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# Acidity control of the gliding arc treatments of aqueous solutions: application to pollutant abatement and biodecontamination

D. Moussa<sup>1</sup>, F. Abdelmalek<sup>1,2</sup>, B. Benstaali<sup>1,2</sup>, A. Addou<sup>2</sup>, E. Hnatiuc<sup>1,3</sup>, and J.-L. Brisset<sup>1,a</sup>

<sup>1</sup> Laboratoire d'Électrochimie (L.E.I.C.A.), UFR des Sciences de l'Université de Rouen, 76821 Mont Saint-Aignan, France

<sup>2</sup> Laboratoire des Sciences et Techniques de l'Environnement et de la Valorisation (S.T.E.V.A.), Faculté des Sciences de l'Ingénieur, BP 188, Mostaganem, Algeria

<sup>3</sup> George Asashi Technical University, 51–53 Boulevardu Mangeron, 66000 Iasi, Romania

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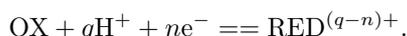
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**Abstract.** A tight control of acidity is needed for performing oxidation–reduction reactions of organic compounds dissolved in liquid media, since the relevant reactions often involve the occurrence of protons; the matching kinetics are therefore acidity dependent. This feature holds for plasma treatments of aqueous wastes which are intended to abate the concentration in organic pollutants. Exposure of aqueous solutions to a gliding arc plasma in humid air induces acid and oxidising reactions in the condensed phase. Acid effect results from the occurrence of NO species formed in the plasma and leads to the formation in water of nitrous and nitric acids, which are responsible for a steep pH fall. Using selected buffers allows accurate controlling of the acidity, which is necessary for most of the plasma-chemical or plasma-biochemical reactions.

**PACS.** 52.80.Mg Arcs; sparks; lightning – 52.80.Tn Other gas discharges

## 1 Introduction

Most of the reactions involving organic compounds and occurring in aqueous phase are governed by the proton concentration, or more commonly by the *pH* value in aqueous solutions. This is the particular case for oxidation-reduction reactions, typically:

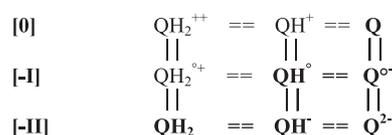


The associate equilibrium is governed by the Nernst's law involving the activities  $a_i$  of the solute species  $i$  and the normal oxidation-reduction potential  $E^\circ(\text{OX}/\text{RED})$  of the system OX/RED in the standard state (i.e., usually atmospheric pressure,  $T = 298$  K and unit activity of the species). For dilute solutions, it is suitable to approximate the activities  $a_i$  by the concentrations  $C_i$ . The Nernst's law then gives the potential of the solution, namely:

$$E(\text{OX}/\text{RED}) = E^\circ(\text{OX}/\text{RED}) + \frac{2.303RT}{nF} \log \frac{a_{\text{OX}}}{a_{\text{RED}}} a_{\text{H}^+}^q$$

with  $R$  and  $F$  the gas and Faraday constants (respectively  $8.314 \text{ J.K}^{-1}\text{mol}^{-1}$  and  $96487 \times 10^4 \text{ C.mol}^{-1}$ ), so that  $(2.303 RT/F) = 0.059 \text{ V} \approx 0.06 \text{ V}$  at 298 K.

The chemists use to consider the formal potential  $E'^\circ$ , given for unit concentrations of OX and RED, and ionic



**Fig. 1.** Jacq's matrix for the Quinone (Q)/Hydroquinone (QH<sub>2</sub>) system involving the intermediate oxidation state [-I]. Proton exchange equilibria are indicated in columns, and electron exchange equilibria in lines. The main species involved depend on the acidity of the medium. For example, in basic media, the protonated species may be neglected, so that the scheme then involves only 6 (neutral or anionic) species (in bold) while in acid medium the neutral and protonated species are concerned.

strength different from zero, by:

$$E'^\circ(\text{OX}/\text{RED}) = E^\circ(\text{OX}/\text{RED}) - \frac{0.06}{n} pH$$

where *pH* refers to the decimal logarithm of the proton activity (i.e.,  $pH = -\log a_{\text{H}^+}$ ). They also use to plot the  $E'^\circ$  function vs. *pH* to illustrate the acidity dependence of the solution potential. A good example is given by the oxidation-reduction system involving quinone as the oxidising species and dihydroxybenzene (hydroquinone) as the matching reducer. Figure 1 reports the relevant Jacq's diagram [1,2] involving three oxidation numbers, i.e., [0], [-1] and [-2] usually involved for the first steps of the

<sup>a</sup> e-mail: Jean-Louis.Brisset@univ-rouen.fr

oxidation-reduction processes. Lines are devoted to proton exchange equilibrium and columns to electron exchange equilibrium. Figure 2 is relevant to basic media, where protonated species may be neglected: the sketch shows the major species concerned, with the variations of the formal potential  $E'^{\circ}$  of the systems with  $pH$ , according to the order of the acidity constants. Figure 2 thus illustrates the fact that oxidation reduction processes strongly depend on acidity, even with simplified assumptions.

Since oxidation reduction reactions in solution involve the occurrence of an oxidising species from a given system A and of a reducing species from another system B, the formal potentials of both systems are likely  $pH$ -dependant, and so does the difference  $E'^{\circ}(A) - E'^{\circ}(B)$ , which is related to the formal Gibbs free energy  $\Delta G'^{\circ}$  of the reaction. For thermodynamically allowed reactions, the larger is  $\Delta G'^{\circ}$ , the easier is the reaction, and consequently the larger is its rate. Such a feature is of major importance for plasma processing of aqueous solutions in view of pollution abatement, as well as for some plasma surface treatments of polymers.

A key for most of the chemical reactions in aqueous or non-aqueous solution is thus provided by acidity control. This feature is particularly glaring when reagents are organic chemicals such as organic pollutants or in the case of biological reactions, since the proton concentration is often involved in the reaction mechanisms. An interesting case is provided by the spreading use of the plasma techniques at atmospheric pressure for pollution control, water treatment and disinfecting. A steep control of the acidity is thus necessary and enables to compare given plasma treatments with conventional chemical treatments in the same conditions.

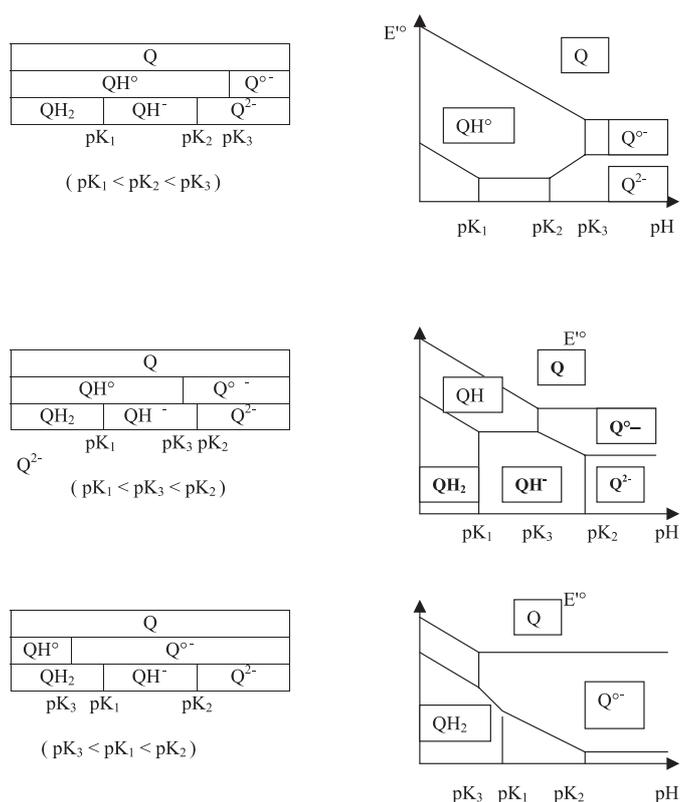
In this paper, we first examine the effect of a plasma treatment on aqueous alkaline solutions at atmospheric pressure and quasi-ambient temperature by following the  $pH$  variations with the treatment time and with various given working parameters. Then we test the use of selected buffers in the same working conditions and underline numerous situations where buffered targets are required for reliable plasma treatments.

