

# Alkaloid decomposition by DC pin-hole discharge in water solution<sup>\*</sup>

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**Abstract.** DC diaphragm discharge generated in a batch reactor was used to decompose two selected model alkaloids, caffeine and quinine in concentrations ranging from 10 to 50 ppm or 5 to 15 ppm, respectively. UV-vis spectrometry was utilized in evaluation of H<sub>2</sub>O<sub>2</sub> production during the process as well as degradation of caffeine. Fluorescence spectrometry was used for quantification of quinine. High rates of decomposition were reached in both cases in the anode part of the reactor. On the other hand, up to four times lower decomposition was observed in the cathode part. Total removal efficiency gained up to 300 mg/kWh for caffeine and 210 mg/kWh for quinine.

## 1 Introduction

One of the most challenging issues in environmental science is water purification. Wastewater treatment from industrial plants needs to be addressed. Smaller, but important issue is rising in household water contamination by a wide range of organic substances. Their removal could allow reuse of the water. One of possible treatments is utilization of discharges in water. This method belongs to advanced oxidation processes (AOPs), since it leads to production of various highly reactive radicals (e.g., OH·, H·, O·, HO<sub>2</sub>·) as well as molecular species (e.g., H<sub>2</sub>O<sub>2</sub>, H<sub>2</sub>·, O<sub>2</sub>·). Together with chemical species, strong electric field, UV and VUV radiation, heat and shock waves can be also produced by these discharges with synergetic effect on decomposition process [1]. Energy input density and composition of the environment have deciding effects on the relative importance of these direct and in-direct mechanisms [2]. These discharges can have broader field of use – not only water treatment, but also biomedicine, surface modifications and nanoparticle synthesis [3–6].

Caffeine is considered as an indicator of human pollution in the environment due to large amounts of coffee, tea and energy drinks consumption. Caffeine is widely metabolized by humans, the disposal of unconsumed coffee and caffeinated soft drinks being the predominant source of caffeine introduced into the wastewater treatment systems [7]. As a psychotropic agent, it has adverse effects on water and soil organisms and can influence the repair of

their DNA damage. Caffeine belongs to purine, methylxanthine alkaloids. Quinine was extensively used as an anti-malaria drug and against leg-cramps [8], but in Europe, its main use nowadays is as an additive in soft drinks with rising usage in cosmetics [9].

## 2 Experimental

A batch polycarbonate reactor (Fig. 1) with total volume of 4 L was used in the experiment. A nonporous diaphragm made from Shapal<sup>TM</sup>-M ceramics was mounted in the center. Diaphragm thickness was 3 mm, diameter of the orifice in its center was 1 mm. The orifice serves for increase of current density and electric field intensification [10] and discharge propagates from this spot towards both stainless steel electrodes, which were placed symmetrically to the diaphragm in the distance of 2 cm. In this configuration, plasma channels do not reach the electrode surface. Power was supplied in a DC regime with maximal voltage of 3 kV. Electrical parameters were continuously monitored by a Tektronix TDS1012 oscilloscope with Tektronix P6015 A high voltage probe. Passing current was monitored by a voltage drop at 5.13 Ω ballast resistor. Experiment was conducted for 60 min at average power reaching 135 W. Cooling system consisting of stainless steel containers filled with mixture of ice and water was renewed throughout the process and ensured temperature below 30 °C during the plasma treatment. Samples were taken every 10 min, with an extra one taken in the fifth minute to see the initial phase in more detail.

Solutions of the alkaloids in distilled water were freshly prepared in concentrations of 10, 25 and 50 ppm in the

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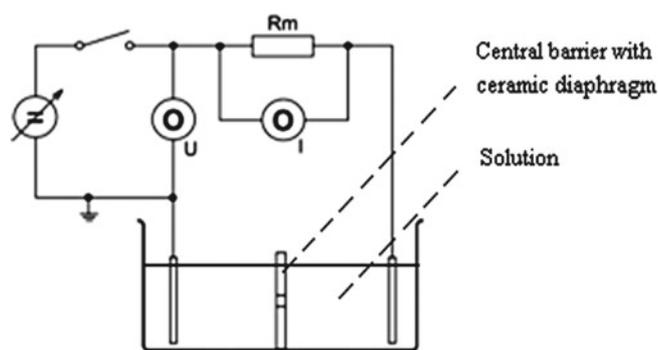


Fig. 1. Simplified reactor scheme.

