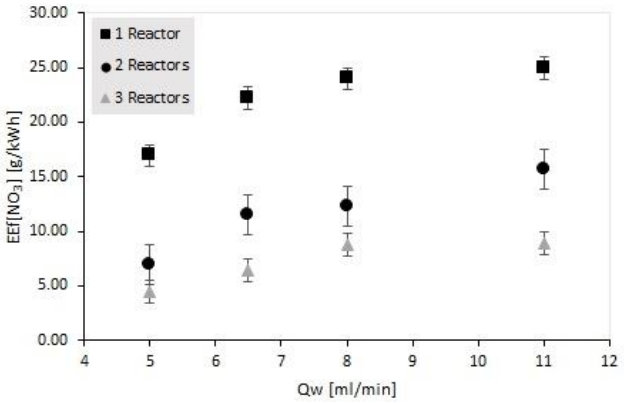

Fig. 10 − The evolution of the NO_3 efficiency production yield for different water flow rates in SDR reactors assembly.

The highest value of the NO_3 production efficiency are for the case with one SDR reactor and they are insignificant differences for different water flow rates (20 g/kWh – 25 g/kWh). Contrary, there are important differences between one reactor working and other two cases, two and three reactors working in series. For the same power, as in the previous case, the evolution of NO_3 production efficiency is constant.

Measurements were made for different frequencies, in order to calculate the efficiency production yield for both reactive species H_2O_2 and NO_3. The next figures (Fig. 11 and Fig. 12) present a comparison of efficiency production yield for different water flow rates in SDR reactors assembly, for two frequencies (Delair *et al.*, 2001).

In the paper were considered two frequencies (240 Hz and 360 Hz) in order achieve stable discharges in all reactors assembly.

As peroxide productions yields are better with three reactors configuration SDR, Fig. 11 shows efficiency production yield for these reactive, for different frequencies.

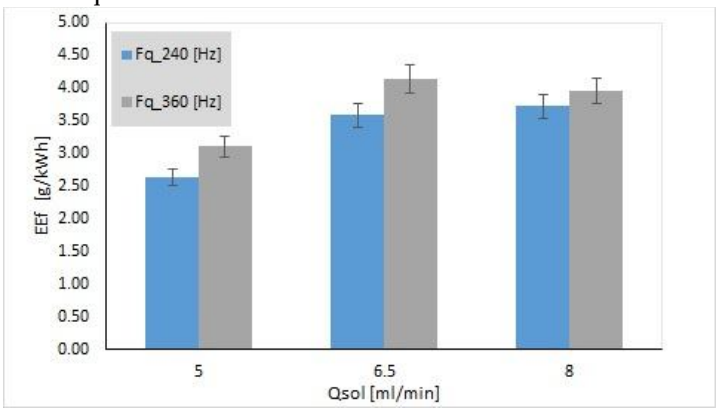

Fig. 11 − The evolution of the H_2O_2 efficiency production yield for different water flow rates and different frequencies in SDR reactors assembly- three reactors.

Similar in Fig. 12 are shown the evolution of efficiency production yield for nitrates, this time for one reactor configuration SDR.

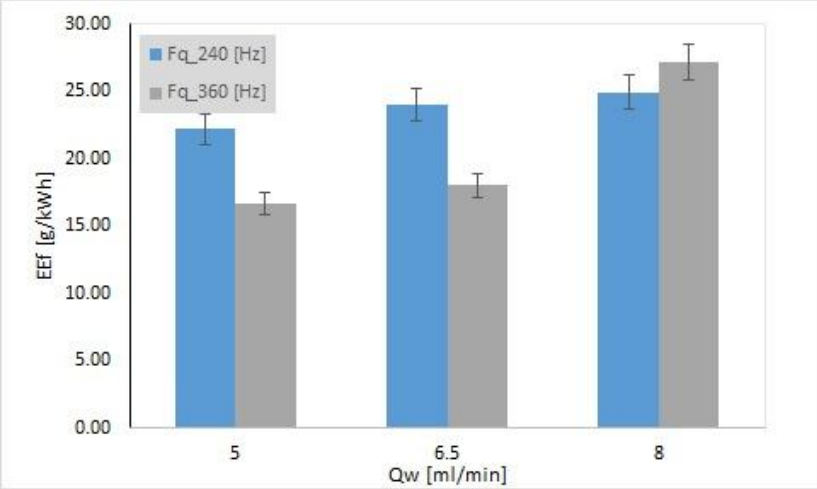

Fig. 12 − The evolution of the H_2O_2 efficiency production yield for different water flow rates, and different frequencies in SDR reactors assembly – three reactors configuration.

3. Conclusions

The generation of molecular reactive species, by NTP in SDR reactors, depends, significantly, on the electrical power of the discharge, the water flow rate and the configuration of the reactors.

The hydrogen peroxide concentration has the highest value when all three reactors are working in series, while the nitrates concentration is highest when only one reactor is used for the treated water.

The series configuration of SDR offer the possibility to control the concentration ratios of reactive species formed in treated water. The parameters are the treated water flow rate, the frequency and the number of reactor SDR configuration.

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EFECTUL PLASMEI NON-TERMICE ÎN FORMAREA SPECIILOR MOLECULARE ÎN SOLUȚII

(Rezumat)

Sunt prezentate, din punct de vedere hidrodinamic şi electric, rezultatele experimentale cu privire la producția de nitrați şi peroxid de hidrogen în apă la trecerea printr-unul sau mai multe reactoare de PNT (Plasmă Non-Termică), conectate în serie. Montajul experimental este o structură modulară, cu reactoare de PNT, identice. Un reactor PNT conține doi electrozi de oțel inoxidabil plasaşi într-un tub de sticlă, care generează o descărcare pe suprafață. Această abordare permite tratarea, aceluiaşi eşantion de apă, prin trecerea succesivă prin una, două sau trei coloane PNT identice. Au fost determinate concentrațiile de nitrați şi peroxid de hidrogen şi s-a măsurat pH-ul apei tratate. A fost de asemenea evaluată eficiența producției de nitrați şi peroxid de hidrogen, în apa tratată în reactoare PNT.