To avoid any thermal effect, and for the sake of simplicity, we selected a non-thermal plasma provided by a gliding arc discharge at atmospheric pressure, and an aqueous solution as the plasma treated target. Also, we concentrate on treatments in air because they are inexpensive and well accepted for industrial applications.

## 2 Basic considerations

### 2.1 The active species in a plasma gas

The composition of non-thermal plasmas was thoroughly studied. Even for high pressure and low temperature discharges, such as corona or DBD discharges, numerous authors reported on the composition of the gas. Surprisingly, only limited information is available on the plasma formed in a gliding arc discharge although the device was largely



**Fig. 2.** Simplified models of Jacq's diagram for quinone/hydroquinone systems in *basic* media, (where the protonated species  $QH_2^{2+}$ ,  $QH^+$  and  $QH^{\circ+}$  may be in negligible concentration). The remaining species present Bronsted acid/base character which is quantified by the relevant  $pK_a$  value. For example the intermediate  $Q[-I]$  is represented by  $QH^{\circ}$  and  $Q^{\circ-}$  which are the conjugate partners in the acid base system:  $QH^{\circ} \rightleftharpoons Q^{\circ-} + H^+$  characterised by the acidity constant  $K_3$  (or  $pK_3 = -\log K_3$ ).

$$K_3 = \frac{C_{Q^{\circ-}} \cdot C_{H^+}}{C_{QH^{\circ}}}$$

In acid medium (i.e., for large concentrations in solvated protons), and more usually for  $pH < pK_a$ ,  $C_{QH^{\circ}}$  is markedly superior to  $C_{Q^{\circ-}}$ , so that  $QH^{\circ}$  is the predominant species involved in oxidation/reduction reactions. For  $pH > pK_3$ , the basic species  $Q^{\circ-}$  is predominant and must be considered in the oxidation-reduction equilibrium. For  $pH = pK_a$  the matching acid and base species have equal concentration (e.g.,  $C_{QH^{\circ}} = C_{Q^{\circ-}}$  for  $pH = pK_3$ ). The left sketch thus illustrates the distribution of the main species with  $pH$ . For example, when  $pK_1 < pK_2 < pK_3$ , and for  $pH < pK_1$ , the main species to be considered in the Nernst equations are  $Q$  and  $QH^{\circ}$  for the  $Q[0]/Q[-I]$  system and  $QH_2$  for the  $Q[-I]/Q[-II]$  system respectively. We have always  $pK_1 < pK_2$ , but the  $pK_3(QH^{\circ}/Q^{\circ-})$  value is usually unknown, so that its position must be considered with respect of  $pK_1(QH_2/QH^{\circ})$  and  $pK_2(QH^{\circ}/Q^{\circ-})$ . The right sketches are relevant to the  $E'^{\circ}$  vs.  $pH$  plots for the considered  $Q[0]/Q[-I]$  and  $Q[-I]/Q[-II]$  oxidation-reduction systems. The standard potentials of the various oxidation-reduction systems are assumed to be very different.

developed by Czernichowski et al. for industrial applications [3–5].

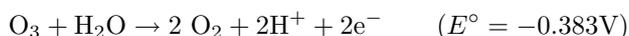
Spectral analysis [6, 7] of the gliding arc discharge in humid air showed the occurrence of two major species, i.e.,  $\text{HO}^\circ$  and  $^\circ\text{NO}$ . The species were identified from their emission bands and the population was quantified.  $^\circ\text{NO}$  was characterised by the  $[\text{A}^2\Sigma^+-\text{X}^2\Pi, \Delta v = -1, -2, -3]$   $\gamma$ -system around 237 nm and  $\text{HO}^\circ$   $[\text{A}^2\Sigma^+-\text{X}^2\Pi, \Delta v = 0]$  at 306 nm. The matching molecular ion  $\text{N}_2^+$  was also found.

The co-generation of  $\text{O}_3$  and  $\text{H}_2\text{O}_2$  in the electric discharge was just mentioned by Velikonja et al. [8] for AC dielectric barrier discharges in humid air, as it was considered by Peyroux et al. [9, 10] several years ago for corona discharges and by Morgan et al. [11] for DBD in humid air. The question was summed up [12].

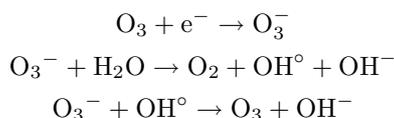
## 2.2 Oxidising species formed in aqueous solutions exposed to the discharge

The species formed in the discharge are responsible for the main chemical properties that can be observed in an aqueous solution exposed to the discharge, namely the oxidising and acidifying effects we are dealing with.

The occurrence of other species of interest was also identified in the liquid target, for example  $\text{H}_2\text{O}_2$  which forms coloured complexes with V(V) or Ti (IV) moieties. Ozone is also suspected to be present in the target solution, but its very low concentration is due to its decomposition into oxygen



according to a reaction which increases the acidity of the medium. Additionally, electrochemical studies [13, 14] at a bright platinum electrode dipped in alkaline media suggest that the reaction involves the occurrence of an intermediate ozonide anion  $\text{O}_3^-$ , which later reacts with water molecules and  $\text{OH}^\circ$ :



and combining the reactions accounts for the decomposition of ozone.

Nitric acid which is also formed in the discharge presents a strong oxidising character which must also be taken into account.

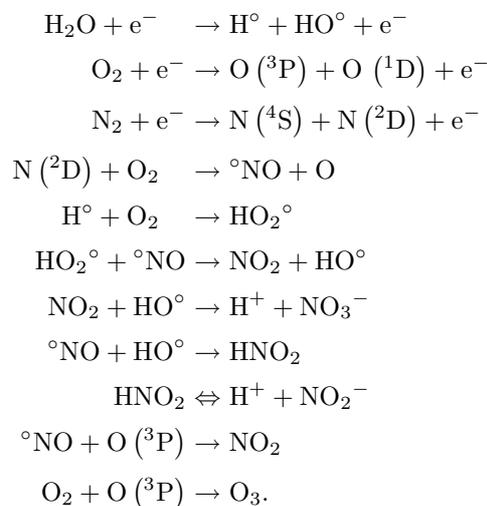
## 2.3 Origin of the acid effects in solution

The acid effects of a plasma treatment were already evidenced and quantified a decade ago [15–17] on exposing aqueous solutions or indicators trapped in a gel to the neutral species of a corona discharge in ambient air.