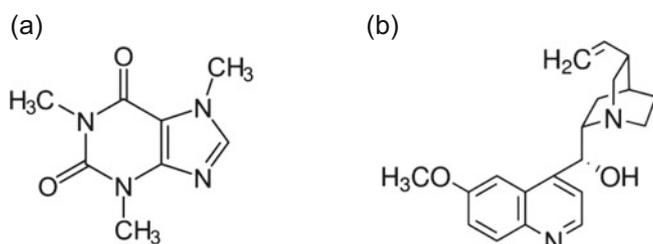


Fig. 2. Chemical structure of used alkaloids: (a) caffeine; (b) quinine.

case of caffeine; 5, 10 and 15 ppm in the case of quinine. Initial conductivity was set by NaCl to 400  $\mu\text{S}/\text{cm}$ . Sodium chloride is the most often used salt as a supporting electrolyte to adjust the initial conductivity of solutions [2, 11–13], even though it is known to affect the OH radical production [14]. The conductivity value was based on preliminary experiments testing three values (400, 750 and 1000  $\mu\text{S}/\text{cm}$ ), with the lowest reaching the best results (see Fig. 3). NaCl solution of the chosen conductivity was also used as a reference for hydrogen peroxide production measurements. This was determined by UV-vis spectroscopy of a yellowish complex formed by  $\text{H}_2\text{O}_2$  and titanium reagent, method was described in more detail in reference [15]. OH radical has been confirmed as the strongest oxidative species present in diaphragm discharge system by optical emission spectroscopy [16] and its measured intensities are independent on alkaloid concentration. Caffeine concentration was observed by UV-vis spectroscopy after recording a calibration line. Peak absorbance was read at 273 nm [17]. Quinine is supposed to be detectable by this method as well, but to avoid effects of re-emission, fluorescence spectroscopy of samples with added sulphuric acid was utilized; excitation wavelength of 350 nm, emission wavelength 450 nm [18].

An example of voltage and current waveforms recorded during discharge operation is displayed in Figure 3, which is typical for DC diaphragm configuration [16]. It is apparent that the discharge is not completely regular due to self-pulsing character with non-reproducible pulses as described in reference [10] in detail. For power input calculations, values averaged over 1 s were used. The waveforms are not affected by addition of alkaloid.

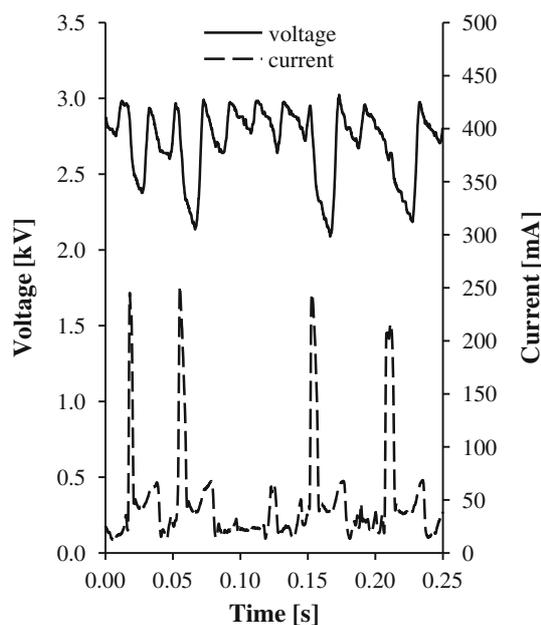


Fig. 3. Example of voltage and current waveforms of the discharge.

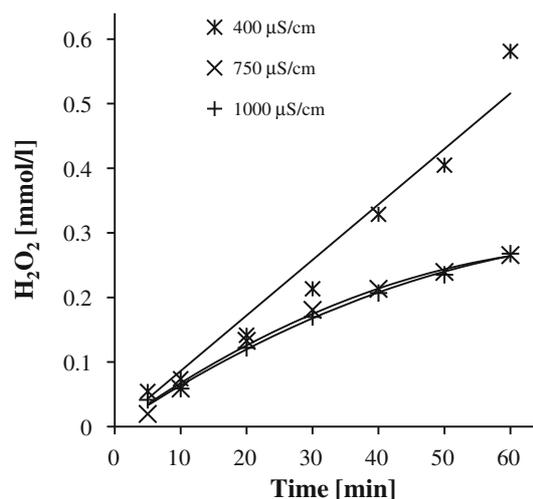


Fig. 4. Hydrogen peroxide production in reference solution with different initial conductivity, cathode part.

