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Chemical Reactivity of Discharges and Temporal Post-Discharges in Plasma Treatment of Aqueous Media: Examples of Gliding Discharge Treated Solutions

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Environmental applications of electric discharges are being considered increasingly more often: they imply the chemical properties of the activated species generated in and by the discharge. An overview of the resulting chemical effects is presented, based on rationalized classification, i.e., acid—base effects, oxidizing properties, complex forming reactions, and radical reactions. The gliding discharge is considered to be a specifically suitable plasma source for the treatment of liquids for pollutant abatement in the scope of sustainable environment, and this justifies an overview of the chemical properties. Special emphasis is devoted to temporal post-discharge reactions (TPDRs), which occur when the target is no longer exposed to the plasma source, and several typical examples are detailed. These recently evidenced TPDRs seem to present some general character. They are the key parameters to estimating the efficiency of a discharge treatment; they also have major technical and economical importance for the application of the plasma treatment to pollutant and/or micro-organism abatement at atmospheric pressure and quasi-ambient temperature.

1. Introduction

Electric discharges occupy a special place among the new technologies developed in the scope of sustaining development, because they allow one to create active species that are able to react with selected target molecules. This feature is specially interesting for the destruction of pollutants or hazardous molecules.

Among the new emerging techniques available, the ones operated at atmospheric pressure are largely favored for their ease of use and simplicity. The use of electric discharges is probably one of the most promising techniques available to solve environmental problems. We will focus on discharges in gases at atmospheric pressure used for pollutant abatement in liquid targets, and we will especially address gliding discharges, with an emphasis on the huge range of their possible applications. In addition, some recently evidenced features (i.e., the postdischarge phenomena) that make specific devices particularly attractive will be detailed.

Electrical discharge in gases is the source of electrochemical reactions: therefore, they are governed, as any electrochemical process would be, by (i) the nature of the (active) electrode(s) and its (their) interaction with the surrounding medium, (ii) the nature and composition of the medium (i.e., the fed gas in the

present case; the aqueous and nonaqueous solvent for electrochemistry in liquid media), (iii) the particular properties of the target molecules (i.e., organic compounds dispersed in an aqueous phase for the considered cases), and (iv) the electric energy displayed to the electrochemical reactor. These points will be considered hereafter in the scope of gas discharges.

A matching consequence is the occurring continuity between classical electrochemistry¹ in the liquid phase and the various types of electrical discharges in gases. This feature is illustrated with the characteristic plots of current i versus applied potential U, which underlines the relevant character of each type of discharge.

On applying a weak potential drop (usually <5-6 V) between two electrodes that are usually dipped in a conducting solution, classical electrochemical phenomena occur and a current of limited intensity (<1 A for laboratory work) is observed, because of the electrode material or solvent oxidation. These phenomena will not be examined anymore, although they account for the first and second principles that have been previously mentioned and are relevant to the interaction between the active conductor and its environment. An increase in the potential drop U applied to the electrodes induces changes in the current-versus-potential drop (i-U) characteristic plot (see Figure 1): in the range of 100 V < U < 600 V, a transition between classical electrolysis and electric discharges in gas (due to local heating of the solvent) occurs.

The electrical discharges in gases are obtained for higher applied potentials and the characteristic U vs i plot (see Figure 2), which are roughly independent of the gas. We are then to focus on discharges in gases at atmospheric pressure and especially on those used for pollutant abatement in liquid targets.

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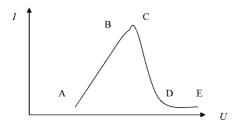


Figure 1. Characteristic current—voltage plots (arbitrary units) for the transition between electrochemistry and electric discharges: \overline{AB} , conventional electrochemistry; \overline{BC} , current intensity saturation; \overline{CD} , instability zone; and \overline{DE} , electrode effects region.