As mentioned, the spectral analysis of the discharge in the gas phase showed the occurrence of  $\text{HO}^\circ$  and

$^\circ\text{NO}$  species, which must be involved in the chemical effects observed in the target solutions. Since the matching analysis [18] of distilled water exposed to the discharge shows the presence of large quantities of nitrate and nitrite ions,  $^\circ\text{NO}$  is therefore directly concerned with the acidifying effects of the discharge, but other species are likely involved. For instance the occurrence of oxoperoxonitrate (1-) as a precursor of the nitrate ion  $\text{NO}_3^-$  is assumed in particular conditions [18].

We can then consider a limited series of reactions in the gas phase which involves the starting components of the plasma gas (i.e.,  $\text{O}_2$ ,  $\text{N}_2$  and  $\text{H}_2\text{O}$  for humid air) and yield atoms by breaking the bonds of the concerned molecules. The formed species are likely concerned with the chemical properties of the solvent, which may consequently affect those of the solutes.



Most of these reactions are probably overall reactions (and particularly the formation of nitric acid) and they are assumed to take place in the gas phase, at least at the plasma/liquid interface. Some chemical kinetics data relevant to humid air plasma are reviewed [19]. The reaction products formed at the gas/liquid interface diffuse in the condensed phase where they can react with the solutes. The above reactions thus account for the species present in solution. We are concerned with the resulting species and their relevant chemistry *in solution* for environmental applications.

## 2.4 Influence of acidity on the oxidation reduction properties of the activated species of the plasma

The main activated species, which are present in a discharge in humid air or able to form in the immediate neighbourhood of the arc, are oxygenated species, such as  $\text{OH}^\circ$ ,  $\text{HO}_2^\circ$ ,  $\text{H}_2\text{O}_2$ , and related species, which present acid-base properties, additionally to  $\text{O}_3$  and nitrogen containing species, such as  $^\circ\text{NO}$ . Tables 1 and 2 gather the relevant physical-chemical data, such as the normal oxidation-reduction potentials  $E^\circ$  in the standard state of the electron exchanger systems and the acidity constants  $pK_a$  of pertinent acid-base couples. Figure 3 illustrates the electrochemical behaviour of the systems in the

**Table 1.** Thermodynamic potentials  $E^\circ$  (V/HNE) of various electrochemical systems of interest at zero ionic strength and in standard  $T$  and  $P$  conditions. [Data from: M.S. Anthelmann and F.J. Harris, *The Encyclopedia of Chemical Electrode Potentials*, Plenum, 1982; (a) K. Rajeshvar, J.G. Ibanez, *Environmental Chemistry*, Academic, 1997; (b) A.J. Bard, R. Parsons and J. Jordan, *Standard Potentials in Aqueous Solution*, M. Dekker, 1985.] Indexes g, liq or aq are respectively relevant to gaseous, liquid or aqueous.

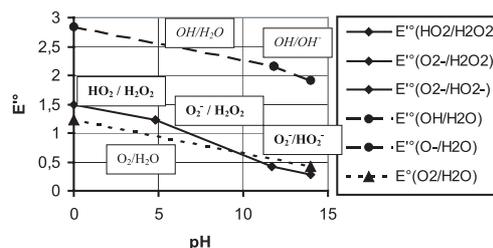
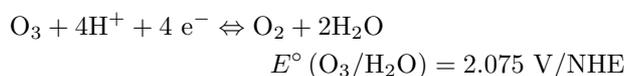
Oxidation – reduction reactions	$E^\circ$ (V /HNE)
$O_2 + H^+ + e^- = HO_2^\circ$	- 0.13; - 0.30 (a); -0.046 (b)
$O_2 (g) + 2H^+ + 2 e^- = H_2O_2 (liq)$	0.68
$H_2O_2 (liq) + H^+ + e^- = OH^\circ (g) + H_2O$	0.71
$HO_2^\circ + O_2 + H^+ + e^- = O_3 + H_2O$	0.813 (b)
$O_2 + 4 H^+ + 4 e^- = 2 H_2O (g)$	1.19
$O_2 + 4 H^+ + 4 e^- = 2 H_2O (liq)$	1.23
$HO_2^\circ (liq) + H^+ + e^- = H_2O_2 (liq)$	1.50; 1.44 (b)
$O_3 + 6 H^+ + 6 e^- = 3H_2O$	1.51 (a)
$O(g) + H_2O + 2 e^- = 2 OH^-$	1.602
$HO_2^\circ (liq) + 3 H^+ + 3 e^- = 2 H_2O$	1.70 (a); 1.65 (b)
$H_2O_2 + 2 H^+ + 2 e^- = 2 H_2O$	1.78; 1.68 (a)
$O_3 + 2 H^+ + 2 e^- = O_2 + H_2O$	2.07
$O^\circ (g) + 2 H^+ + 2 e^- = H_2O$	2.42
$OH^\circ + H^+ + e^- = H_2O$	2.85; 2.38 (b)
<hr/>	
$2 NO + 2 H^+ + 2 e^- = H_2N_2O_2$	0.70
$2 NO_3^- + 4 H^+ + 2 e^- = N_2O_4 (g) + 2 H_2O$	0.80
$NO_3^- + 3 H^+ + 2 e^- = HNO_2 + H_2O$	0.94
$NO_3^- + 4 H^+ + 3 e^- = NO + 2 H_2O$	0.96
$HNO_2 + H^+ + e^- = NO + H_2O$	1.00
$N_2O_4 + 2 H^+ + 2 e^- = 2 HNO_2$	1.07
$NO_2 + H^+ + e^- = HNO_2$	1.09
$2NO_3^- + 12 H^+ + 10 e^- = N_2 (g) + 6 H_2O$	1.25 (b)
$2HNO_2 (aq) + 4 H^+ + 4 e^- = N_2O (g) + 3 H_2O$	1.29
$2HNO_2 + 6 H^+ + 6 e^- = N_2 + 4 H_2O$	1.45
$H_2N_2O_2 + 2 H^+ + 2 e^- = N_2 + 2 H_2O$	2.65

**Table 2.** Acidity constants  $pK_a$  ( $pK_a = -\log [C_{base} \cdot C_H / C_{acide}]$ ) of various Bronsted acid-base systems Acid = Base +  $H^+$ . [Data from A.J. Bard, R. Parsons and J. Jordan, *Standard Potentials in Aqueous Solution*, M. Dekker, 1985.]

Acid = Base + $H^+$	$pK_a$
$H_2O_2 = HO_2^- + H^+$	11.7
$HO_2^- = O_2^{2-} + H^+$	$16 < pK < 18$
$HO_2^\circ = O_2^- + H^+$	4.8
$OH^\circ = O^- + H^+$	11.8
$HNO_2 = NO_2^- + H^+$	3.3

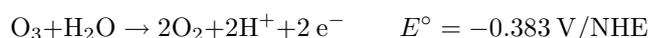
usual  $E'^\circ$  vs.  $pH$  diagram and shows that the oxidising properties of the species are strongly dependent on acidity.

Ozone presents a strong oxidising character, which is exceeded in acid solution by fluorine, atomic oxygen  $^\circ OH$  and few other species:



**Fig. 3.** Theoretical  $E'^\circ$  vs.  $pH$  diagrams relevant to the systems  $O_2H$  (or  $O_2^-$ )/  $H_2O_2$  (or  $HO_2^-$ ),  $OH$  (or  $O^-$ )/ $H_2O$  and  $O_2/H_2O$ .

but  $O_3$  is unstable in solution and decomposes into oxygen,



according to a clearly established decomposition process [20].

