Decomposition of caffeine by DC pin-hole discharge in water solutions

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Abstract: Decomposition of caffeine as a model alkaloid by a DC diaphragm discharge is studied. Production of H$_2$O$_2$ during the discharge and decomposition of caffeine was evaluated by UV-VIS spectrometry starting with initial concentration of 10, 25 or 50 ppm of alkaloid. Decomposition is practically complete after 1 hour for the lowest caffeine concentration, with better energy efficiency for two higher concentrations (300 mg/kWh).

Keywords: pin-hole discharge, diaphragm, alkaloid, caffeine, decomposition.

1. Introduction

Wastewater treatment poses a challenging issue in environmental science. Household wastewaters include a wide range of organic substance that should be removed to allow reuse of the water. One of possible ways is treatment of the water by discharges in water or water-based solutions. These belong to so-called Advanced Oxidation Processes (AOPs), as they lead to production of various highly reactive species including radicals (e.g. OH·, H·, O·, HO$_2$·) and molecular species (e.g. H$_2$O$_2$, H$_2$, O$_2$). Together with chemical species, strong electric field, UV and VUV radiation, heat and shock waves can be also produced by these discharges [1]. The relative importance of these direct and in-direct mechanisms is strongly dependent on the energy input density to the system as well as on the composition of the reacting environment [2]. There are various configurations that can be utilized in order to achieve discharge in a liquid. They are often based on densification of the electric field on a tip of an electrode. In the case of pin-hole discharge, this process takes place in a small orifice in a dielectric barrier, separating two electrode chambers. This configuration allows measurement under both polarities at the same time. Generally, electrohydraulic discharges are utilized not only in water or wastewater treatment [3], but can be also applied for nanoparticle synthesis, in biomedicine or for surface modifications [4]–[6].

Caffeine is considered as an indicator of human pollution in the environment due to large amounts of coffee, tea and energy drinks consummation. Caffeine is widely metabolized by humans, the disposal of the unconsumed coffee and caffeinated soft drinks being the predominant source of caffeine introduced into the wastewater treatment system [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.

2. Experimental

A batch reactor (Fig. 1) with total solution volume of 3.6 litres was used. A ceramic nonporous diaphragm (Shapal$^{TM}$-M) was placed in the centre of the reactor, with a small orifice (diameter of 1 mm, thickness 3 mm). In this orifice connecting both discharge chambers, plasma discharge with corona-like or glow discharge characteristics can be ignited under certain conditions. Stainless steel electrodes were placed symmetrically to the central barrier at the distance of 2 cm from barrier so plasma did not reach to their surface. A DC power source with voltage supply up to 2 kV was used for the discharge generation. Electrical parameters were continuously monitored using a Tektronix TDS1012 oscilloscope with Tektronix P6015A high voltage probe. Passing current was monitored by voltage drop at 5.13 $\Omega$ ballast resistor. Total time of solution treatment was 60 minutes with sampling time of 10 min., with extra sample taken after the first five minutes of the discharge operation. Average power supplied to the system was 135 W. Cooling of the system was mediated by stainless steel containers with ice-water mixture that was renewed during the experiment, otherwise thermally sensitive compounds (such as hydrogen peroxide) might decompose.

Solutions containing 10, 25 or 50 ppm of the alkaloid (Fig. 2) were prepared fresh for each measurement, with initial conductivity set to 400 $\mu$S/cm by NaCl. This value was chosen after pilot experiments with the selected diaphragm – hydrogen peroxide production was studied for 400, 750 and 1000 $\mu$S/cm solution; with the best results for the lowest conductivity. The NaCl solution of this conductivity was used as a reference for hydrogen peroxide measurement.

UV-VIS spectroscopy was utilized to study the hydrogen peroxide production by absorbance
measurements of complex formed with a specific titanium reagent (method described in more detail in [8]).

Calibration line of caffeine absorption was recorded as well. Absorption spectra were also used to follow the decomposition of the studied compound. An absorption peak value was read at 273 nm, which represents the strongest absorbance of caffeine molecule in the UV-VIS region.

Fig. 2. Caffeine structure.

3. Results

The experiments revealed strong dependence of alkaloid decomposition on polarity of the reactor chamber. As proved before [9], production of hydrogen peroxide is more efficient in the cathode part. The measured concentrations can be seen in Fig. 3. For 750 and 1000 µS/cm, the equilibrium values are reached at lower values.