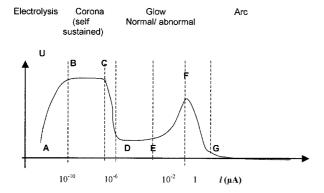


Figure 2. Typical U vs i plot, showing a rough classification of the discharge.²

An increase in the applied potential leads to several domains, which are illustrated in Figure 2:

- (1) The low applied potential domain is the field of electrochemistry in aqueous, nonaqueous, or molten salts media. In the matching AB zone of the characteristic plot, the voltage U rapidly increases with the current intensity i and is almost a linear function $U = f(\ln i)$. This domain is related to the oxidation wall observed in classical solution electrochemistry. The energy transferred to electrochemical reactions is limited, and the degradation process of a solute molecule is usually governed by electrolysis laws.
- (2) The Townsend or Corona discharge (zone BC), where the self-sustained current increases without a significant increase in the voltage drop;t this area is often called the "Townsend plateau".
- (3) A steep transition zone (CD) to the glow discharge for high current intensities, where sparks occur.
- (4) The glow discharge identified by Okazaki et al.³ for gases at atmospheric pressure. It involves (i) the normal glow discharge (DE) for $U \approx 200$ V and current intensity (1–10 mA) and (ii) the abnornal glow discharge (EF), which corresponds to a large increasing voltage with i.
- (5) A transition zone (FG) from the glow discharge to the arc, which is a discontinuous process that is characterized by a steep decrease of the voltage with increasing current.
- (6) The arc domain (GH) for high current intensity values and rather low applied voltage close to the gas ionization potential.

Other discharges are identified and mainly developed for pollutant abatement purposes. Improved devices use pulse energy sources.

(1) For example, the dielectric barrier discharges in gases (DBDs) are usually corona or streamer discharges that have been fitted with an isolating membrane between the electrodes that acts as a separate compartment and prevents the reaction products from mixing.

Table 1. Electron Distribution in the External Orbital HOMO for different excited states of Dioxygen

	Energy		electron d	istribution	Lifetime		
species	kJ/mol	eV/mol	in HOM	O $(2\pi_{xy})$	in gas	in solution	
$O_2(^1\Sigma_g^+)$	156.9	1.63	-1-	-\-	7-12 s	10 ⁻¹² s	
$O_2(^1\Delta_g)$	94.4	0.98	↑↓		45 min	$4 \times 10^{-6} \text{ s}$	
$O_2(^3\Sigma_g^-)$	0	0	-1-	- ↑-			

(2) The electrohydraulic discharges involve one electrode disposed in the gas phase and the other(s) in the treated solution. An excellent review of this topic was recently published,⁴ and our intention is not to duplicate it. 4,5 However, these devices require special attention, because they illustrate the continuity between discharges burning in liquid media and in gas media. This large family of discharges involves contact glow discharge electrolysis (CGDE), which was explored by Sengupta et al.,6 Tezuka et al., Gao et al., and others; these devices are operated at limited voltage drops (~500 V). The active point electrode is placed just at the liquid surface, and the discharge occurs between the point electrode and the (conducting) liquid. Immersed corona or arc discharges also belong to this group of discharges. The phenomena are similar to those associated with discharges in gases, except that extra electrolysis phenomena likely occur at the electrodes and make the processes much more complex.

As developed below, we will focus on discharges depicted by the FG line, in the upper region close to the peak F. In this domain, one gets arc discharges with the relevant advantage of a rather important available energy, compared to the corona or glow discharges. The selected device of gliding discharge is actually a *quenched* plasma, which presents both the properties of a thermal plasma (for the gas composition) and those of a nonthermal plasma (i.e., the macroscopic temperature remains close to ambient, which enables to expose thermosensitive targets and even organic liquids to the discharge). The device used for the gliding discharge (or "glidarc") is described in the experimental section.

The third principle is related to the nature of the target molecules, which are mostly organic compounds. Their oxidizing degradation leads to carbon oxides and water, and their oxidation potential is usually limited (e.g., <0.5 V/NHE), so that the compounds are sensitive to strong oxidizers. They are also able to participate in specific chemical reactions.

The fourth basic principle involves energy. The energy amount displayed in the discharges that we are interested in is roughly <1000 kJ/mol ($\sim10 \text{ eV}$), so that only reactions that require low energies could be expected.