In the case of waste waters treatments, the  $pH$  of the solution depends on the nature and the concentration of the solutes. Hence, the degradation of organic solutes

which results from oxidation by the plasma species is in part controlled by the acidity of the liquid target.

Kinetic studies are very often  $pH$ -dependent. A recent illustration is provided by Alexeev et al. [21] in their study of the plasma oxidation of phenol in water.

### 3 Experimental section

The plasma device used for this study is a gliding arc system which was largely described [3,4] and already used for pollution abatement of liquid effluents [22,23]. A special HV transformer (9 kV-100 mA without charge) provided the electric power. The plasma was fed with a water-saturated airflow (Fig. 4).

An arc forms at the minimum gap. Due to the gas flow, the arc feet move along the diverging electrodes until the arc is short-circuited by a new one. The plasma plume is disposed close enough to the liquid target, so that it licks the liquid surface, and allows the chemical reactions to take place at the interface. The contact surface is increased by means of magnetic stirring.

The working parameters were identified as the electrode gap  $e$ , the distance  $L$  between the electrode neck and the liquid surface, the gas flow rate  $Q$ , and the nozzle diameter  $D$  which delivers a cylindrical gas flow.

The influence of the current intensity was examined with the help of a special control unit [24].

Chemicals were analytical grade commercially available reagents. They were dissolved in distilled water and aliquots of 125 mL were disposed in a thermostatted vessel, magnetically stirred at constant speed to improve diffusion and homogenise and exposed to the plasma discharge for various time periods. Acidity was measured by conventional  $pH$ -metry techniques, i.e., by means of a glass or alternatively by an ISFET test electrode. Both files of results were in close agreement.

### 4 Results and discussion

The set of reactions listed in Section 2 shows that exposing an aqueous target to an air plasma induces the formation of NO, which gives rise to nitrous and nitric acid in the solution. The acidity of the solution is thus increased, and the  $pH$  substantially lowered. This “acid effect” depends on the main working parameters and may be easily quantified.

Among the chemical properties induced in the solution by a plasma treatment in air, acidity measurements are an easy-to-operate diagnostic. An increase in the acidity of the solvent target exposed to a humid air plasma is observed and confirms previous observations on the corona discharge [15–17]. We now focus on the treatment of aqueous solutions by a gliding arc in humid air.

#### 4.1 Quantifying the acid effect

Alkaline aqueous solutions prepared from group Ia and IIa elements, such as NaOH, KOH,  $\text{Ca}(\text{OH})_2$  or even qua-

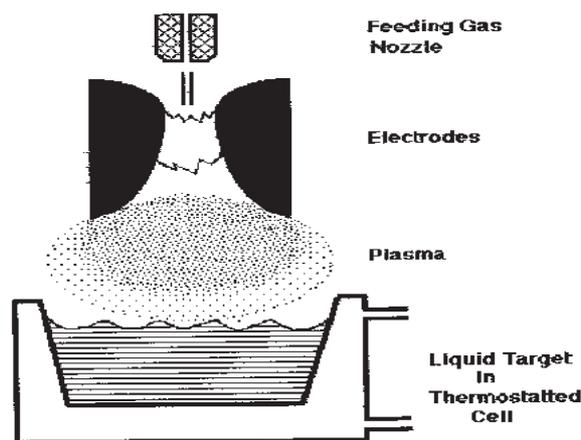


Fig. 4. Scheme of the gliding arc device.

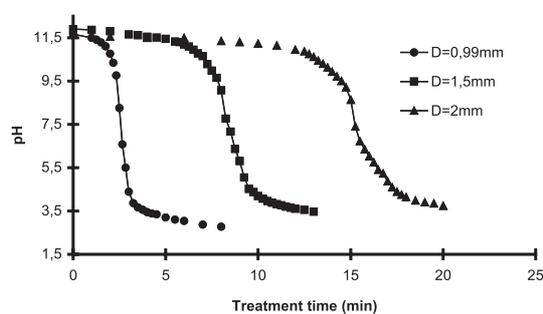


Fig. 5. Evolution of  $pH$  of the target solution with the treatment time for various nozzle diameters  $D$  (mm). The “equivalent time”  $t_{eq}$  linearly depends on the square of the nozzle diameter. Resulting correlation:  $t_{eq} = 4.1386 D^2 - 1.3243$ ;  $r^2 = 0.9987$ .

ternary ammonium solutions, are considered as strong bases in water. The  $pH$  of the solution is thus high ( $7 < pH < 14$ ) and depends on the concentration of the solute.

Exposing to the discharge known volumes of such solutions of given concentration (e.g. 125 mL of NaOH  $5 \times 10^{-3}$  M) for the time  $t^*$  induces a marked  $pH$  lowering by several  $pH$  units. The  $pH$  decreases as  $t^*$  increases, so that the relevant plots  $pH$  vs.  $t^*$  are similar to a mere titration plot of a strong base by a strong acid (Fig. 5). The plasma treatment of the solution is thus characterised by the exposure time  $t_{eq}$  needed to get  $pH = 7$ , i.e., the time needed by the discharge to form enough protons to neutralise exactly the excess in  $\text{OH}^-$  ions initially present in the target solution.

This feature is thus related to the neutralisation of the  $\text{OH}^-$  ions introduced in solution by the impinging species formed in the plasma phase. The relevant parent species were identified as NO, one of the major components of the plasma, which reacts at the water surface and yields nitrous and nitric acids.

One can also observe that exposing pure water to the discharge also induces an immediate  $pH$  lowering from  $pH$ : 6–7 to 2–3, since no extra hydroxyl ion is present in the solution and the plot  $pH$  vs.  $t^*$  is characterised by a  $pH$

fall occurring as soon as the discharge is switched on (so that  $t_{eq}$  cannot be precisely determined).

Exposing known volumes of ( $5 \times 10^{-3}$  M) NaOH solutions to the discharge showed that  $t_{eq}$  linearly depends on the volume of the target. Matching experiments performed with fixed target volumes, but various solute concentration accounted that the  $t_{eq}$  values actually linearly varied with the solute concentration. A direct relationship is thus stated between the number of protons formed in the discharge for the treatment time  $t_{eq}$  and those which are able to neutralise at the surface the hydroxyl ions introduced in the exposed liquid.

#### 4.2 Acidity measurements are a possible test for the efficiency of a reactor

The  $pH$  vs.  $t$  plots are thus characterised by the equivalent times  $t_{eq}$ , i.e., by the exposure times to the plasma needed to lower  $pH$  to neutrality ( $pH = 7$ ) according to a standard titration process. The huge  $pH$  fall can thus be considered as an easy-to-operate test for the chemical efficiency of the plasma device, since the shorter is  $t_{eq}$  needed to get  $pH = 7$  (in given working conditions), the more efficient is the energy transfer from the electric source to the gas to form NO and hence  $HNO_3$ , and the more efficient is the reactor.

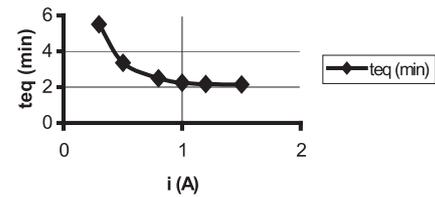
Quantifying the acid effect may be a useful and simple tool for estimating the efficiency of the reactor in a very first step. We have also to keep in mind that other parameters, electric or aero-hydrodynamic nature, should also require attention.