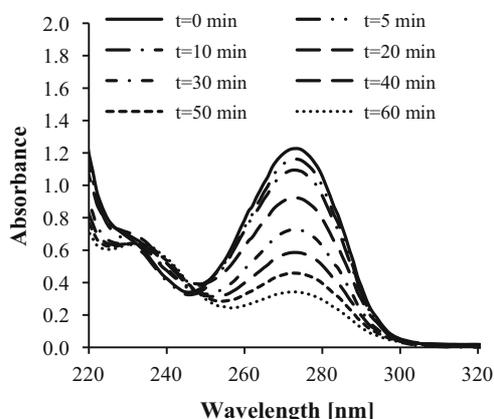
### 3 Results and discussion

Alkaloid decomposition is strongly dependent on the polarity of the reactor chamber. Production of hydrogen peroxide is more efficient in the cathode part, as in agreement with previous work [19]. Concentration of  $\text{H}_2\text{O}_2$  in NaCl reference solution is shown in Figure 4 in the cathode reactor chamber; for 750 and 1000  $\mu\text{S}/\text{cm}$ , the equilibrium values are reached in shorter time. Efficiency of  $\text{H}_2\text{O}_2$  production in 400  $\mu\text{S}/\text{cm}$  solution is about 340 mg/kWh. Further results are thus presented for solutions with initial conductivity set to 400  $\mu\text{S}/\text{cm}$ , if not stated otherwise.

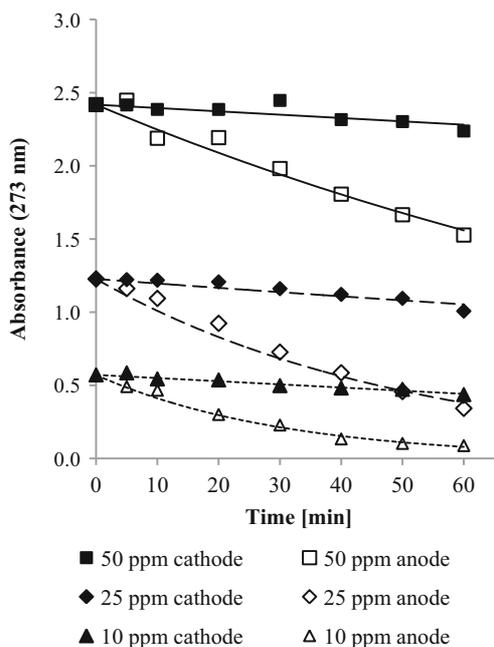
Production of hydrogen peroxide in solutions containing alkaloids is summarized in Table 1 together with data from the reference solution at 30th and 60th minute of

**Table 1.** Concentration of hydrogen peroxide generated during the experiment.

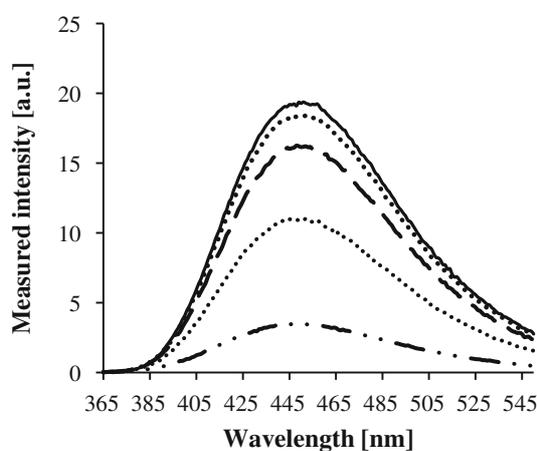
| Concentration [ppm] | Time [min] | H <sub>2</sub> O <sub>2</sub> concentration [μmol/l] |         | Time [min] | H <sub>2</sub> O <sub>2</sub> concentration [μmol/l] |         |  |
|---------------------|------------|--|---------|------------|--|---------|--|
|                     |            | Anode  | Cathode |            | Anode  | Cathode |  |
| Caffeine            |            |  |         |            |  |         |  |
| 10                  | 30         | 40   | 100     | 60         | 65   | 210     |  |
| 25                  |            | 30   | 100     |            | 50   | 210     |  |
| 50                  |            | 35   | 90      |            | 50   | 205     |  |
| Quinine             |            |  |         |            |  |         |  |
| 5                   | 30         | 50   | 65      | 60         | 100  | 210     |  |
| 10                  |            | 80   | 150     |            | 90   | 220     |  |
| 15                  |            | 70   | 130     |            | 115  | 235     |  |
| Reference solution  |            |  |         |            |  |         |  |
| –                   | 30         | 85   | 210     | 60         | 165  | 580     |  |