In particular, very low energy transfers induce a modified electron repartition on the external (highest occupied molecular orbital, HOMO) orbitals, which confer on the excited species new and particular chemical properties. This feature is illustrated by the oxygen molecule (Table 1): the electron-free $2\pi_{xy}$ HOMO of singlet oxygen enables this moiety to welcome an electron pair and, thus, act as a Lewis acid.

Gliding discharges in air allow O^+ and N^+ cations to form in the most energetic zone (i.e., at the minimum electrode gap, where arcing occurs). The relevant basic data have been gathered in Table 2.

The use of pulse sources is intended to display higher energy for a limited time; therefore, it enables more-numerous active species to form.

2. The Chemical Reactivity of the Activated Species

2.1. An Overview of the Plasma-Chemical Reactions. The various types of elementary plasma-chemical reactions are listed

Table 2. Enthalpy Values for Dissociation and Ionization of Air Major Components

		Enthalpy, ΔH°						
	(O_2	O N_2		N_2	N		
	kJ/mol	eV/mol	kJ/mol	eV/mol	kJ/mol	eV/mol	kJ/mol	eV/mol
dissociation: $M_2 \rightarrow 2M$ ionization: $P \rightarrow P^+ + e^-$	497 1167	5.2 12.1	1310	13.6	945 15.05	9.8 15.6	1400	14.5

Table 3. Typical Reactions Occurring in the Discharges (Plasma Phase)

type of reaction	reaction	type of reaction	reaction
Excitation		Recombination	
heavy particles	$A + B \rightarrow A^* + B$	atoms	$A + A + B \rightarrow B + A_2$
photon	$A + h\nu \rightarrow A^*$	e ⁻ /ion	$A^+ + e^- \rightarrow A + h\nu$
electron	$A + e^- \rightarrow A^* + e^-$	ion/ion	$A^- + B^+ \rightarrow AB$
transfer	$A + B^* \rightarrow A^* + B$	radicals	$R^{\circ} + H^{\circ} \rightarrow RH$
		ion/molecule	$A^+ + B \rightarrow AB^+$
De-excitation/photon	$A^* \rightarrow A + h\nu$	Charge transfer (oxidation-reduction)	$A + B^+ \rightarrow A^+ + B$
Ionization by:		Dissociation by:	
heavy particles impact	$A + B \rightarrow A^+ + B + e^-$	heavy particles impact	$A_2 + B \rightarrow A + A + B$
electron attachment	$A + e^- \rightarrow A^-$	electron attachment	$A_2 + e^- \rightarrow A + A + e^-$
photon impact	$A + h\nu \rightarrow A^+ + e^-$	photon impact	$A_2 + h\nu \rightarrow A + A + h\nu$
electron impact	$A + e^{-} \rightarrow A^{+} + 2e^{-}$	1	_

Table 4. Example of the Main Species Expected to Form in a Discharge in Humid Air

parent species	primary species	secondary species
O ₂ , N ₂ , H ₂ O	H, OH, O_x , N_y , and ions	H_xO_y , NO_x , HNO_2 , $HOONO$, HNO_3 , and ions

in Table 3: the involved species often concern activated species. These reactions are the key to the formation of secondary species.

2.2. Selectivity of the Chemical Effects of the **Discharges.** Table 3 shows that a huge number of reactions occur in a plasma treatment. One can guess that all of them will not be useful for the process.

A well-known aim for chemists is to perform specific reactions, i.e., reactions with 100% yields that allow all the treated molecules to be exclusively and completely transformed into the desired product. This is quite a hopeless attempt in plasma chemistry, because the distribution of the activated species is dependent on the energy provided to the source and on that which is transferred to the discharge, so that it is quite difficult to get specific reactions instead of competitive reactions. This explains two well-known features: (i) why 100% yields are so scarce for chemical reactions, even in conventional chemistry, and (ii) why plasma chemistry is so complicated and the forecasting of products is so risky.

The order of magnitude of the energy provided to the considered discharge is $\sim 6-9$ eV (450–900 kJ): this means that both activated species—radicals and ions—are usually formed in the discharge (see Table 2). The so-called *primary* species are able to react with other primary species or with the surrounding gas molecules. They form then *secondary products*, which may be able to react at the target molecules.