#### 4.3 Dependence of $t_{eq}$ on the main working parameters

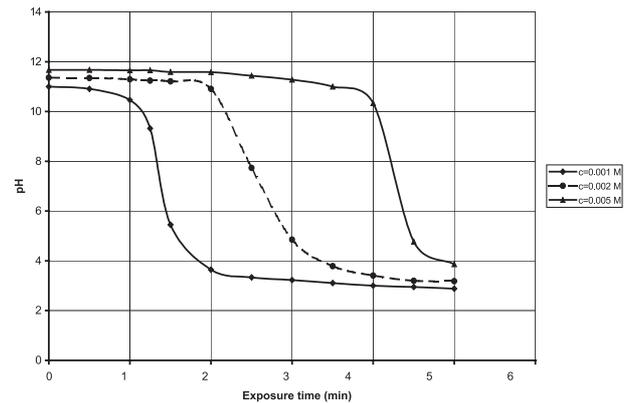
Previous investigation of the influence of various working parameters showed that  $t_{eq}$  directly depends on the concentration of hydroxyl ions in the target solution (for given working parameters). The influence of some working parameters was investigated:  $t_{eq}$  also depends on the distance  $e$  between the electrodes, on the distance  $L$  from the electrodes to the liquid surface and on the square of the nozzle diameter ( $D^2$ ). Additionally  $t_{eq}$  is an increasing linear function of the inverse of the feeding gas flow (i.e.,  $Q^{-1}$ ), and a decreasing function of the measured current intensity in the range 0.1–1 A. All these features are illustrated by Figures 5–11. These experimental results will be considered hereafter, in view of showing that  $t_{eq}$  is a suitable indicator for estimating the efficiency of the reactor.

All these reported features strongly suggest that an overall process close to the electrolysis process takes place. A very simplified model may be derived from the rough following assumptions:

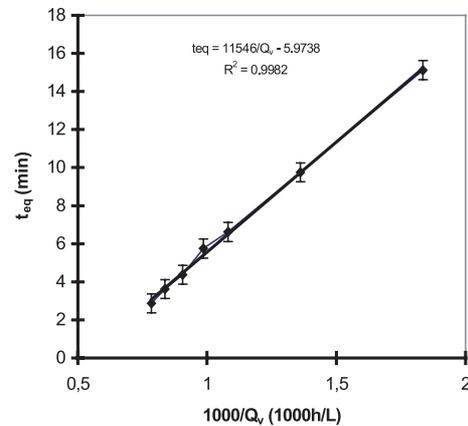
- the current efficacious intensity is constant for a period,
- the active species result from electrochemical reactions involving the feeding gas and the discharge. Incidentally, one can consider that this feature may be related



**Fig. 6.** Evolution of the “equivalent” time  $t_{eq}$  with the current intensity, for given working parameters [ $Q = 975$  L/h;  $D = 2$  mm;  $H = 20$  mm]. Resulting relation:  $(1/I) = 0.7323 \cdot t_{eq} - 0.63$ ;  $r^2 = 0.9871$ .



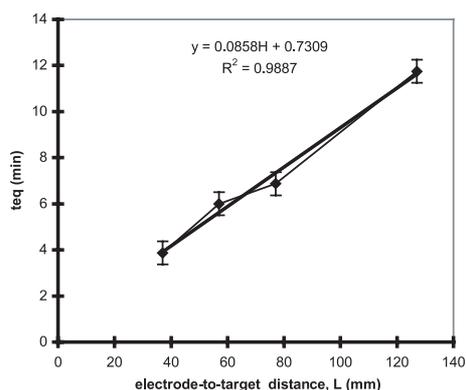
**Fig. 7.** Evolution of the “equivalent” time  $t_{eq}$  with the concentration of the target solution, for given working parameters [NaOH concentrations:  $10^{-3}$ ;  $2 \times 10^{-3}$  and  $5 \times 10^{-3}$  M]. Resulting correlation:  $t_{eq} = 699.23 \cdot C_{OH^-} + 0.8654$ ;  $r^2 = 0.9773$ .



**Fig. 8.** Evolution of the “equivalent” time  $t_{eq}$  with the reverse of the gas flow  $10^{-3}Q$  (liters per h), for given working parameters. Resulting correlation:  $t_{eq} = 11546/Q - 5.9738$ ;  $r^2 = 0.9882$ .

to electrolysis phenomena which are based on the Faraday’s laws (i.e., the number of transformed species is directly related to the electric charge) with the following restriction that electrolysis processes are usually performed either at fixed potential or at constant current intensity,

- let  $m_0$  refer to the number of hydroxyl ions added in the target solution and  $N_0$  be the number of active particles involved in acidification produced in the



**Fig. 9.** Evolution of the “equivalent” time  $t_{eq}$  with the distance  $L$  between the electrode neck and the surface of the liquid target, for given working parameters ( $t_{eq} = 0.0858H + 0.7309$ ;  $r^2 = 0.9887$ ).

discharge per unit time. It can be assumed that  $N_0$  is proportional to the plasma power in the energy range of our device, (see discussion in Sect. 4.1), hence to the current intensity. The  $N_0$  active species are transported to the liquid surface by the gas flow, so that  $L/v$  is their residence time in the gas phase, where  $L$  is the distance to the aqueous solution and  $v$  the gas flow velocity. On their way some of them are transformed into other (and useless) species, so they have a lifetime  $\tau$ . The flux of active species impinging at the surface and able to react with the target molecules is thus affected by the weakening factor  $\exp[-L/(v\tau)]$  inferior to unit. So, with proceeding time  $t$ , we get

$$n_0 = N_0(P)^* \exp[-L/(v^*\tau)]^* t$$

particles for acidification at the liquid surface. Neutralisation is then reached if  $n_0 = m_0$ , and occurs for  $t = t_{eq}$ .

This results in

$$t_{eq} = m_0 \{N_0(P)^* \exp[-L/(v^*\tau)]\}^{-1} \\ \sim [m_0/N_0(P)]^* (1 + L/v^*\tau)$$

since  $L/v \ll \tau$ , which accounts for experimentally observed results.

#### 4.4 Relevant model to account for the acid effect

The experimental results satisfactorily agree with the consequences of a very simplified model, which can thus be considered as a first step in modelling the plasma treatment of liquids, and limited to non chemical considerations. The reported results are also an easy to check set of tests to appreciate the chemical efficiency of a gliding arc reactor.

The species present in the plasma and considered as responsible for the acid effect are the nitrogen oxides, among which the most important is NO, which was incidentally identified from emission spectroscopy analysis [7].

The overall reactions then involve air nitrogen and oxygen as the starting species:



We may then consider that the formation of protons takes place at the gas-liquid interface, and that protons and the matching nitrates drift to the bulk solution. This assumption is backed up by two arguments: (i) the occurrence of nitrate ions in the target solution exposed to humid air plasma and (ii) similar discharges in humid oxygen induce no acid effect.

The second assumption is related to NO and in connection with its quantification. The overall reaction (1) was thoroughly studied; it involves the occurrence of  $N$  atoms, which come from electron impact on  $\text{N}_2$  inducing the dissociation of the molecule. Hence, the more important is the electric current (or the electron flow), the higher is the proton concentration. We have then a linear correlation between the quantity of electricity involved in the discharge and the number of formed active species, i.e., the protons in the present case.

