ACIDITY CONTROL OF THE OXIDATION REACTIONS INDUCED BY NON-THERMAL PLASMA TREATMENT OF AQUEOUS EFFLUENTS IN POLLUTANT ABATEMENT PROCESSES

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Abstract. The acid properties of a non-thermal plasma in humid air (e.g., a gliding arc device) induced in an aqueous solution may deeply affect the efficiency of the matching oxidising properties, especially when the aqueous targets involve organic solutes. Hence, their oxidation rate may be strongly modified. A series of buffers is proposed to control the pH of aqueous target for at least one-hour treatments. The selected acid-base systems were selected for their inertia towards oxidation reaction, to cover a very large range of acidity.

The reported results are essential from both fundamental and applied points of view. They first allow the acute controlling of the degradation rate of organic compounds. They also enable estimating the efficiency of the gliding arc process in pollutant abatement pollutants, which is one on the main applications of the gliding arc treatments in environmental applications. Besides, they allow getting reliable data on the bactericidal effect of the plasma treatments, which are a merging application of the electric discharges.

1. INTRODUCTION

One of the major world problems of the XXI Century is related to environment, so that large efforts are devoted by many countries to promote new emerging techniques for pollution abatement. Electric discharges at atmospheric pressure and quasi-ambient temperature are carefully studied in ours Laboratories, as matching techniques to advanced oxidation processes. We focus on gliding arc discharges, which are actually quenched thermal plasmas. The chemical properties of the active species formed in the plasma are identified and quantified, in view of application to pollution abatement. The best working conditions to degrade pollutants imply a careful control of the acidity of the plasma treated targets.

2. EXPERIMENTAL SECTION

The gliding arc device used (Fig.1) for this study is close to that originally proposed by Czernichowski and Chapelle [1]. An arc, corresponding to thermal plasma, forms at the electrode "neck" (i.e., at the minimum electrode gap), moves along the electrodes, due to an air flow, then breaks when a new arc forms and gives rise to a quenched plasma. The gas flow is introduced in the reactor through a nozzle of calibrated diameter, along the axis of the reactor.

A special feeding electric device was drawn by one author (E.H.) and tested to vary the current intensity.

Magnetically stirred aqueous solutions (125 mL) are disposed as targets in front of the gas flow, so that the impinging plasma species react with the solutes at the liquid surface. The aqueous targets are analysed according to classical analytical procedures (pH-metry, UV-visible absorption spectrometry, gas chromatography).
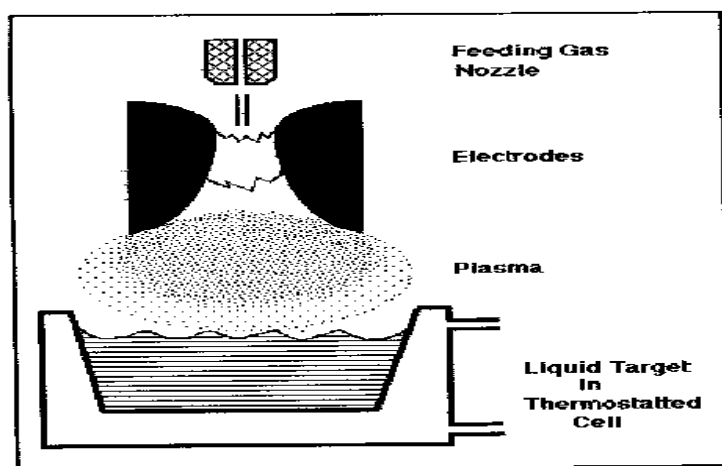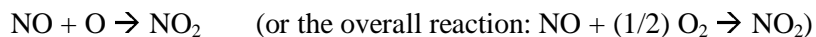
FIGURE 1. General scheme of the gliding arc device

3. RESULTS AND DISCUSSION

3.1. Chemical properties of a gliding arc plasma

Emission spectroscopy investigations show that the main active species formed in a gliding arc ("gli-darc") discharge in humid air are the radicals NO and OH. These species are respectively responsible for acidifying and oxidising effects on impinging the plasma treated solution. NO gives rise to nitrous and nitric acids according to the general scheme: the relevant anions were identified and quantified according to standard procedures. Overall reactions are the followings:

$$N_2 \rightarrow 2N \quad \text{and} \quad O_2 \rightarrow 2O$$

$$N + O \rightarrow NO \qquad \text{(or the overall reaction: } N_2 + O_2 \rightarrow 2\,NO)$$