Table 4 lists some primary and secondary species in the case of a discharge over aqueous targets, and Table 5 report characteristics of some excited species.

The number of primary reactive species formed (that are able to react readily and directly or indirectly at the target) is dependent on the quantity of energy provided to the discharge. It is desirable to have the largest quantity of energy available to get an increased number of activated species and to shorten the treatment time as far as possible. However, energy is expensive and secondary effects such as thermal effects may

Table 5. Some Metastable States

		Excitation	Energy	
species	metastable state	(kJ/mol)	(eV)	lifetime (s)
N_2	$A^3\Sigma_u$ +	598	6.2	2
	$\mathrm{B}^3\Pi_\mathrm{g}$	695	7.2	1.7×10^{-6}
	$C^3\Pi_u$	1080	11.2	3.2×10^{-8}
Н	$2^{2}S_{1/2}$	984	10.2	1

be unexpected. High-energy plasma sources (e.g., plasma torches) are also expensive devices that require special care for isolating. A compromise must be found between the cost of the process and its theoretical and technical yields.

3. The Gliding Discharges: Experimental Section

3.1. Historical Background and Models. The gliding discharge (or "glidarc") was proposed by Lesueur et al. 10,11 and developed by Czernichowsky et al. 12-18 for the treatment of gases. For example, the gliding arc technique was used for removing hydrogen sulfide (H₂S)^{12,13} or N₂O¹⁴ from gases of industrial interest. The technique was also applied to the partial oxidation and conversion of light hydrocarbons 15,16 or more directly to the preparation of syngas 17,18 and the destruction of VOCs. 19

A model of the discharge was proposed some years later by groups led by Cormier and Fridman.^{20,21} Other models that focused on various aspects of the discharge were proposed, 22-27 to account for a complicated system generated by a simple device.

3.2. Description of the Basic Reactor. The reactor consists of two or more diverging conductors (see Figure 3), i.e., the electrodes, disposed in a gas at atmospheric pressure and connected to a suitable energy source, generally a HV transformer (5–10 kV). An arc forms at the narrowest gap between the electrodes. A gas flow directed along the axis of the electrodes gently pushes the arc feet along the conductors, so that its length increases until it breaks in a plasma plume, i.e., when the arc is short-circuited by a new one. Because the length of the arc (which is actually a thermal plasma) increases, the temperature of the ionized gas decreases, so that it becomes a nonthermal quenched plasma upon breaking into a plasma plume.



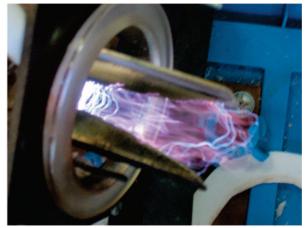


Figure 3. Gliding discharges with one pair of electrodes.



Figure 4. Standard 1-L reactor used for the degradation of tributylphosphate (TBP) in batch mode. The reactor is filled with a lower aqueous phase (red) and upper organic phase (colored blue), to illustrate the phase separation of TBP and water.

The basic reactor is fitted with a couple of electrodes. The reactor volume (a jacketed Pyrex cylinder, with an inner diameter of 7.7 cm) enables the batch treatment of aqueous solutions with a volume of 170 mL. We rapidly standardized a 1-L reactor (shown in Figure 4) (with an inner diameter of 100 mm, large enough to avoid wall effects) and fitted with a circulating system for work in circulating and batch modes. The circulating system is interesting, because it enables the treatment of very large volumes (see Figure 5).

Microreactors were also built and operated for bacterial inactivation. The useful volume of the Pyrex vessel was \sim 25 mL. The most-recent reactors involve a stainless steel cover to hold the electrodes.

In batch reactors, the liquid target was disposed in the reactor with its surface perpendicular to the gas flow. In circulating reactors, the target liquid was injected into the reactor between the electrodes by a nozzle, while, for gas reactors, the fed gas was enriched in volatile organic compounds (VOCs), to be destroyed before being injected.