#### 4.5 Attempts of modelling the liquid-plasma interaction

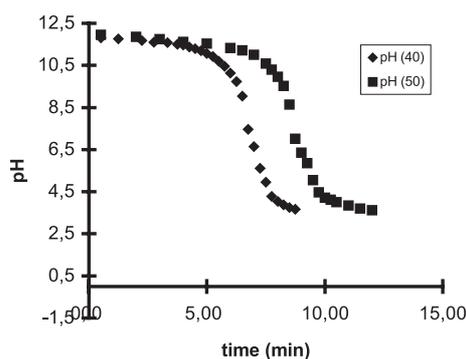
We intend to realise specific reactions in solution with increased yield, by selecting suitable activated species. These species present different reactivity, as illustrated by the singlet and triplet  $\text{O}_2$  molecules and also by the different reduction potentials of the  $^{\circ}\text{NO}/\text{NO}^-$  systems: that involving the triplet state is by 740 mV higher than that of the singlet one. Unfortunately, we are still unable to do so with the available electric sources.

It is assumed as a first approximation that all the active species are formed in the gas phase with a number directly related to the power of the discharge and that they react at the liquid surface with the solute molecules. A simple model is given [22].

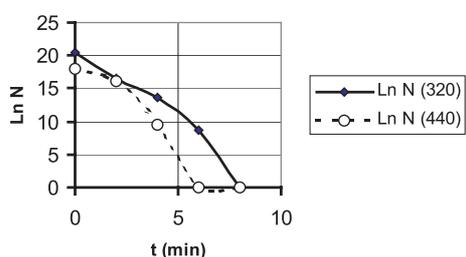
#### 4.6 Reaction orders in solution

A simplified mechanism results from the above considerations.

- For large concentrations of solute (or for pure solvent),  $C_M$  remains nearly constant, and the kinetic rate only depends on the impinging flux of A at the surface. Then, the reaction becomes a zero-order mechanism in M: the rate is then constant for given working conditions, and depends on the current intensity of the discharge.
- For small concentrations of solute M (or towards the end of the reaction), the limiting species of the reaction are then M, which drift to the surface by diffusion from the bulk solution. The kinetics is governed by diffusion process and obeys a first-order law.



**Fig. 10.** Influence of the electrode length on the “equivalent time”  $t_{eq}$ . The considered electrode lengths are respectively 40 and 50 mm.



**Fig. 11.** Plasma inactivation of exponentially growing *E. Coli* (strain MG 1655). [Working conditions  $L = 120$  mm;  $Q = 320$  and  $440$  L/h.]

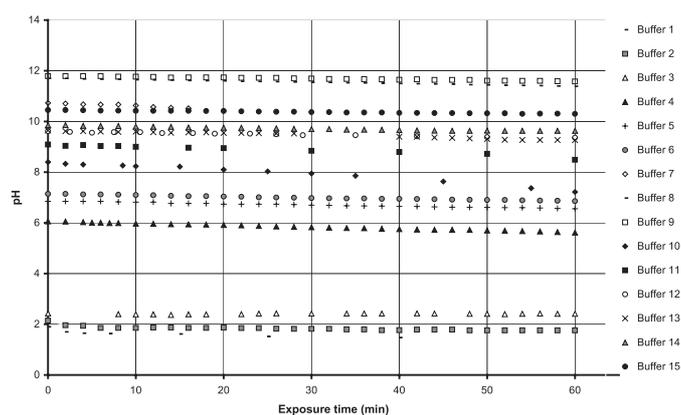
Changes in the kinetic law were experimentally confirmed. For example the degradation of spent non aqueous solvents, such as tributylphosphate, obeys a zero-order kinetic law except towards the end of the reaction, when the liquid surface becomes poor in target molecules [22]. Treatment of alkaline cyanide solutions also showed the matching couple of kinetic behaviours according to the starting concentration in  $CN^-$  ions [25].

## 5 Acidity buffers

All the above reported examples underline the acid effect of the plasma treatment by electric discharges in humid air, in connection with oxidation phenomena. We must point out at the juncture that a similar discussion would hold on considering reducing effects, provided the plasma gas be modified, for example by using electric discharges in hydrogen or in hydrocarbon vapours.

As previously mentioned, a number of chemical reactions need a sharp control of acidity. Plasmachemical oxidation is thus often accompanied by acidifying effects when performed in humid air. It is thus necessary to fix acidity to control the matching kinetic rates. This means that acidity buffers should be used to operate at fixed acidity of the target solution.

Using acidity buffers is a convenient way to control acidity, and the technique may be suitable for plasma treated aqueous targets, provided side reactions do not occur. Most of usual buffers are however unsuitable, since



**Fig. 12.** Evolution of the  $pH$  of selected buffer solutions (see Tab. 3) with the exposure time to the plasma (standard operating conditions: buffer solution 50 mL; nozzle diameter 1 mm; air flow rate  $Q = 975$  L per h; distance  $H = 80$  mm).

either the acid or basic forms may be oxidised (or reduced). We have thus to consider chemical compounds that hardly oxidise or degrade under plasma conditions. This feature is realised with phosphoric, carbonic or boric acid derivatives, which involve the elements P, C and B at their maximum usual oxidation number.

We thus prepared a series of concentrated solutions of acids and matching base, in the ratio 3/1; 1/1 or 1/3 to enlarge the range of available buffers. The stirred solutions (50 mL) were exposed to the plasma for 1 h and the  $pH$  was measured every 2 minutes to follow the acidity increase. A general  $pH$  decrease by less than 0.5  $pH$  units per hour was generally recorded, which satisfactorily illustrates the buffer effect.

Additionally, the plots  $pH$  vs.  $t$  (min) are reasonably linear decreasing functions over 1 h treatments (Fig. 12).

Other acid/base ratios than 3/1, 1/1 and 1/3 may be prepared as valuable buffers, provided that the buffer index (or buffer capacity  $dC_{Base}/dpH = -dC_{Acid}/dpH$ ) be high enough. Efficient buffers may be experimentally realised in a  $pH$  range of about 2 units around the  $pK_a$  value of the relevant acid/base system. For very high or very low acidity, one can use the so-called pseudo-buffers that are only concentrate solutions of strong base or acid. We have now a reliable tool for fixing and controlling acidity in all levels of the acid/base scale in water.

## 6 Matching oxidising properties

### 6.1 Treatment of liquids

Additionally to the acid changes of the solutions exposed to the plasma, a matching reaction is identified and also concerns solutes, which may be oxidised. Evidence lies in the formation of  $NO_3^-$  ions in the solution which result from oxidation of molecular nitrogen  $N_2$  present in air. Oxidation phenomena are identified and quantified in the same way as the acid effects. They are mainly attributed

