Diaphragm Discharge in Liquids: Fundamentals and Applications

František Krčma, Zdenka Stará, Jana Procházková
Faculty of Chemistry, Brno University of Technology, Purkyňova 118, 612 00 Brno, Czech Republic
E-mail: krcma@fch.vutbr.cz

Abstract. Paper describes results of our research on DC diaphragm discharge creation in water solutions of electrolytes from the viewpoint of its principles, properties and applications. The thermal theory of discharge ignition in bubbles of evaporated solution has been confirmed by both high speed camera and sound records. Static current-voltage characteristics revealed a significant dependence of discharge breakdown on the solution conductivity. Determined breakdown parameters lay in the range of 900–1300 V and 40–100 mA, respectively, for NaCl solution conductivity varying from 150 to 1300 µS·cm⁻¹. Time resolved electrical characteristics showed a simultaneous appearance of current, voltage and sound oscillations as well as a light emission. Plasma diagnostics by optical emission spectroscopy confirmed formation of reactive species (hydroxyl, hydrogen and oxygen radicals) and excitation of metallic atoms presented in the solution. Moreover, rotational temperature was calculated from the obtained OH spectrum. Experiments focused on the diaphragm discharge applications are outlined in the paper. Results of hydrogen peroxide production, organic dye decomposition and treatment of humic acid solutions are compared from the viewpoint of experimental conditions.

1. Introduction
Electrical discharges generated in liquids are in an intensive research focus for a few last decades. Many scientists deal with various types of discharge configuration and several kinds of applied high voltage. The most frequent electrode geometry used for discharge creation is point-to-plane or coaxial [1-3] together with the application of DC pulsed voltage of about 20 kV. Other experiments in liquids have been carried out with capillary [4] or diaphragm discharge [5]. Discharge generation using AC [6] or RF [7] voltage is also possible as well as a hybrid system with one electrode above water surface [8].

The diaphragm discharge, presented in this paper, is formed in reactor containing two electrodes separated by diaphragm in which the pin-hole is made. The DC high voltage is applied on the electrodes. Consequently, the high electric field between two planar electrodes is concentrated just in the pin-hole. If the electric field is sufficiently high, the discharge is formed in the bubbles of evaporated water in and/or near the pin-hole made in the diaphragm. Two kinds of plasma streamers of the opposite polarity are created in two parts of reactor separated each other by the insulating wall containing diaphragm, as it is shown in Fig. 1. The difference in properties of plasma channels propagating towards the electrodes is not only in their shape, but foremost in the velocity of electrons accelerated by the applied electric field and the energy dissipation in channels [9]. For better understanding of streamer propagation, there is an analogy between the generation of the diaphragm
discharge and corona discharge in point-to-plate electrode configuration. The pin-hole behaves as a point electrode of both polarities each one for two separated parts of the reactor. In the part with the plane cathode, electrons are accelerated towards the positively charged pin-hole (like to the point anode) and the remaining positive space charge at the end of the streamer is further enhancing the electron velocity. Thus created streamers represent long plasma channels. This form of plasma is called in text as the “positive discharge”. Contrary to this, electrons propagating from the negatively charged pin-hole (like from the point cathode) towards the plane anode are dragged by the positive space charge and their velocity decreases. The final shape of negative streamers is represented by shorter bush-like plasma channels having a spherical shape and we called them the “negative discharge” [10], (see Fig. 1).

Figure 1. Simplified scheme of diaphragm discharge formation: 1 – anode, 2 – cathode, 3 – negative plasma channels, 4 – positive plasma channels, 5 – electrolyte solution.

Electrical discharges belong to the so-called Advanced Oxidation Processes (AOP’s) that can be utilized for different applications. Their main importance is in the formation of highly reactive species (especially radicals) and production of UV radiation. Subsequently, initiated processes lead to the excitation, ionization and decomposition of particles and compounds contained in treated solution. Thus methods based on electrical discharges are often used in water treatment, surface modification or other applications.

