Pulsed positive corona in water

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Abstract

High voltage pulses are applied to an underwater point-to-plane corona discharge. The energy content of the corona discharge pulses is measured and it is found that it is for a large part determined by the pulsed power supply. The shape of the current indicates that tap water behaves resistive and deionized water discharge-like. Conversion of phenol is measured to be higher in tap water than in deionized water. Addition of oxygen at the anode increases the conversion rate. A conversion of 70% of phenol starting at 2 mg/L is observed with 30 mJ pulses at 50 Hz during 30 minutes, during this period the heating of the water is less than 2 K..

Introduction

New technologies are required either to prevent or to solve waste water-problems. Prevention is of course the best way but many environmental problems already exist and need to be solved. Conventional technologies are not always adequate because in some cases they only displace the problem (e.g. carbon or fabric filters) or it is damaged by the waste (toxic organic compounds may destroy biofilters, for example). Therefore research is started in search of such new methods for water treatment [1-3]. Strong, oxidative methods are required which decompose molecules to harmless substances such as CO_2, H_2O and minerals. Examples of such processes are treatment with O_3, H_2O_2 and/or UV radiation, supercritical oxidation [1,2] and non-thermal plasmas [3].

The non-thermal plasmas are distinguished in two categories: electron beams and atmospheric gas discharges. Application of these processes for gas treatment is well known [3], but there are also possibilities to use them in water purification and desinfection [3-5]. There is, however, very little fundamental knowledge of pulsed discharges in water. Removal of phenol is demonstrated in [4], but not even the energy consumption is determined. The necessity of a cooling bath suggests, however, a high power input. In our laboratory, our experience with pulsed discharges in gas [6] enables us to measure the electric power input into corona pulses under water and the breakdown of phenol.

Electrical measurements

Pulsed corona is created under water in a glas cup with a content of 0.5 liter. On the bottom is a metal plate or wire which is used as the cathode. The anode is a metal wire with a sharp point. In the case of oxygen addition a hypodermic needle is used, where the oxygen is bubbled through. The pulses are created from a charged capacitor of 55 pF which is switched by a spark gap. The circuit and the procedures for voltage and current measurement is similar to the one we used for the corona reactor with gas flow [6].

The first measurements have been performed in tap water. Fig. 1 shows the voltage and current for two cases of the applied voltage, i.e. 15 and 30 kV (on the DC supply that charges the capacitor). The point-plane distance of the electrodes is 18 mm in this case. Fig. 1a shows a current peak during the rise of the voltage. This is the capacitive current as is shown by a computer analysis where the voltage derivative is calculated ($I=C\cdot dV/dt$). The decay of the current follows the shape of the voltage, so it is a resistive current. The value of the resistance is in the order of 50 kΩ. Above 15 kV light emission is seen at the anode and a ticking sound is heard with each pulse. In Fig. 1b the voltage and current are given for the case of a 30 kV pulse. A similar capacitive current peak is observed initially. Then, after 200 to 300 ns a second current peak shows up. This second peak comes simultaneously with light emitted from the region near the anode point which was detected with a photomultiplier. This proves that a discharge is created in the water. The charge and energy of a pulse are also calculated by a computer program by integrating the current and the product of current and voltage respectively, where the capacitive current is subtracted.

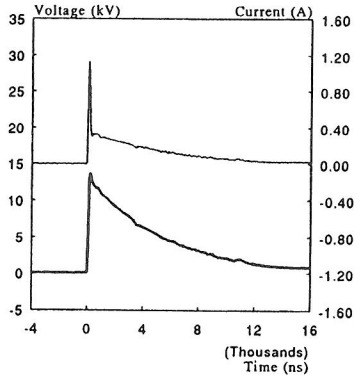

Fig. 1a. The voltage (lower, thick line) and current (upper, thin line) of a 15 kV pulse in water, i.e. below discharge inception. The current peak at t=0 is capacitive.

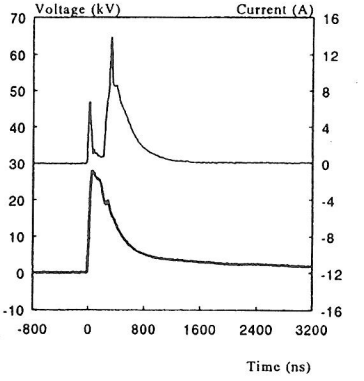

Fig. 1b. The voltage and current (as in Fig. 1a) of a 30 kV pulse in water. The corona discharge current starts at t≈200 ns.