**Table 3.** Selected examples of available buffers.

Nr	Buffer composition	$pH$ for $t = 0$ min	$pH$ for $t = 60$ min
15	HCO <sub>3</sub> Na (0.05 M) + CO <sub>3</sub> Na <sub>2</sub> (0.15 M)	10.45	10.3
14	HCO <sub>3</sub> Na (0.1 M) + CO <sub>3</sub> Na <sub>2</sub> (0.1 M)	9.86	9.62
13	HCO <sub>3</sub> Na (0.15 M) + CO <sub>3</sub> Na <sub>2</sub> (0.05 M)	9.65	9.25
12	HBO <sub>2</sub> (0.05 M) + BO <sub>2</sub> Na (0.15 M)	9.62	9.36
11	HBO <sub>2</sub> (0.1 M) + BO <sub>2</sub> Na (0.1 M)	9.09	8.49
10	HBO <sub>2</sub> (0.15 M) + BO <sub>2</sub> Na (0.05 M)	8.4	7.22
9	HPO <sub>4</sub> Na <sub>2</sub> (0.05 M) + PO <sub>4</sub> Na <sub>3</sub> (0.15 M)	11.8	11.6
8	HPO <sub>4</sub> Na <sub>2</sub> (0.1 M) + PO <sub>4</sub> Na <sub>3</sub> (0.1 M)	11.7	11.4
7	HPO <sub>4</sub> Na <sub>2</sub> (0.15 M) + PO <sub>4</sub> Na <sub>3</sub> (0.05 M)	10.73	10
6	H <sub>2</sub> PO <sub>4</sub> Na (0.05 M) + HPO <sub>4</sub> Na <sub>2</sub> (0.15 M)	7.14	6.86
5	H <sub>2</sub> PO <sub>4</sub> Na (0.1 M) + HPO <sub>4</sub> Na <sub>2</sub> (0.1 M)	6.85	6.56
4	H <sub>2</sub> PO <sub>4</sub> Na (0.15 M) + HPO <sub>4</sub> Na <sub>2</sub> (0.05 M)	6.06	5.62
3	H <sub>3</sub> PO <sub>4</sub> (0.05 M) + H <sub>2</sub> PO <sub>4</sub> Na (0.15 M)	2.43	2.41
2	H <sub>3</sub> PO <sub>4</sub> (0.1 M) + H <sub>2</sub> PO <sub>4</sub> Na (0.1 M)	2.16	2
1	H <sub>3</sub> PO <sub>4</sub> (0.15 M) + H <sub>2</sub> PO <sub>4</sub> Na (0.05 M)	1.9	

to the occurrence of °OH radicals, which are also identified by emission spectroscopy analysis of the plasma. The normal potential of the °OH/H<sub>2</sub>O system is close to 2.8 V, one of the highest potential values under that of the fluorine system. The very strong oxidising power of °OH justifies its use in advanced oxidation processes for pollution abatement of aqueous solutions.

The oxidising effect is observed for a variety of solutes exposed to humid oxygen-containing plasmas, i.e., air or oxygen plasmas, which confirms that °OH radical is definitely responsible for the relevant chemical effect.

The oxidation reduction potential of the °OH/H<sub>2</sub>O system depends on the acidity and decreases by 60 mV per  $pH$  unit (at ambient temperature). The  $pH$  dependence of the systems may explain why thiourea is degraded in acid medium and not in basic solution [26]. Also, plasma degradation of chlorocarbons leads to the formation of chlorine or chloride according to the low or high  $pH$  value, which agrees with the well known dismutation of chlorine in basic medium. The influence of acidity on the degradation rate is also illustrated by the treatment of 20 mL samples of 1.1.1.-trichloroethane dispersed in 150 mL of aqueous phase: the degradation is much faster in strongly basic (NaOH 1M) or buffered ( $pH = 8.3$ ) medium than in acidic (HNO<sub>3</sub> 1M) medium [27].

## 6.2 Application to the corrosion of metals

The occurrence of a thin water layer at the surface of materials is involved in the corrosion phenomena which concern metallic materials and in the degradation of organic polymers exposed to a natural air plasma, since the relevant chemical reactions involve the plasmachemistry of an aqueous surface. Selected examples are given as suitable illustration.

Exposure of aluminium plates as the grounded electrode in a negative corona discharge [28] showed that corrosion phenomena take place at the anode electrode. A new examination of the experimental results shows that oxidation phenomena occur as they usually do for classical corrosion processes in solution. Aluminium plates oxidise while other species reduce at the cathode at the same time. In the present case, and due to the presence of a thin water layer at the surface of the material, the protons may easily reduce to hydrogen gas.

Gliding arc treatments of metals in natural air also result in the formation of oxide layers such as for copper, zinc or iron [29,30]. Stainless steel is also affected by the plasma treatment in humid air: short treatments by few minutes induce a steep fall in the contact angle with water droplets [31] which confirms that the surface acidity largely increases.

*All these features are easily related to the increase in the Bronsted acidity, which favours corrosion phenomena, by moving the reduction branch of the proton reduction towards positive potentials in the characteristic curve current density  $j$  vs. potential  $E$ , and thus increasing the corrosion current.*

## 6.3 Bio-decontamination

A forthcoming application of the non-thermal plasmas is given by bio-decontamination. Most of the basic human activities and industries require products of improved quality, especially for food and pharmaceuticals industries. Bacteriae were thus the favourite targets for various decontamination techniques, long before the plasma techniques became available. The standard techniques mostly used for years involved oxygen derivatives, e.g., ozone or hydrogen peroxide, which easily form in an electric discharge.

The first reported works dealing with plasma bacteria interaction were performed with low pressure plasma device, and some industrial apparatus were evaluated in hospitals. More recently, a limited number of papers and communications [32–36] were devoted to the use of atmospheric plasmas, and especially the corona discharge, as direct sources of lethal stress for the bacteria. Industrial pilots device were also built for industrial applications purpose.

Exposure of a bacteria to a plasma source may induce a drastic stress. Apart from the thermal effect, which is not concerned in the case of using non thermal plasmas, three major sources of stress must be considered: the acid and the oxidising effects, which are chemical stresses, additionally to the electric field effect, which actually induces a physical stress.

Successful experiments performed with a gliding arc device [37–39] allowed us to discard the thermal and acid effects, since we exposed to the plasma a thermostatted cell filled with a buffered solution of *E. Coli*. The influence of the electric field is probably limited, because the target solution is disposed out of the electrode gap, in a low electric field area. Complete inactivation of *E. Coli* (Fig. 11) is realised within a few minutes for exponentially or steady (stationary) growing conditions of the bacteria. Our results relevant to the model bacteria *E. Coli* are confirmed by the behaviour of other bacteria, such as *St. Epidermidis* or *Erwinia cc* [39] exposed to a plasma treatment; they are thus strong arguments in favour of the determining influence of the oxidising neutral activated species of the plasma, additionally to other proposed mechanisms [34].

## 7 Further applications and conclusion

This study first reports that a very simple series of tests based on *pH* measurements allows to account for the chemical efficiency of a plasmachemical reactor involving an electric discharge in humid air.

Apart this important result, numerous examples of acidity dependant reactions are mentioned, most of them involve the plasma degradation of organic pollutants. For most of the cases, the use of buffers is necessary to control both the process and the kinetics of organic pollutant abatement. Preparing available buffer solutions is easily feasible for the treatment of a number of industrial solutes, such as dyes or waste solvents and needs using selected oxidised acid/base systems.

Applied research must be undertaken and developed to optimise the acidity conditions for removing such pollutants. Incidentally, the control of acidity is essential when highly toxic chemicals are concerned (e.g., the plasma degradation of cyanide ions), either as target solutes or as potential intermediates.

Also, the biochemical applications of non thermal plasma are just coming to light and appear to be a promising field of application for the technique. Since life media are always buffered media, we should consider that any investigation in the field needs the use of acidity buffers to provide reliable results.