2. Experimental

2.1. Discharge reactor
A specially constructed batch discharge reactor was used in the study of diaphragm discharge formation, properties and applications (Fig. 2) [11]. The main chamber was divided by an insulating wall into two spaces with one electrode (stainless steel or platinum) in each part. A changeable diaphragm made of inert material (PET, thickness of 0.25 mm) was fixed in the centre of the barrier. Both electrode spaces were connected by a small orifice in the diaphragm (initial diameter of 0.2 mm) where the discharge was ignited. DC high voltage source providing constant power supply up to 300 W was used. Water solutions containing supported electrolyte (NaCl, NaBr, NaNO₃, Na₂HPO₄·12H₂O or Na₂SO₄; their concentration varied according to the needed conductivity) were split per 1.5 liters into both parts of the reactor. Addition compounds such as organic dyes (textile: Direct Red 79, Direct Blue 106, Direct Yellow 29, food: Acid Blue 74, Acid Red 14; initial concentration of 12-30 mg·l⁻¹) or humic acids (HUMIN-P 775, initial concentration of 35 mg·l⁻¹) were added when degradation effects of the discharge were investigated. Both mixing and cooling systems were used to keep experimental conditions homogeneous and constant during the whole process.
2.2. Plasma diagnostic and analytic methods
Breakdown moment of the diaphragm discharge as well as its further behaviour was studied from electrical characteristics (static and time resolved). For that purpose, two and four channel digital oscilloscopes Tektronix TDS 1012B and TDS 2024B were used. Signals of discharge voltage (using the HV probe Tektronix P6015A), current, sound and emitted light were recorded. Plasma diagnostics was carried out by optical emission spectroscopy using the spectrometer Jobin Yvon Triax 550 in the range of 200–700 nm. Subsequently, rotational temperature was calculated from recorded OH radical spectra.
Detection of hydrogen peroxide generated by the discharge was done by colorimetric method using a specific titanium reagent [12]. In the case of decomposition experiments, concentration of dyes and humic acids was determined by absorption spectroscopy. Moreover, fluorescence spectroscopy was carried out to obtain a humic index of treated humic solutions [11].

3. Results and discussion

3.1. Breakdown and formation of diaphragm discharge in electrolyte solution
According to the thermal theory of discharge initiation in liquid [10], breakdown appears in bubbles of evaporated water solution which is strongly heated by the applied electric field. To confirm this hypothesis in our device, series of photos from high speed camera was correlated with current and sound time resolved records. Obtained pictures showed on the bubble formation [13]. Moreover, determined amplitudes of sound closely corresponded to recorded current peaks (see Fig. 3). This sound effect could be related to the discharge creation represented by a rapid current increase.
3.2. Diaphragm discharge electric characteristics

Ignition of DC diaphragm discharge in electrolyte solutions highly depended on the initial conductivity of the liquid phase. Too low conductivity (adjusted by concentration of dissolved electrolyte) meant low amount of charge carriers and subsequently, weak current was insufficient for liquid heating and bubble creation. At the higher conductivities, the system resistance was lower and current was higher. Also the voltage drop in liquid was significantly smaller and thus the discharge breakdown was observed at lower voltage and higher current. Based on these assumptions, breakdown parameters (mean voltage and current) were determined from VA characteristics measured in electrolyte solutions of initial conductivity 50–1400 µS·cm⁻¹. A typical VA characteristic of the diaphragm discharge in the NaCl solution is shown in Fig. 4. The moment of the discharge ignition is represented by the breakpoint of the VA curve (about 1100 V in this case). Further, the comparison obtained for two electrolytes (NaCl and KCl) is given in Fig. 5. It is obvious that in the middle range of tested conductivities (300–1300 µS·cm⁻¹) breakdown voltage was slightly decreasing with the increasing conductivity while breakdown current significantly increased with more or less the same trend in both electrolytes [13]. The extreme values of tested conductivities had a remarkable effect on breakdown appearance foremost due to the consequent discharge instability.