3.3. Developments. 3.3.1. Development of the Reactor for Gas Treatment. Several people have worked on improving the gliding discharge reactor for gas treatments, and the first one among them was actually Czernichowski. He proposed

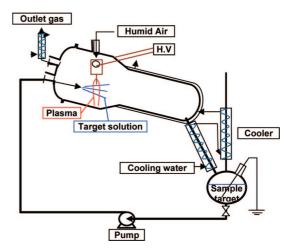


Figure 5. Sketch of a gliding discharge reactor used in circulating mode with the pump-fed liquid target introduced in the discharge.

using various settings of the electrodes and claimed using a three-phase, three-electrode device for removing H₂S¹¹ as early as 1993. He multiplied the number of stages and that of electrodes; for example, the Glidarc II was fitted with 4 stages and 16 electrodes. The device was successfully used for the destruction of VOCs.²⁸

Cormier and co-workers, ^{29–31} and, more recently, Fridman's group³² and others, ³³ concentrated on rotating discharges, i.e., a device which derives from the gliding discharge. They focused on the physical aspects of the discharge and its relative stability.

Pellerin et al.³⁴ and Burlica and Locke³⁵ examined bidimensional gliding arc reactors, both from the theoretical point of view³⁴ and from the chemical effects.³⁵ Burlica and Locke³⁵ compared the efficiencies of this system with that of a standard three-electrode reactor, in terms of mineralization, and concluded in favor of the standard reactor.

3.3.2. Development of the Electrical Source. In Poland, Stryczevska and Janowski^{36–38} worked for years to improve the plasma source (i.e., the source of electric energy transferred to the discharge and used for chemical purposes). They were also interested in three-electrode gliding discharge reactors.

Hnatiuc et al.^{2,39-41} were concerned with controlling the discharge by means of an extra power source and extra auxiliary electrodes. The system was also successfully used for rotating discharges.

3.4. Treatment of Condensed Targets. The device initially proposed by Czernichowski et al.10 was later adapted to the treatment of other targets, mainly liquids and solids. When the

arc is short-circuited, the resulting quenched plasma plume is in contact with the desired target, i.e., the liquid or solid surface and the activated species are then able to react at the surface.

- 3.4.1. Treatment of Solids. The plasma-chemical treatment of solids was related to the formation of barrier layers for protecting metallic materials from corrosion^{42–45} or to the modification of the surface properties of the substrate, 46,47 in view of modifying the adhesion properties of bacteria on organic polymers. Other works^{48–50} have reported on the treatment of solid catalyst particles.
- **3.4.2. Treatment of Liquids.** The treatment of liquids was mainly concerned with liquid waste treatments. It was mainly developed in France^{51–53} and Algeria.^{54–56} Now this easy-touse technique is developed in the United States, ^{57,58} the Far East, ^{59,60} Cameroon, ^{61,62} and eastern Europe ^{63–65} for pollutant abatement of wastewaters.

Several factors are implied in the process: the fed gas, the nature of the electrodes, and the nature of the target molecule dissolved as an aqueous solute.

The fed gas used is water-saturated air. Air is provided by a compressor and passes through a bubbling Duran flask that is filled with distilled water and becomes saturated. The choice of this gas is governed by economy and by the nature of the expected chemical properties of the mixture O₂, N₂, and H₂O. It is now accepted that the occurrence of water vapor (or a spray) enhances the efficiency of the treatment.

The target is an organic solute, the fate of which is dependent on its own chemical properties.

The electrodes are made of aluminum, but other metals or alloys were tested (e.g., copper, stainless steel, nickel).

In standard working conditions, the current intensity in a discharge driven by an Aupem-Sefli 9000 HV transformer (9000 V/100 mA under open conditions) is \sim 160 mA and the voltage drop is close to 600 V.

The reactor is fitted with a thermostatted jacket, which allows one to keep the temperature of the target solution close to ambient, and then kinetic rates reasonably favored by the very limited temperature increase. In case of volatile or flammable liquid targets, evaporation or fire risks may thus be limited using a cooling source.

Several reactor types were built and operated for batch and circulating operations. They were developed from the reactor devoted to the degradation of TBP^{51} (gas flow = 545 L/h). Other reactors were later operated in circulating mode, so that a quasi infinite volume could be treated. For batch treatments, the reactors (inner volume close to 1.2 L) were fitted with a stainless steel lid that also acted an as electrode holder. A scheme of a gliding arc reactor operated in circulating mode is presented in Figure 5.