**Fig. 5.** Caffeine absorption spectra in anode part, initial concentration of 25 ppm.



**Fig. 6.** Caffeine peak absorbance in dependence on solution treatment time.



**Fig. 7.** Quinine fluorescence in time.

the experiment. In the cathode part with caffeine, there is about the same decrease in H<sub>2</sub>O<sub>2</sub> concentration regardless the concentration of the alkaloid and it is about a half of the value reached in the reference solution. In the anode part, the situation seems to be similar for lowest and highest caffeine concentrations (that is 10 and 50 ppm), with slightly lower results for 25 ppm of this alkaloid, reaching approx. one third of the reference value. However, the measured concentrations are close to the detection limit of 10 μmol/L; therefore the difference might not be reproducible. For quinine, smaller difference in H<sub>2</sub>O<sub>2</sub> concentration is detected. The decrease in hydrogen peroxide concentration is more pronounced after longer treatment time.

Conductivity increase was observed in both polarities after the experiment. In cathode part, rise of 80–200 μS/cm was measured in all cases; in anode part the increase is even higher, in range of 200–550 μS/cm. Based on values measured in final solutions, pH of tested solutions rises in cathode part up to values of 10.7 from the initial state of 5.5–7.5, while in the anode part,

**Table 2.** Summary – degradation of caffeine and quinine.

| Initial caffeine concentration | Decrease of caffeine absorbance in anode part |      | Decrease of caffeine absorbance, cathode part  |      | Total removal efficiency ( $\pm 15$ mg/kWh) |
|--------------------------------|---|------|--|------|---|
| [ppm]                          | [%]   | [mg] | [%]  | [mg] | [mg/kWh]                                    |
| 10                             | 92  | 16.6 | 25   | 4.5  | 160   |
| 25                             | 73  | 33.0 | 15   | 6.9  | 310   |
| 50                             | 30  | 27.4 | 7  | 6.2  | 260   |
| Initial quinine concentration  | Decrease of quinine absorbance in anode part  |      | Decrease of quinine absorbance in cathode part |      | Total removal efficiency ( $\pm 10$ mg/kWh) |
| [ppm]                          | [%]   | [mg] | [%]  | [mg] | [mg/kWh]                                    |
| 5                              | 98  | 9.2  | 20   | 1.9  | 85  |
| 10                             | 85  | 15.6 | 22   | 4.0  | 150   |
| 15                             | 87  | 24.4 | 11   | 3.1  | 210   |

acidification takes place with pH decreasing down to 3.2, mainly because of reactions on the electrode surface [16, 20]. This differentiation can take place when no buffer is used and the initial pH of the solution is approximately neutral. The pH values are stable after treatment for at least several days in closed container. The pH change can affect the decomposition of caffeine significantly. The degradation path may be similar to the one proposed in reference [21] for two different values of pH together with pH dependent degradation products. The ring opening at the double bond of the purine structure (in right-hand cycle of the molecule structure in Fig. 2a) is probable as a first step of the process.

UV absorption spectra recorded for 25 ppm of alkaloid in the reactor anode part are shown in Figure 5 for the spectral range of 220–320 nm. This decay represents a typical result obtained also with other starting concentrations. The data suggest exponential decay. These values are corrected to the measured background data for solution without caffeine. Time evolution of maximal peak absorbance is comprehended in Figure 6.

In the cathode part, the caffeine degradation is negligible and does not exceed 20%, while reaching only approx. 8% for the most concentrated solution.

In the anode part, up to 85% of the caffeine is degraded during the treatment. These values are based on the decrease of absorbance at the wavelength of the maximal peak. However, presence of degradation products that would absorb in the same region cannot be excluded, even though a very little peak shift can be observed in the measured spectra.

For quinine, fluorescence measurements give better and more reliable results compared to UV-vis spectrometry. Typical fluorescence spectra corrected to both source and detector properties can be seen in Figure 7 for initial concentration of 15 ppm of quinine in the solution with initial conductivity of 400  $\mu$ S/cm.

Efficiency of caffeine and quinine degradation based on spectroscopic measurements is summarized in Table 2.