![Figure 4](image1.png)

**Figure 4.** Typical VA characteristic of the diaphragm discharge in the 4 mM NaCl solution.

![Figure 5](image2.png)

**Figure 5.** Breakdown values of voltage (left) and current (right) as a function of solution conductivity. Comparison is given for two electrolytes (NaCl and KCl).

An example of characteristics time evolution obtained in NaCl solution during the breakdown moment is demonstrated in Fig. 6. Increasing the input power into the reactor, voltage and current were slightly
increasing and no light emission was recorded until the breakdown moment. Getting over this value, intensive peaks of current appeared together with light flashes while voltage mean magnitude remained more or less constant.

**Figure 6.** Time resolved characteristics of diaphragm discharge. Given result represents simultaneous records of voltage, current and light signal during the breakdown moment in 4 mM NaCl solution.

### 3.3. Plasma optical diagnostics

Plasma properties were measured by optical emission spectroscopy in the range of 200–1000 nm. Strong emission of OH radicals as well as other reactive species (H and O atomic lines) was determined in the spectrum. Emission spectrum of metallic atoms coming from the dissolved electrolyte was observed, too. The overall spectrum of the diaphragm discharge ignited in the NaCl electrolyte is demonstrated in Fig. 7. Obvious emission of OH radicals as well as H atoms was identified. Moreover, strong emission of sodium atomic lines was recorded.

**Figure 7.** Emission spectrum of diaphragm discharge in 4 mM NaCl solution (input power of 120 W).

Fig. 8 shows the dependence of sodium atomic line intensity on the concentration of NaCl electrolyte in the solution. The result that the Na intensity was directly proportional to the Na concentration in the solution can be applied as a determination method in the analytical chemistry [14]. A weak signal of Na atomic lines at very low NaCl concentration resulted from the unstable discharge generation at these conditions. Integral emission intensity of OH radicals remained constant over the whole tested concentration range. Additionally, rotational temperature was calculated from OH spectrum and its obtained value was 500–900 K depending on the solution conductivity, applied power and electrolyte kind.
3.4. Examples of diaphragm discharge applications

Diaphragm discharge generated in water solutions by constant DC voltage can be applied in more fields of utilization. The possibility of an excitation source for determination of metallic atoms in the solution has been already mentioned above [14].

Next useful process studied by our works is production of hydrogen peroxide [15]. Fig. 9 demonstrates its formation in both electrode spaces of the reactor. It is evident that electrode polarity played a significant role in this process. Concentration of hydrogen peroxide increased almost linearly in time in both parts of the reactor. However, remarkably higher production was achieved in the part with the negative electrode, i.e. were positive plasma streamers were propagated. This result is in a good agreement with studies focused on the pulsed corona treatment where the positive corona discharge was also more effective in $\text{H}_2\text{O}_2$ formation than the negative one [10]. Hydrogen peroxide concentration reached after one hour of the experiment was about 1.8 mmol·l$^{-1}$ in the cathode space and only 0.3 mmol·l$^{-1}$ in the anode space (i.e. six times lower).

Formation of hydrogen peroxide by DC diaphragm discharge was influenced by several important parameters. Especially input power supplied into the reactor from the HV source determined the final peroxide production. Fig. 10 (left) represents the final $\text{H}_2\text{O}_2$ concentration produced after one hour of the discharge as a function of the input power. It is clear that the increasing power enhanced hydrogen
peroxide production with the more or less directly proportional tendency. These results are presented for the cathode space, only, because H$_2$O$_2$ production in the anode space was negligible.

Figure 10. Left: Final H$_2$O$_2$ concentration after one hour discharge treatment in the cathode space as a function of the input power (4 mM NaCl). Right: Final concentration after one hour discharge treatment in the cathode space as a function of the initial solution conductivity (260 W).