Most recent developments concern the plasma source and the control of the discharge, which is made easier by an increased number of electrodes (e.g., two main electrodes and two auxiliary electrodes, as illustrated in Figure 6 or three main electrodes and one auxiliary electrode for control). These devices are described in ref 2 Other devices were tested for VOC treatment, 2,41 and particular rotating discharges 32,41 are allowed to operate with gas flows up to $6-8 \text{ Nm}^3/\text{h}$.

The electric source was also modified using a 5-6 kV HV commercial transformer delivering high current intensities, because this parameter seems to be essential, and an intensity control unit.

The standard techniques used for determining the solute concentration are classical analytical methods, such as HPLC, TOC or absorbance spectroscopy measurements and standard

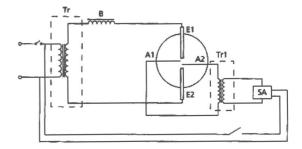


Figure 6. Sketch for a 2 + 2 reactor (two main electrodes (E1 and E2) and two auxiliary or control electrodes (A1, A2)). Tr denotes a AUPEM type-HV (high voltage) transformer and SA indicates an auxiliary source.² (Reprinted from ref 2. Copyright 2002, Tec & Doc, Paris.)

methods in microbiological analysis, e.g. plate numeration of bacterial population.

4. The Chemical Effects of the Species Formed in the Discharge and Their Control

The parent gaseous species are provided by the ambient gas when no discharge is switched on. For a reactor operated with humid air, these species are O_2 , N_2 , and H_2O .

The primary species are formed in the burning discharge: they are occasionally able to react at the target. However the major effect of the plasma treatment of a target comes from the interaction of secondary species with the target molecules.

These secondary species result from reactions involving primary species only or primary species and parent species.

The chemical effects induced by the discharge and concerning the solutes depend on the activated species directly or indirectly formed in the discharge, i.e., the primary and secondary species.

4.1. The Primary Species. Spectroscopy emission analysis demonstrated^{66–68} that the most numerous species formed in the discharge in humid air are NO and OH radicals. Their distribution is obviously dependent on the sampling position.

At the neck (which corresponds to the smallest electrode gap and the largest energy transfer to the ambient gas), the discharge actually behaves as a thermal plasma and O+ and N+ are present⁶⁸ in large quantities but no NO band is observed.

OH radical results from the decomposition of H₂O by electron impact, which also yields H:

$$H_2O + e^- \rightarrow H + OH + e^- \tag{1}$$

Thus, one can expect that the formed species exhibit antagonist properties, related to the respectively reducing and oxidizing character of these moieties.

4.2. The Secondary Species. In other respects, analysis of the quenched plasma plume shows no atomic line. The second positive system of N₂ (C³ $\Pi_u \rightarrow B^3\Pi_g$) and NO (A² $\Sigma^+ \rightarrow X^2\Pi$) are predominant. 66 Also, the molecular ion N_2^+ is detected but is not present in noticeable quantity. OH, NO, N_2^* , and N_2^+ are clearly identified in the plume. These latter species will come into contact with the surface of the liquid target and react with the solute molecules present at the surface.

In addition, the group of the secondary species is completed by the reaction products of some known reactions, among numerous others:

$$H_2O + e^- \rightarrow H + OH + e^- \tag{1}$$

$$H + NO \rightarrow N + OH$$
 (2)

or

$$H + NO \rightarrow O + NH \tag{3}$$

Figure 7. Typical pH vs t^* plots for the plasma treatment of 120 mL of 6 \times 10⁻³ M NaOH solutions in dry air for various current intensities: the time $t_{\rm eq}$ required to exactly neutralize the number of OH⁻ anions in excess in the target (and, thus, to get neutrality at pH 7) decreases as the intensity of the current increases for a given energy range.