$$NO + O \rightarrow NO_2 \qquad \text{(or the overall reaction: } NO + (1/2)\,O_2 \rightarrow NO_2)$$

$$NO_2 + OH \rightarrow HNO_3 \rightarrow H^+ + NO_3^-$$

$$NO + OH \rightarrow HNO_2 = H^+ + NO_2^-$$

OH is one of the strongest oxidising agents after fluorine. Due to its high potential, the hydroxyl radical $[E°(OH°/ H_2O) > 3$ V/NHE] is able to degrade most of the solutes. In the particular case of organic compounds, referred to as Red, oxidation of Red may be performed up to CO_2 as the ultimate product. Formally:

$$Red \rightarrow \dots \rightarrow CO_2 + qe\text{-} + r\,H^+ \qquad OH + e\text{-} + H^+ \rightarrow H_2O$$
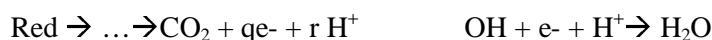
Oxidising degradation reactions of organic compounds often involve protons; thus, the kinetic rate very often depends on acidity. In works relevant to solution chemistry, acidity of the medium is usually fixed by using buffers, so that reaction mechanisms may be derived from kinetic data performed under controlled conditions. The lack of controlling acidity in the plasma treatment of organic solutes makes thus very difficult to estimate its efficiency.

Additionally, such a feature is of major interest for industrial applications, when organic pollutants dispersed in solution must be removed by plasma treatment.

We have just to summarise the main experimental results related to the acid effect.

3.2. Acid effects

Aqueous NaOH solutions were exposed to humid air plasmas; a steep pH lowering by more than 10 pH units for few minutes treatments results, due to the formation of nitrous and nitric acids. The pH vs

treatment time plots are thus typical titration curves of a strong base by acid (Fig. 2). These plots are characterised by the equivalent point, for pH = 7, where all the present OH⁻ anions initially introduced in the solution are neutralised by the impinging species, that is when the number of plasma formed acid species balance the remaining hydroxyl ions. The equivalent point, or the neutral pH (i.e., pH=7), is reached for the particular treatment time t_{eq} in given working conditions.
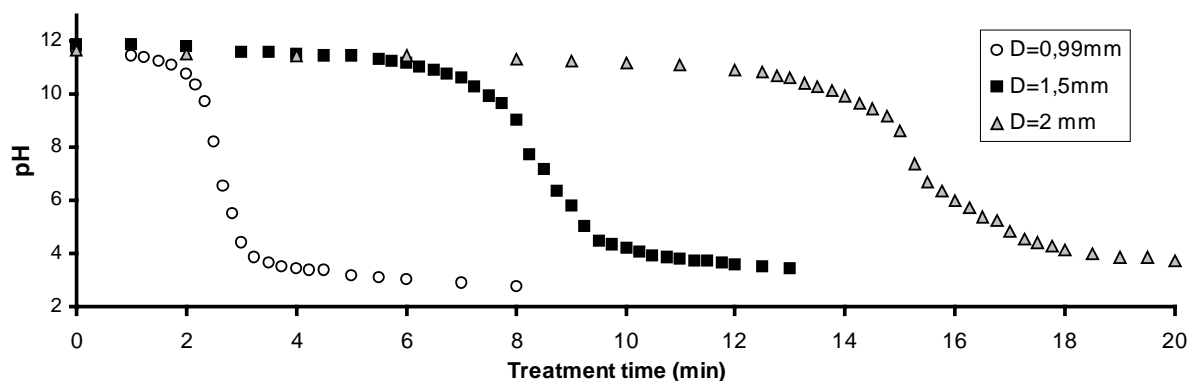

FIGURE 2. Plasma neutralisation of NaOH solutions for several electrode to liquid distances (D mm)

As previously reported [2,3], the t_{eq} values linearly depend on:

♦ the starting concentration $C°$ of the NaOH solution,

♦ the volume of treated solution,

♦ the distance D between the electrodes and the liquid target (Fig.3),

♦ the reverse of the gas flow rate Q (Fig. 4),

♦ the square of the nozzle diameter Φ : teq = 4.1388 Φ^2 - 1.3243 (r^2 = 0.9987)
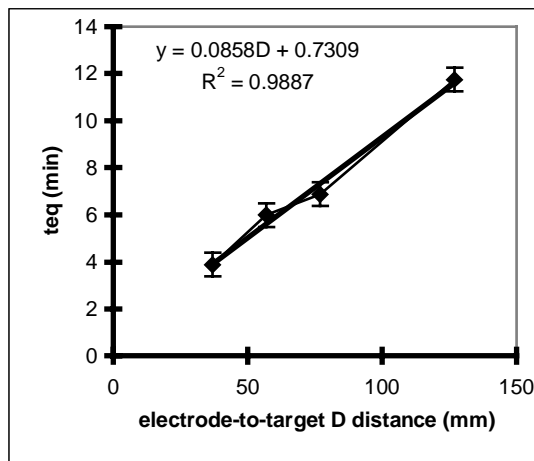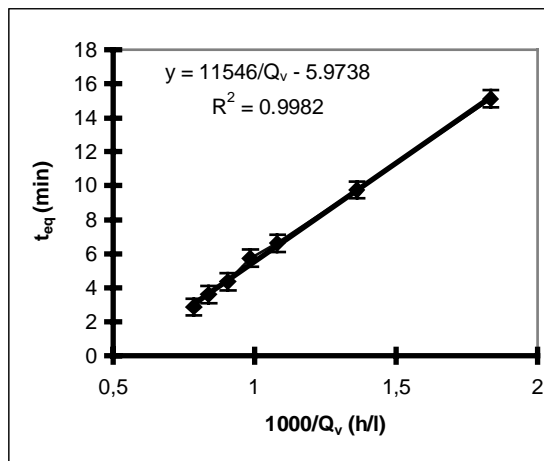
**FIGURE 3.** t_{eq}=f(D)   **FIGURE 4.** t_{eq} = f(1/Qv)

All these features easily account for the residence time of the active species formed in the plasma.

3.3. Acidity control by using selected buffers

The acid and oxidising matching effects of discharges in humid air were underlined: We wished to control acidity, so that oxidation processes could be performed in controlled conditions, which strongly suggests to use buffered media. To avoid degradation of the buffers, we had to select particular acid/base systems, which are little oxidation sensitive (5). For example, o-phosphoric acid and its conjugate bases was a suitable candidate, as were carbonic and boric acids, additionally to strong acids

and strong bases.

Table 1 gathers data relevant to selected buffered solutions exposed to the plasma for 1 hr. Emphasis is devoted to initial and final pH values, which only differ by few tenths of pH unit. This feature shows that the buffer effect actually occurs for times long enough to achieve pollution abatement by means of gliding arc treatment. Additionally, Figure 6 illustrates an example of limited and continuous pH decrease for plasma treated solution. By the way, the increasing acidity shows that the plasma treatment actually occurred.
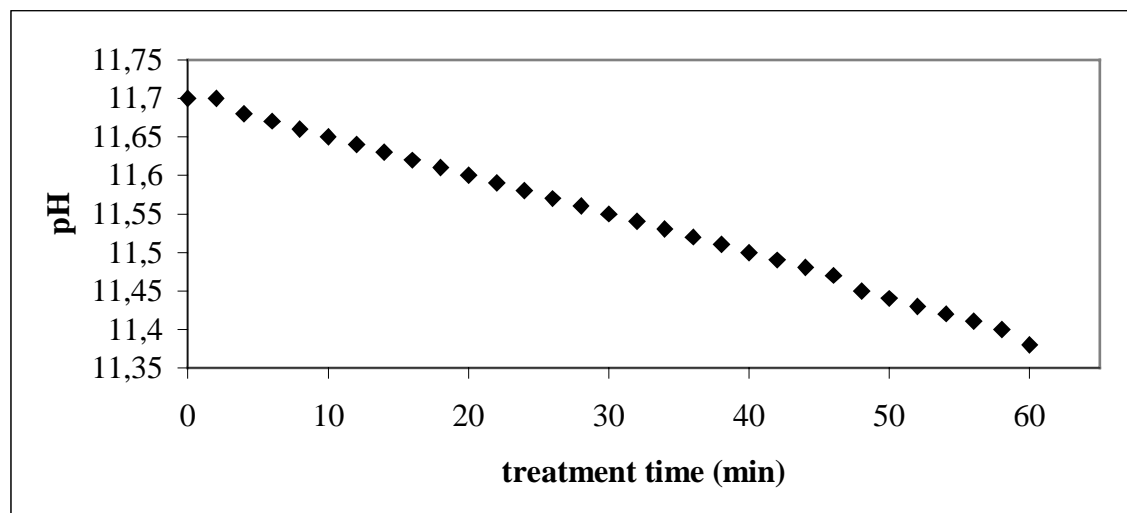
FIGURE 6. Typical behaviour of a buffered solution exposed to the gliding arc discharge. Buffer composition: Na_2HPO_4 (0.1 M) + Na_3PO_4 (0.1 M)

Table 1 also presents data relevant to buffers involving base/acid ratios different from 1:1. The limited pH evolution in this case is similar to that observed for 1:1 buffers, which confirms that the buffer effects holds again. This suggests that a large series of non-equimolar buffers can be prepared and satisfactorily used, so that the whole pH range may be now controlled.