The second case, shown is Fig. 2, is pulsed corona in deionized water. It can be seen in Fig. 2a that the current behaves very different compared to tap water (conditions 30 kV supply voltage and 18 mm gap distance). The current consists of a munber of spikes, correlated in time with light emission pulses. On photographs it is seen that the discharge paths in deionized water are less numerous but much longer than the ones in tap water. There appears to be no current proportional to the voltage, so the deionized water does not show a resistive behaviour. At low voltage its resistance was measured to be about 10 times higher than for tap water. It was noticed, however, that the energy per pulse in deionized water was not very reproducible, which turned out to be due to an aging effect. Fig. 2b shows the voltage and current of a pulse in deionized water after 3 hours of pulsing at 50 Hz repetition rate. Besides the current sparks there is now also a base current which has the shape of the decreasing voltage pulse. The DC conductivity is also lowered considerably at this time.

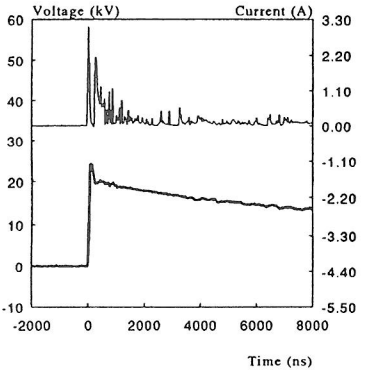

Fig. 2a. Voltage (lower line) and current (upper line) of pulsed corona in deionized water at 30 kV supply voltage and 18 mm gap distance.

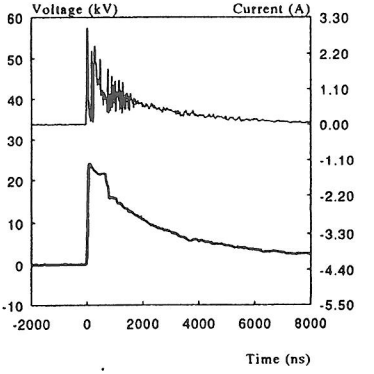

Fig. 2b. Voltage and current (as in Fig. 2a) after three hours. A conductive current shows up. The current spikes indicate discharge behaviour.

In Fig. 3 and 4 the charge and energy are given for corona pulses in tap water and deionized water as a function of the applied voltage (as indicated on the DC supply). In all cases a correction for the capacitive part is carried out. In Fig. 3a the charge is plotted together with a straight line which is fitted by the computer. It is observed that the line almost goes through the origin. In Fig. 3b the energy is plotted with a fit of a parabolic curve. This fit goes even more exactly through the origin (not imposed in the fit).

Fig. 4 shows the energy of pulses in deionized water. In Fig. 4a the gap distance is 18 mm, in Fig. 4b it is 36 mm. It can be seen that for the same gap distance tap water and deionized water have almost the same energy content per pulse. Also it is noticed that at different gap distances but the same applied voltage the energy of pulses in deionized water is almost the same. The fits of

parabolic functions cross the voltage axis at a large positive value, indicating a threshold behaviour as is always observed in gas discharges.

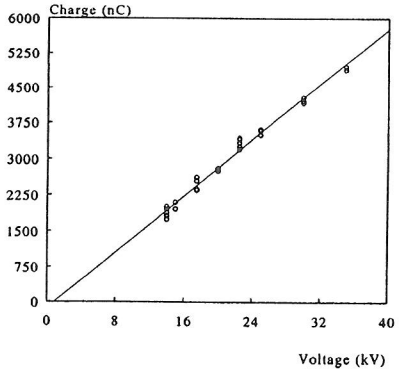

Fig. 3a. Charge content of corona pulses in tap water as a function of the applied voltage. The line is a linear fit through the data points.

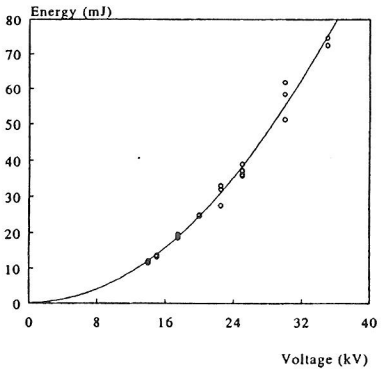

Fig. 3b. Energy content of the pulses of Fig. 3a. The line is a fit of a quadratic curve.

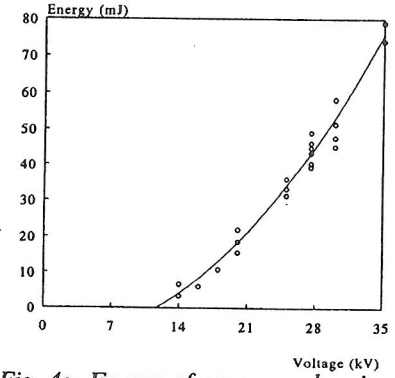

Fig. 4a. Energy of corona pulses in deioned water as a function of the applied voltage. The line is a quadratic function fitted through the data points.

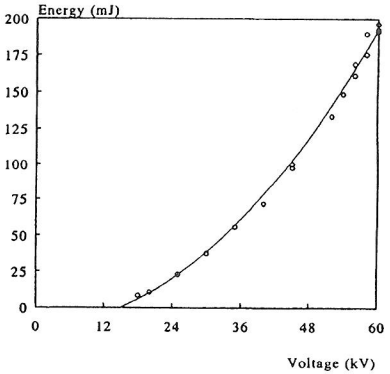

Fig. 4b. Energy of corona pulses in deionizedwater with increased gap distance (36 mm vs 18 mm in Fig. 4a).