Further basic applications are also important: for example, the plasma degradation of urea and thiourea can be considered as simple models for the plasma treatment of proteins. Additionally, possible applications of the plasma treatments to the degradation of viruses can easily be imagined and considered as a valuable aim: the plasma treatments should provide a cheap and easy way to clean syringes and other surgery tools, and consequently to limit the spreading of diseases.

The reported results show that we have now the opportunity to control acidity of plasma treated solutions. With such a tool, we can afford investigating pH-dependant reactions, and in particular reactions involving organic compounds or biochemical reactions. This is an essential feature in the scope of applying plasma treatments to microbiological remediation.

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## References

1. J. Jacq, *Electrochim. Acta* **12**, 1 (1967)
2. H. Lund, M.M. Baizer, in *Organic Electrochemistry* (M. Dekker, New-York, 1991), Chap. 2
3. H. Lesueur, A. Czernichowski, J. Chapelle, *Fr. Pat.* 2 639 172 (1988)
4. G. Fillon, A. Czernichowski, H. Lesueur, *Fr. Pat.* 90-11278 (1990)
5. P. Jorgensen, J. Chapelle, A. Czernichowski, K. Meguernes, *Fr. Pat.* 2 620 436 (1987)
6. B. Benstaali, B.G. Chéron, A. Addou, J.L. Brisset, *Proc. ISPC-14 (Praga, Czech Rep., 1999)*, edited by H. Hrabovskii, M. Konrad, V. Kopecki, pp. 939–944
7. B. Benstaali, P. Boubert, B.G. Chéron, A. Addou, J.L. Brisset, *Plasma Chem. Plasma Process.* **22**, 553 (2002)
8. J. Velikonja, M.A. Bergougnou, G.S.P. Castle, W.L. Cairns, I.I. Inculet, *Ozone Sci. Eng.* **23**, 467 (2001)
9. R. Peyrous, *Ozone Sci. Eng.* **12**, 41 (1990)
10. R. Peyrous, R.M. Lapeyre, *Atmos. Environ.* **16**, 959 (1982)
11. W.L. Morgan, M. Jacob, E.R. Fisher, *Proc. ISPC-12 (Minneapolis, USA, 1995)*, pp. 741–746
12. E.M.F. Van Veldhuizen, *Electric Discharges for Environmental Purposes: Fundamentals and Applications* (Nova Science Pub., New York, 2000)
13. J.P. Hoare, in *Standard Potentials in Aqueous Solution*, edited by A.J. Bard, R. Parsons, J. Jordan (M. Dekker, New-York, 1985), Chap. 4, p. 59
14. C. Fabyan, *Monatsh. Chem.* **106**, 513 (1975), quoted in [13]
15. J.L. Brisset, A. Doubla, J. Amouroux, *Proc. ISPC-8 (Tokyo, Japan, 1987)*, pp. 1793–1798
16. J.L. Brisset, A. Doubla, J. Amouroux, *Rev. Int. Hautes Temp. Réfract. Fr.* **26**, 199 (1990)
17. J.L. Brisset, J. Lelièvre, A. Doubla, J. Amouroux, *Analisis* **18**, 185 (1990)
18. F. Abdelmalek, A. Addou, J.L. Brisset, to be published (2005)
19. J.T. Herron, D.S. Green, *Plasma Chem. Plasma Proc.* **21**, 459 (2003)

20. J.A. Roth, D.E. Sullivan, *Ozone Sci. Eng.* **5**, 37 (1983)
21. N.V. Alexeev, A.V. Samokhin, E.V. Troiskaya, A.N. Belivtsev, V.T. Zhavoronkova, *Proc ISPC-16 (Taormina, Italy, 2003)*, p. 761
22. D. Moussa, J.L. Brisset, *J. Hazard. Mat. B* **102**, 189 (2003)
23. D. Moussa, J.L. Brisset, S. Barguès, *Fr. Pat.* 98-13439 (1998)
24. E. Hnatiuc, in *Procédés électriques de mesure et de traitement des polluants*, edited by E. Hnatiuc coord. (Tec&Doc, Paris, 2002), Chap. 10
25. F. Moras, J.L. Brisset, *Proc. 4th Int Congress GRUTTEE (Limoges, France, 2001)*, pp. 231–234
26. A. Doubla, E. Tsagou-Sobze, D. Moussa, R. Burlica, E. Hnatiuc, J.L. Brisset, *Rev. Sci. Eau* (submitted)
27. J. Fanmoe, J.-O. Kamgang, D. Moussa, J.-L. Brisset, *Phys. Chem. News* **14**, 1 (2003)
28. M. Goldman, R.S. Sigmond, *J. Electrochem. Soc.* **132**, 2842 (1985)
29. N. Bellakhal, J.L. Brisset, *Proc. 7th Int. Symp. High Pressure Low Temp. Plasma Chem. "Hakone VII" (Greifswald, Ge, 2000)*, edited by H.E. Wagner, J.F. Benke, Vol. 2, pp. 460–464
30. B. Benstaali, J.M. LeBreton, A. Addou, B.G. Chéron, J.L. Brisset, *Phys. Chem. News* **5**, 87 (2002)
31. Y. Rutter, Rapport de DESS, Université de Bretagne Sud, 2002
32. M. Yamamoto, N. Nishioka, M. Sadakata, *Proc. ISPC-15 (Orléans, France, 2001)*, edited by A. Bouchoule, J.M. Pouvesle, A.L. Thomann, J.M. Bauchire, E. Robert, Vol. 2, pp. 743–748
33. V. Yu. Bazhenov, A.I. Kuzmichev, V.I. Kryzhanovski, I.L. Milno, A.V. Ryabtsev, I.A. Soloshenko, V.A. Khomish, V.V. Tsiolko, A.I. Schredin, *Proc. ISPC-15 (Orléans, France, 2001)*, edited by A. Bouchoule, J.M. Pouvesle, A.L. Thomann, J.M. Bauchire, E. Robert, Vol. 7, pp. 3005–3010
34. M. Laroussi, J.P. Richardson, F.C. Dobbs, *Proc. ISPC-15 (Orléans, France, 2001)*, edited by A. Bouchoule, J.M. Pouvesle, A.L. Thomann, J.M. Bauchire, E. Robert, Vol. 2, pp. 729–734
35. A. Soloshenko, V.V. Tsiolko, V.A. Khomich, V. Yu. Bazhenov, A.V. Ryabtsev, A.I. Shchedrin, I.L. Mikhno, *Proc. ISPC-15 (Orléans, France, 2001)*, edited by A. Bouchoule, J.M. Pouvesle, A.L. Thomann, J.M. Bauchire, E. Robert, Vol. 2, pp. 735–742
36. M. Moisan, J. Barbeau, S. Moreau, J. Pelletier, M. Tabrizian, L'H. Yahia, *Int. J. Pharm.* **221**, 1 (2001)
37. H. Vitrac, J. Guespin, J.L. Brisset, *Proc. 7th Int. Symp. High Pressure Low Temp. Plasma Chem. "Hakone VII" (Greifswald, Ge, 2000)*, edited by H.E. Wagner, J.F. Benke, Vol. 2, pp. 393–397
38. M. Moreau, J.M.G. Feuilloley, N. Orange, J.-L. Brisset, *J. Appl. Microbiol.* (in press)
39. J.O. Kamgang, R. Briandet, Y. Rutter, J.M. Herry, M.N. Bellon-Fontaine, J.L. Brisset, *Proc. Congrès de la S. Fr. Biochim. (Bordeaux, Fr., 2004)*