(depending on the temperature range)

$$N + NO \rightarrow N_2 + O$$
 (at low temperature) (4)

$$O + NO (+M) \rightarrow NO_2 (+M)$$
 (5)

$$OH + NO(+M) \rightarrow HONO(+M)$$
 (6)

(which is a reaction that is largely involved in atmospheric chemistry)

$$O_2H + NO \rightarrow OH + NO_2 \tag{7}$$

(which is a key reaction in troposphere chemistry)

$$OH + NO2 (+M) \rightarrow HNO3 (+M)$$
 (8)

$$OH + NO_2 \rightarrow HO_2 + NO$$
 (9)

This set of reactions accounts for the formation of acid species HONO and NO_2 (and, hence, the derived nitric acid). In addition, the combination of two OH radicals leads to hydrogen peroxide.

- **4.3. The Main Chemical Properties of the Secondary Species.** The chemical reactions induced by the discharge in the solution are classified according to the usual scheme:
- (1) Acid effects and the matching presence of NO_2^- and NO_3^- in the solution,
- (2) Oxidizing effects due to the occurrence of OH and NO derivatives,
- (3) Complex formation reaction of H_2O_2 with Ti(IV) or V(V) ions, and
 - (4) Radical reactions involving OH and NO.

Representative reactions of each type have been identified in aqueous targets. $^{69-71}$

4.3.1. The Acid Effect. The acidic effect was first evidenced and carefully studied by Moussa et al., ^{69,70} because of its key importance in the control of almost all the organic oxidation—reduction reactions. ⁷¹ The study was extensively completed with the behavior of efficient acidity buffers, ⁷⁰ the pH of which decreased by 0.2 pH units only for 1 h of exposure to the discharge, which enables one to achieve many plasma treatments at stabilized pH.

The exposure of strong base solutions to the discharge induced a large acidity increase, which is caused by a decrease in pH (pH $\approx -\log C_{\text{H}^+\text{aq}}$) by several units, e.g., ~ 8 pH units. The relevant plot was that of the titration of a strong base by a strong acid (Figure 7). This is evidence that protons are formed in the liquid phase and neutralize the hydroxyl ions present as the target before being in large excess. The exact neutralization is obtained for a particular exposure time $t_{\rm eq}^*$ for which, the pH of

the solution is neutral (pH 7). Thus, an essential parameter to check the efficiency of the reactor is the "equivalent" exposure time t_{eq}^* needed to exactly neutralize the starting OH⁻ concentration, i.e., to get neutrality (pH 7).

Similar results are obtained with humid and dry air (see Figure 7). This may result from water evaporation and vapor stripping, which saturate the local atmosphere.

The influence of the working parameters on $t_{\rm eq}$ was considered. The variable $t_{\rm eq}$ is linearly related to (i) the quantity of OH⁻ present in the treated target (which means that, for given volume of the solution, with all other parameters constant, $t_{\rm eq}$ is proportional to the number of introduced hydroxyl ions OH⁻, and for a given OH⁻ concentration, $t_{\rm eq}$ is proportional to the volume of treated solution), (ii) the distance between the electrodes and the target, (iii) the square diameter of the input gas nozzle, (iv) the reverse of the input gas flow (Q) over a large range of Q values (given in units of L/h), and (v) the current intensity of the discharge (for intensities of <0.5 A).

The influence of the electrode gap was also considered from the point of view of electric power^{69,70} and the thickness of the electrodes. The plasma treatment is also characterized by the increase in the concentration of nitrite and nitrate ions in the solution, which appear as the matching ions to the protons. Numerous works account for an increase in the conductivity of the treated solution with the exposure time t^* . Thus, the parent species N_2 and the primary species NO can be considered to be basically responsible for the acid effect.

4.3.1.1. Acidity Buffers. A large number of organic reactions, and, in particular, oxidation-reduction reactions, involve the proton concentration in the reaction medium. Hence, the reaction rate is controlled by acidity, because the formal standard potential E'° is often dependent on pH for organic systems. It is thus essential to control acidity when organic compounds are concerned, which is the case for organic pollutants abatement, as well as the inactivation of micro-organisms. A series of acidity buffers was proposed:⁷⁰ they involve oxidized anions, so that they are not affected by the strong oxidizing power of the plasma. Phosphates, borate, and carbonate anions were selected to cover the entire range of pH available in water. The pH of the selected buffers did not vary by more than 0.4 pH units within 1 h of exposure to the discharge (see Figure 8 and Table 6), i.e., a time long enough to achieve the degradation of the dispersed wastes. Moreover, this allows one to control the degradation kinetics of organic compounds by keeping the pH of the medium quasi-constant for a long period.

