Effects of Diaphragm Discharge in Water Solutions Containing Humic Substances

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Abstract. Preliminary results of research focused on the applications of DC diaphragm discharge in water solutions containing humic substances are presented in this paper. Diaphragm discharge investigated by this work was created in the reactor using constant DC high voltage up to 2 kV that gave the total input power from 100 to 200 W. Presented work investigated decomposition of humic substances by the electric discharge in the dependence of discharge conditions (electrode polarity) as well as solution properties (electrolyte kind, pH). Especially substantial effect of pH on humic acid decomposition has been observed when acidic conditions stimulated the degradation process. Absorption spectroscopy in UV-VIS region together with fluorescence spectroscopy has been used for the detection of changes in humic solutions. Index of humification was calculated from obtained fluorescence spectra and a significant decrease of aromatic components in the humic mixture was determined during the discharge treatment.

1. Introduction
Water pollution is one of the biggest problems of present world. Among these pollutants humic substances are often contained that are otherwise find in soils, ponds and sediments. In the last years, floods are becoming a more frequent phenomenon due to climate changes and tree felling in the surrounding of water flows. Thus, humic acids are more frequent in surface water. Humic acids are not toxic like organic wastes from factories, but they limit water use for purposes in households. In general, humic substances are mixtures of mainly aromatic compounds of high molecular weight (up to 10 000 mass units). Water treatment can be generally realized by three methods: physical, chemical and biological. These methods have disadvantages – insufficient efficiency, production of another ecologically or health risk substances and the resources are too expensive. Therefore interactions of organic compounds with electric discharges are investigated recently. Effects of electric discharges on decomposition of organic dyes [1] or other organic reactants (phenol [2], 4-chlorophenol, etc.) were examined and confirmed. This method is based on the transformation of high electrical energy into an aqueous phase and generation of highly reactive species (hydroxyl radicals, hydrogen peroxide, ozone, etc.) [3]. These species are able to oxidize organic matter and such reactions could lead to destruction of organic pollutants dissolved in water. The main goal is not the full humic acids decomposition but at least the breaking of aromatic ring is necessary for further biological purification.

In this work, degradation of humic substances dissolved in water was investigated by diaphragm discharge, which was generated in a very small orifice in dielectric diaphragm placed between two
planar electrodes. Effects of electrolyte kind and pH value were examined in this work. Aromatic and aliphatic content in humic acid mixture was compared by humification index calculated from fluorescence spectra.

2. Experimental setup

![Figure 1](image.png)

Figure 1. Scheme of the discharge reactor: 1 – diaphragm with pinhole, 2, 3 – electrodes, 4, 5 – cooling boxes.

Diaphragm discharge studied in this work was generated in a batch reactor (figure 1) divided into two parts – cathode and anode space [4]. The DC non-pulsed HV source giving the voltage of about 2 kV was used for the discharge generation. General parameters describing experimental set-up are listed in Table 1. Each part of the reactor contained 2 litres of treated solution containing commercial humic acid HUMIN-P 775 dissolved in demineralised water and electrolyte (NaCl, Na₂SO₄). Solution pH was primary adjusted by the electrolyte kind. As pH significantly changed during all experiments [5], its value was either modified by acid/base adding or it was let without any correction. Analyses of quality changes of treated solutions were carried out by spectroscopic methods (UV-VIS and fluorescence spectroscopy).

| Table 1. General parameters of experiments |
|-------------------------------------------|
| Discharge power                          | 200 W                  |
| Electrodes                               | planar stainless steel |
| Dielectric diaphragm                      | PET, thickness 0.25 mm |
| Pinhole                                  | central, diameter 0.25 mm |
| initial solution conductivity             | 500 μS cm⁻¹             |

3. Results and discussion

First attempts with humic acid decomposition by DC diaphragm discharge have already revealed a remarkably higher HA destruction in the anode space of the reactor [4]. Moreover, a significant decrease of pH value in the anode space and an increase of pH value in the cathode space were detected during the discharge treatment. Therefore we came up to attempts focused on pH value maintenance at a neutral value by the method of dropping the definite amount of surfactant (acid or base) to the both parts of the discharge reactor during the reaction.