3.4. Application to the bactericidal effect

As mentioned, numerous reactions involving organic compounds are pH-dependant. It is the case of common pollutants, such as phenols, for which the 1st oxidation step involves the formation of catechols, which are very quickly oxidised to quinones.

A matching important field of application of the plasma treatments refers to microbiology. Previous studies in ozone applications demonstrated the strong bactericidal effect of the gas (6,7). Preliminary report (8) of using a gliding arc discharge showed the bactericidal effects of the plasma treatment.

TABLE 1. pH of selected buffers exposed to the gliding arc

Composition	pH (t = 0 min)	pH (t= 60 min)
H_3PO_4 (0.1 M) + H_2PO_4Na (0.1 M)	2.16	2.0
H_2PO_4Na (0.1 M) + HPO_4Na_2 (0.1 M)	6.85	6.56
HPO_4Na_2 (0.1 M) + PO_4Na_3 (0.1 M)	11.7	11.4
H_2PO_4Na (0.15 M) + HPO_4Na_2 (0.05 M)	6.06	5.62
HPO_4Na_2 (0.15 M) + PO_4Na_3 (0.05 M)	10.73	10
HCO_3Na (0.1 M) + CO_3Na_2 (0.1 M)	9.86	9.62
HBO_2 (0.1 M) + BO_2Na (0.1 M)	9.18	8.81

Strain MG 1655 of *Escherichia Coli* were cultivated in a suitable medium (LB) and exposed to the discharge for various working conditions before numeration. The number of surviving bacteria N decreases as the exposure time increases, and the relevant plot (Figs. 7, 8) agrees with a 1st order kinetic law ($k \approx 5$ min^{-1}). The influence of the treatment parameters was underlined from the inactivation time of the bacteria in suitable buffered solutions, according to a technique which allows to discard the acid effect of the plasma treatment on the living matter.
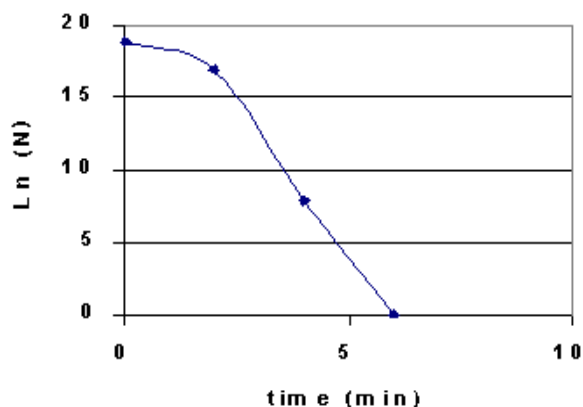

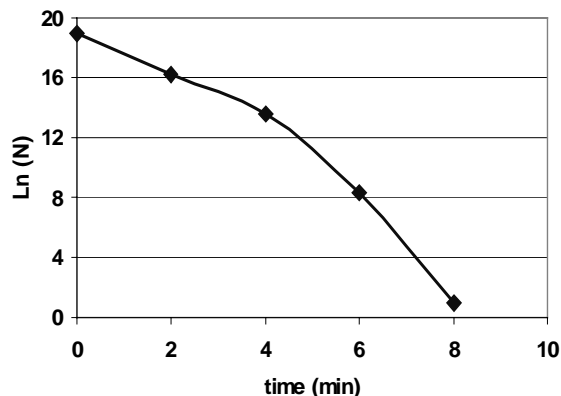**FIGURE 7.** *E. Coli* abatement [d=12 cm; Q=440L/h]   **FIGURE 8.** *E. Coli* abatement [d=12 cm; Q=320L/h]

4. CONCLUSION

A series of buffers, which can be used under plasma conditions, are now available. Their efficiency was tested for 1 hr plasma treatments. They enable us to control the acid effect induced by plasma exposure of aqueous solutions. As a first and direct consequence, we can now perform acute measurements of the kinetic constants of degradation reactions involving organic solutes, which are often controlled by acidity. A second consequence such is related to organic pollutants: we are now able to assess the efficiency of the gliding arc technique for pollution abatement, and even for microbiological inactivation, which appears to be an interesting and new field of application.

ACKNOWLEDGEMENTS

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