Chemical measurements

In Fig. 5 our results are summarized of the first experiments on the breakdown of phenol. All cleaning experiments are performed with pulses of 30 kV applied voltage and 50 Hz repetition rate and with an initial phenol concentration of 2 mg/L. Both types of water are used here (Fig. 5a and 5b deionized water, Fig. 5c and 5d tap water) and in both cases without (Fig. 5a and 5c) and with (Fig. 5b and 5d) oxygen addition. The figures show that the conversion of phenol is faster in tap water and its rate is increased by adding oxygen.

So the best result, obtained in tap water with oxygen, is a conversion of 70% after 30 minutes. During this time the water is heated by only 1 to 2 K.

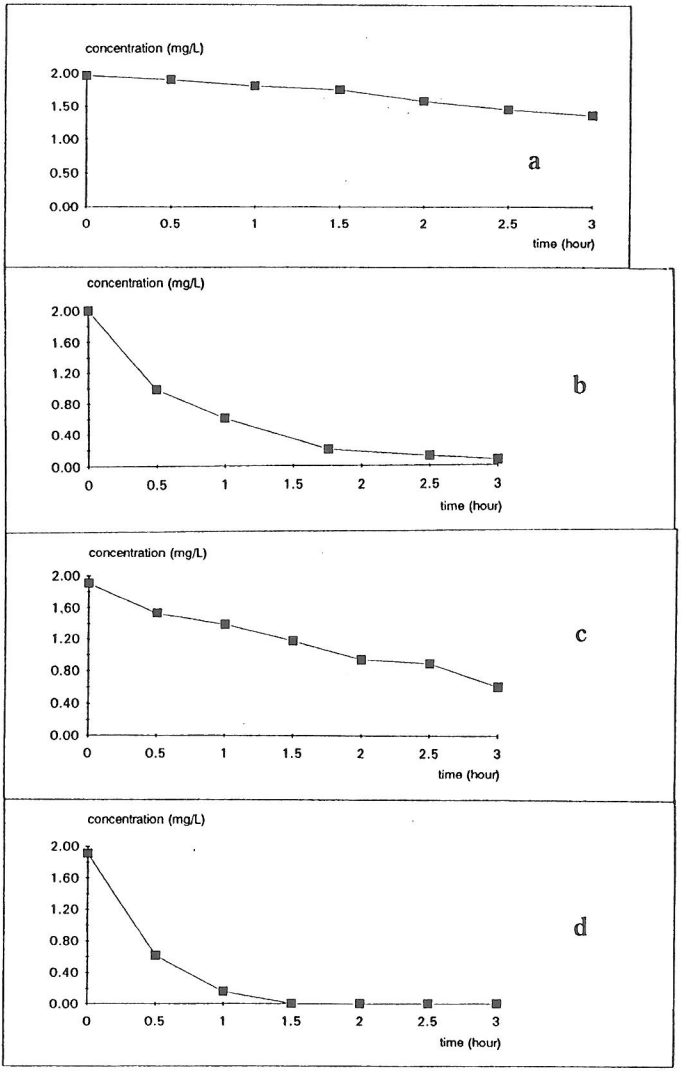

Fig. 5: The degradation of phenol induced by corona pulses of 30 kV amplitude and 50 Hz repetition rate. a and b are in deioniz water, in b oxygen is added through a hollow anode. c and d are in tap water, in d also oxygen is added.

Discussion and conclusions

From Figs. 1-4 an interesting feature is observed. The underwater pulses behave resistive in the case of tap water and they behave like a gas discharge in demineralized deionized water. This is seen from the shape of the discharge current and from the dependence of charge and energy on applied voltage. The aging effect, shown in Fig. 2b, leads to the conclusion that the conductivity of the water plays a major role in this effect. After several hours the deionized water becomes more conductive and the current pulse behaves more like that in tap water. Above 20 kV the energy per pulse is very similar in all cases (at the same voltage) so it is probably mainly determined by the power supply.

It is interesting to note that the best cleaning is obtained in tap water. This is of course an advantage for the application. The reason for this may be that ions in tap water (Fe^{2+} probably) increase the amount of oxidizing radicals (Fenton's reaction, [1,4]). This result is unexpected from the point of view from gas discharges. There one would expect the discharge in deionized water to have higher electron energy and therefore to be more effective in creating radicals. It seems that the chemistry in oxidation in liquids is even more complicated than that in gases and more knowledge is required. A rough energy analysis learns that the energy consumption of the pulsed discharge method is in the same order of ozonation and lower than for ultrasonics. Because corona discharges can be made at the desired place, it has good chances for the future.

Acknowledgement

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