Fig. 3. Hydrogen peroxide production in solutions with different conductivity.

Hydrogen peroxide production in the solution of caffeine with different initial alkaloid concentration is shown in Table 1 together with data for the reference solution for 30 and for 60 minutes of the discharge operation. Maximum hydrogen peroxide concentration was – as expected – in the reference solution, where there was no extrinsic compound that could withdraw the molecules for its decomposition. The efficiency of H₂O₂ production in this case was about 240 mg/kWh.

In the cathode part, the consumption of hydrogen peroxide for the caffeine decomposition appears to be approximately the same regardless the initial concentration of the alkaloid. The concentration of H₂O₂ measured in this electrode part was about half of the value reached in the reference solution in all cases. 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 alkaloid. However, the measured concentrations are close to the detection limit, therefore the difference might not be reproducible.

Table 1. Hydrogen peroxide concentration

<table>
<thead>
<tr>
<th>Caffeine (ppm)</th>
<th>H₂O₂ [mmol/l]; cathode; t = 30 min</th>
<th>H₂O₂ [mmol/l]; cathode; t = 60 min</th>
<th>H₂O₂ [mmol/l]; anode; t = 30 min</th>
<th>H₂O₂ [mmol/l]; anode; t = 60 min</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.21</td>
<td>0.58</td>
<td>0.08</td>
<td>0.16</td>
</tr>
<tr>
<td>10</td>
<td>0.15</td>
<td>0.27</td>
<td>0.04</td>
<td>0.06</td>
</tr>
<tr>
<td>25</td>
<td>0.15</td>
<td>0.27</td>
<td>0.02</td>
<td>0.03</td>
</tr>
<tr>
<td>50</td>
<td>0.14</td>
<td>0.25</td>
<td>0.05</td>
<td>0.06</td>
</tr>
</tbody>
</table>

Spectra recorded for 25 ppm of alkaloid in the reactor anode part are shown in Fig. 4 for the spectral range of 220 – 250 nm. Caffeine decomposition in time with starting concentrations of 10, 25 or 50 ppm is shown in Figs. 5, 6 or 7, respectively. The data suggest exponential decay. These values are corrected to the measured background data for solution without caffeine.

In the cathode part, the caffeine degradation is negligible and does not exceed 20 %, while reaching only approx. 8 % for the highest 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 peak wavelength. However, degradation product that would absorb in the same region can be expected, absolute concentrations will be detected by HPLC-MS.

In the pin-hole configuration, pH changes are different at each polarity, too. In the anode part, the pH in NaCl solution falls down to about 3, while there is practically symmetrical increase in the cathode part to values about 9 [10]. This differentiation can take place when no buffer is used and the initial pH of the solution is approximately neutral. This can affect the decomposition of the alkaloid. The degradation path may be similar to the one proposed in [11] for two different values of pH together with possible degradation products. Detailed study of the decomposition products using HPLC-MS technique is in progress. Efficiency of caffeine degradation based on spectroscopic measurements is summarized in Table 2.

Fig. 4. Recorded spectra in time; initial c = 25 ppm.
Table 2. Decomposition of caffeine based on absorbance values

<table>
<thead>
<tr>
<th>Initial caffeine concentration [ppm]</th>
<th>Decrease of caffeine absorbance value in anode part [%]</th>
<th>Decrease of caffeine absorbance value in cathode part [%]</th>
<th>Total removal efficiency [mg/kWh]</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>85</td>
<td>24</td>
<td>144</td>
</tr>
<tr>
<td>25</td>
<td>72</td>
<td>18</td>
<td>300</td>
</tr>
<tr>
<td>50</td>
<td>37</td>
<td>8</td>
<td>295</td>
</tr>
</tbody>
</table>

4. Conclusion

The best results with caffeine decomposition by a diaphragm discharge were achieved for the least concentrated solution (initial concentration of 10 ppm). In this case, the decomposition reached about 85% in anode part and about 25% in cathode part. Different pH in each electrode part given by the diaphragm configuration may play the role in the caffeine decomposition process. Hydrogen peroxide concentration measured in caffeine solutions decreases about one half compared to the reference solution, implying consumption of OH radicals or H$_2$O$_2$ for the degradation of the compound. Further detailed study of the decomposition products using HPLC-MS technique is in progress, as well as comparison of the caffeine degradation results with decomposition of other alkaloids.

5. Acknowledgement

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6. References