3.1. Change of pH value during the treatment

At first, it was detected how pH value turned during the decomposition in the dependence on the used electrolyte kind (figure 2). Changes of pH value for sodium sulfate and sodium chloride were almost coincident. It decreased from the value of approximately 6.7 to 3.6 in the anode space and increased to
9.8 in the cathode space after 20 minutes of the discharge treatment. 1M H₂SO₄, HCl and NaOH solutions were used as surfactants because of their ion identity with used electrolytes. Injection step of surfactant was determined on every 2 minute.

![Chart](image)

**Figure 2.** Time evolution of pH value for NaCl and Na₂SO₄ electrolytes by the diaphragm discharge (input power 200 W, initial conductivity 500 µS·cm⁻¹).

### 3.2. Correction of pH value

Experiments with humic matters were carried out by using two different electrolytes – NaCl and Na₂SO₄ (figure 3). In both cases low degradation efficiency of humic acid in the anode space was observed, while in the cathode space a slight degradation improvement was determined in comparison with experiments without pH value correction. It could be assumed that the maintenance of neutral pH value during discharge treatment was inconvenient because it generally lead to lower degradation. On the other hand, it is possible to assume that the low pH value stimulated the degradation process.

![Chart](image)

**Figure 3.** Effect of pH value correction on humic acid decomposition by the diaphragm discharge (initial HA concentration: 35 mg l⁻¹, electrolyte: 4 mM NaCl (left), 2 mM Na₂SO₄ (right), corrected pH 6.7, initial conductivity: 500 µS cm⁻¹).

### 3.3. Analysis – humification index (HIX)

Initial and final samples were analysed by fluorescence emission spectrophotometry, whereas exciting wavelength was adjusted on 280 nm (figure 4). From the ratio of the emission intensity values at 470 and 400 nm, humification index (HIX) was calculated, which indicated the mutual content of aromatic and aliphatic components in the mixture (Table 2). HIXs pointed to decrease of aromatic part at final samples from anode space. Molecules of humic acid were decomposed however, created up to now non-identified by-products distorted the absorption spectra of humic acid.
Figure 4. Fluorescence emission spectra of samples before and after treatment with correction pH (initial HA concentration: 35 mg l^{-1}, electrolyte: 4 mM NaCl (left), 2 mM Na₂SO₄ (right), corrected pH 6.7, initial conductivity: 500 μS cm⁻¹, input power: 200 W).

Table 2: Humification index (HIX).

| Samples – corrected pH | HIX | Samples – uncorrected pH | HIX |
|------------------------|-----|--------------------------|-----|
| NaCl                   |     |                          |     |
| initial                | 1.47| initial                  | 1.47|
| final – anode          | 1.28| final – anode            | 0.55|
| final – cathode        | 1.31| final – cathode          | 1.27|
| Na₂SO₄                 |     |                          |     |
| initial                | 1.44| initial                  | 1.44|
| final – anode          | 0.64| final – anode            | 0.37|
| final – cathode        | 1.06| final – cathode          | 1.40|

4. Conclusion
Commercial humic acids dissolved in water solution were treated by diaphragm discharge. The changes of quality were observed by the absorption spectroscopy and fluorescence spectroscopy. The presented work gave the results about the effect of pH value on the decomposition of humic acid mixture. Processes of degradation became more efficient at lower pH values (acidic medium). Fluorescence analysis provided not so misrepresenting results than absorption analysis (UV-VIS). This discrepancy and finding of ideal analytical method will be an object of our further study as well as a detail analysis of final degradation products.

Acknowledgements
This work has been supported by the Czech Science Foundation, project No. 202/07/P371 and by the Czech Ministry of Education, Youths and Sports, Research Plan No. MSM0021630501.

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