## 4 Conclusion

Practically full decomposition of alkaloids was reached in both cases in anode part of the reactor. Using

spectroscopic measurements, there is a chance of bias of the recorded data by similarly absorbing (by-)products. Peak shift was more apparent in UV-vis spectroscopy of quinine, this method was therefore complemented by fluorescence measurements. Highest removal efficiency was reached in the case of caffeine solution with initial concentration of 5 ppm (over 300 mg/kWh), with highest percentage of caffeine being decomposed in the least concentrated solution with initial concentration of 10 ppm. For quinine, the best percentage of decomposition based on peak fluorescence was reached in the least concentrated solution of quinine (initial concentration of 5 ppm). On the other hand, best total removal efficiency is in the highest concentrated solution (15 ppm), suggesting the limitation of the discharge effects by the available alkaloid. Strong polarity dependence of the decomposition of both alkaloids was shown. This is tied to the changes in pH in a diaphragm discharge configuration. Maximum of only 25 or 20% decomposition was reached in the cathode part for caffeine and quinine, respectively, where the pH becomes basic during the treatment. This is in the opposite of what could be drawn from the production of hydrogen peroxide, which in the used configuration is significantly higher in the negative polarity. Its concentration decreases by about half compared to the reference solution, implying consumption of OH radicals or  $H_2O_2$  for the degradation of the given alkaloid. Further experiments will be carried out for detail study of degradation products using HPLC-MS.

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## References

1. P. Lukes, Ph.D. thesis, Institute of Plasma Physics, AS CR, Prague, 2001
2. B.R. Locke, M. Sato, P. Sunka, M.R. Hoffmann, J.-S. Chang, *Ind. Eng. Chem. Res.* **45**, 882 (2006)
3. S. Ognier, D. Iya-Sou, C. Fourmond, S. Cavadias, *Plasma Chem. Plasma Process.* **29**, 261 (2009)

4. T. Belmonte, A. Hamdan, F. Kosior, C. Noël, G. Henrion, *J. Phys. D: Appl. Phys.* **47**, 224016 (2014)
5. A.I. Maksimov, I.K. Naumova, A.V. Khlyustova, *High Energy Chem.* **46**, 212 (2012)
6. R. Joshi, R.-D. Schulze, A. Meyer-Plath, J.F. Friedrich, *Plasma Processes Polym.* **5**, 695 (2008)
7. D. Tang-Liu, R.L. Williams, S. Riegelman, *J. Pharmacol. Exp. Ther.* **224**, 180 (1983)
8. H.C. Diener, U. Dethlefsen, S. Dethlefsen-Gruber, P. Verbeek, *Int. J. Clin. Prac.* **56**, 243 (2002)
9. R. Gatti, M.G. Gioia, V. Cavrini, *Anal. Chim. Acta* **512**, 85 (2004)
10. Z. Kozakova, F. Krcma, M. Vasicek, L. Hlavata, L. Hlochova, *Eur. Phys. J. D* **69**, 100 (2015)
11. P. Hoffer, Ph.D. thesis, Czech Technical University in Prague, Prague, 2014
12. P. Bruggeman, J. Degroote, J. Vierendeels, Ch. Leys, *Plasma Source. Sci. Technol.* **2**, 17 (2008)
13. P. Bruggeman, Ch. Leys, *J. Phys. D: Appl. Phys.* **5**, 42 (2014)
14. Ch.-H. Liao, S.-F. Kang, F.-A. Wu, *Chemosphere* **5**, 44 (2001)
15. E. Vyhnanekova, Z. Kozakova, F. Krcma, A. Hrdlicka, *Open Chemistry* **13**, 218 (2014)
16. Z. Kozakova, Habilitation thesis, Brno University of Technology, Brno, 2011
17. T. Atomssa, A.V. Gholap, *Afr. J. Pure Appl. Chem.* **5**, 1 (2011)
18. J.E. O'Reilly, *J. Chem. Education* **52**, 610 (1975)
19. Z. Stara, F. Krcma, *Acta Physica Slovaca* **55**, 515 (2004)
20. Z. Kozakova, M. Nejezchleb, F. Krcma, I. Halamova, J. Caslavsky, J. Dolinova, *Desalination* **258**, 93 (2010)
21. R. Rosal, A. Rodriguez, J.A. Perdigon-Melon, A. Petre, E. Garcia-Calvo, M.J. Gomez, A. Aguera, A.R. Fernandez-Alba, *Chemosphere* **74**, 825 (2009)