Next parameter effecting hydrogen peroxide formation was the presence of supported electrolyte. Such electrolyte was added into the treated solution for the adjustment of a particular conductivity value. Generally, the DC diaphragm discharge is very sensitive to the system conductivity – it is not possible to create or maintain a stable discharge in the pin-hole if solution conductivity is either very low or too high [11]. That is why an electrolyte addition was necessary for proper conductivity adjustment. Concentration of supported electrolyte determined solution conductivity. Two selected electrolytes (NaCl and Na$_2$HPO$_4$) providing solution conductivity in the range of 100–1400 µS·cm$^{-1}$ were used for hydrogen peroxide formation. Obtained results, represented by the final H$_2$O$_2$ concentration after one hour discharge treatment, are shown in Fig. 10 (right). It is obvious that in both cases production of hydrogen peroxide reached a particular maximum at a conductivity value different for both electrolytes. If NaCl was used as the supported electrolyte, the highest H$_2$O$_2$ production was achieved in the solution with conductivity around 400 µS·cm$^{-1}$. On the other hand, maximal hydrogen peroxide production in the Na$_2$HPO$_4$ solution was obtained at conductivity of about 900 µS·cm$^{-1}$. Going beyond these conductivity values (to lower or higher magnitudes), formation of hydrogen peroxide significantly decreased. The comparison of produced hydrogen peroxide in these two electrolytes revealed only a slightly higher production in the Na$_2$HPO$_4$ solution than in NaCl. The lower amount of determined H$_2$O$_2$ could be caused by peroxide decomposition by chlorine radicals formed in the NaCl solution by the discharge.

Further application of DC diaphragm discharge is in the field of water treatment. Decomposition of various, especially organic, pollutants is effective due to the simultaneous effect of reactive species (OH radicals), UV radiation emitted by the discharge and electrochemical reactions taking place on electrode if constant DC voltage is applied.

This work focused on the removal of organic dyes commonly used in the textile industry (Direct Blue 106 and Direct Red 79). Decomposition of these dyes in both reactor spaces is represented by the graph in Fig. 11. It is evident that the electrode polarity played again a significant role in this process. However, the degradation process was more effective in the anode space on contrary to the hydrogen peroxide generation. The decomposition rate went more or less exponentially in the anode space and the dye was decomposed from 60 % after 40 minutes of the discharge treatment [16]. On the other hand, dye removal in the cathode space went almost linearly and became only about 10 % after the same time. The substantial effect of electrochemical oxidation on the positive electrode is probably the main reason of the decomposition difference in both reactor parts.
Figure 11. Decomposition rate of the dye Direct Blue 106 (left) and Direct Red 79 (right) achieved by the diaphragm discharge in both electrode spaces (input power of 170 W, 4 mM NaCl).

As the study of hydrogen peroxide formation revealed the significant dependence of the process on the discharge conditions, a series of analogous experiments was carried out to determine these effects on the dye destruction. The obtained dependence of the dye Direct Red 79 removal on the input power is given in Fig. 12 (left). Results are presented for both electrode polarities. As in the case of hydrogen peroxide, the increasing input power significantly enhanced the dye decomposition as well. This enhancement was observed in both reactor parts. However, the process was more sensitive to the power input in the cathode space.

Figure 12. Left: Final decomposition rate of the dye DR79 after 40 minutes of discharge treatment in both electrode spaces as a function of the input power (4 mM NaCl). Right: Final decomposition rate of the dye DR79 after 40 minutes of discharge treatment in the anode space as a function of the initial solution conductivity of four electrolytes (260 W).

Influence of electrolyte kind and its concentration providing definite solution conductivity was investigated on four different inorganic salts (NaCl, NaBr, NaNO₃ and Na₂HPO₄). Obtained results represented by the final relative concentration of the red dye in the solution are given in Fig. 12 (right). From the figure it is evident that both electrolyte kind and solution conductivity significantly effected the dye decomposition during the discharge treatment. In all electrolytes (except Na₂HPO₄) degradation process reached a particular maximum represented by a minimal DR79 concentration at a particular conductivity value. Obtained results were almost similar at NaCl and NaBr solutions and moreover, the decoloration process was remarkably higher than in other electrolytes. The most
effective degradation was determined at conductivity in the range of 500–600 µS·cm⁻¹. On the other hand, the dye removal in the Na₂HPO₄ electrolyte was almost negligible at all tested solution conductivities. The decomposition difference observed in various electrolytes could be also caused by a different pH value before and after discharge treatment. The first three electrolytes (NaCl, NaBr and NaNO₃) provided a neutral initial pH of the solution that significantly decreased to the strong acidic conditions in the anode space during the discharge as a result of electrochemical reactions on the anode. However, Na₂HPO₄ electrolyte adjusted a base solution conditions that remained at higher pH values during the whole experiment. We assumed that acidic conditions of the solution stimulated the dye decomposition process.

Besides organic dyes, humic substances were selected for the diaphragm discharge application in water treatment. Commercial mixtures of humic acids were dissolved in demineralised water to simulate a natural solution of polluted water coming for example from floods. Prepared solutions were treated in the diaphragm reactor in the same way as organic dyes (i.e. with the addition of supported electrolyte and under the same experimental conditions). Obtained samples were analysed by UV-VIS spectroscopy to observe colour changes and by fluorescence spectroscopy to determine the ratio of aromatic and aliphatic components in the mixture. Generally, humic acids have complicated structures containing both long chained hydrocarbons as well as aromatic components. Their destruction and removal from water should lead to the minimum amount of aromatic substances. The ratio of aromatic and aliphatic matters is known as the index of humification (HIX) [17]. It can be calculated from the mutual ratio of the emission intensity at 470 and 400 nm obtained from the fluorescence spectrum excited at 288 nm. Table 1 summarizes these HIX values achieved before and after plasma treatment of humic solution containing two supported electrolytes (NaCl and Na₂SO₄). Moreover, the table compares the result of samples with corrected pH to the samples without any modification. It is obvious that in all cases the plasma treatment of humic solutions lead to the decrease of humification index. That meant the enhancement of aliphatic components and decrease of aromatic substances [17, 18]. However, correction of pH during the discharge treatment (it means its balancing at neutral pH level) strongly decreased the final humic removal. This was another demonstration of the significant pH influence on the degradation process in the diaphragm discharge treatment. Comparing both electrolyte used, sodium sulphate gave better results than the NaCl solution.

<table>
<thead>
<tr>
<th>Table 1: Humification index (HIX) before and after discharge treatment in two electrolytes.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Samples – corrected pH</td>
</tr>
<tr>
<td>NaCl</td>
</tr>
<tr>
<td>initial</td>
</tr>
<tr>
<td>final – anode</td>
</tr>
<tr>
<td>final – cathode</td>
</tr>
<tr>
<td>Na₂SO₄</td>
</tr>
<tr>
<td>initial</td>
</tr>
<tr>
<td>final – anode</td>
</tr>
<tr>
<td>final – cathode</td>
</tr>
</tbody>
</table>

4. Conclusion
Paper describes diaphragm discharge generated using constant DC voltage up to 4 kV in water solutions containing supported electrolytes. Presented text is divided on two main parts focused on the discharge creation itself and its properties and further on the application of the discharge, especially in the field of water treatment.

The thermal theory of the discharge initiation in the solution was confirmed and both static and time evaluated characteristics were presented. The substantial influence of electrolyte (both its kind and concentration) was discussed.

Plasma diagnostics by OES determined rotational temperature in the range of 500–900 K as well as the formation of the main radicals (OH, H, O).
Application of the discharge in the dye and humic acid decomposition, hydrogen peroxide formation and metallic atoms determination was suggested, too. Influence of experimental conditions (input power, electrode polarity) and solution properties (electrolyte kind, solution conductivity and pH) was demonstrated. Generally, it was found that all tested parameters had an important impact on the degradation process as well as on the formation of hydrogen peroxide. Increasing input power enhanced the processes. Generation of hydrogen peroxide was more effective in the cathode space while decomposition process went more effectively on the anode side. However, this effect was closely related to the solution pH and its change during the treatment.

Acknowledgments
This work was supported by the Czech Science Foundation, projects No. 202/03/H162 and No. 202/07/P371.

References