4.3.2. The Oxidizing Effect. This effect is essential for applications relevant to both pollutant and micro-organism abatement, and, in particular, to environmental application. It is attributed to the specific character of OH radicals formed in the discharge and present in the plasma plume, because the OH–H₂O system has the second standard oxidation potential after the fluorine/fluoride system (see Table 7). This potential is much higher than that of the O₂–H₂O water system and a huge majority of the organic systems. This is the basic reason why the OH radical is involved in the advanced oxidation processes.

Secondary species, such as H₂O₂, also participate to the collective oxidizing power of the plasma.

Because the oxidation potential of the polluting organic compounds is usually low and scarcely positive, strong oxidizing chemical agents such as chlorinated compounds, ozone, or hydrogen peroxide have been selected for their ability to degrade pollutants for a long time. The choice of the oxidizer is

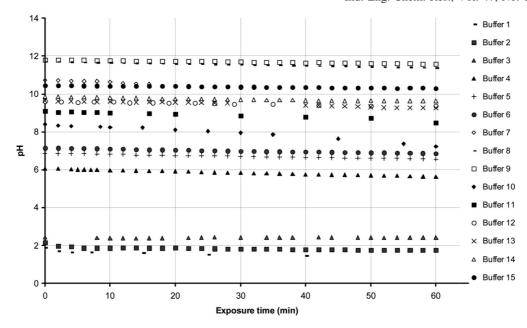


Figure 8. Effect of the discharge on selected concentrated buffers. (Reprinted from ref 70. Copyright 2005, EDP Sciences, Les Ulis, France.) (See matching compositions in Table 6.)

Table 6. Selected Buffer Compositions

		p	Н
		for $t^* =$	for $t^* =$
buffer	buffer composition	0 min	60 min
1	$H_3PO_4 (0.15 M) + H_2PO_4Na (0.05 M)$	1.9	
2	$H_3PO_4(0.1 M) + H_2PO_4Na(0.1 M)$	2.16	2
3	$H_3PO_4 (0.05 M) + H_2PO_4Na (0.15 M)$	2.43	2.41
4	$H_2PO_4Na (0.15 M) + HPO_4Na_2 (0.05 M)$	6.06	5.62
5	$H_2PO_4Na (0.1 M) + HPO_4Na_2 (0.1 M)$	6.85	6.56
6	$H_2PO_4Na (0.05 M) + HPO_4Na_2 (0.15 M)$	7.14	6.86
7	$HPO_4Na_2 (0.15 M) + PO_4Na_3 (0.05 M)$	10.73	10
8	$HPO_4Na_2 (0.1 M) + PO_4Na_3 (0.1 M)$	11.7	11.4
9	$HPO_4Na_2 (0.05 M) + PO_4Na_3 (0.15 M)$	11.8	11.6
10	$HBO_2 (0.15 M) + BO_2Na (0.05 M)$	8.4	7.22
11	$HBO_2 (0.1 \text{ M}) + BO_2Na (0.1 \text{ M})$	9.09	8.49
12	$HBO_2 (0.05 M) + BO_2Na (0.15 M)$	9.62	9.36
13	$HCO_3Na (0.15 M) + CO_3Na_2 (0.05 M)$	9.65	9.25
14	$HCO_3Na (0.1M) + CO_3Na_2 (0.1M)$	9.86	9.62
15	$HCO_3Na (0.05M) + CO_3Na_2 (0.15M)$	10.45	10.3

conditioned by economical costs and occasionally by undesirable side reactions.

4.3.2.1. Oxidation—Reduction Buffers. Humid fed gases are credited with great oxidizing power, which is greatly attributed to OH that is provided by the dissociation of water molecules in the discharge. This is a feature of key importance for the degradation of recalcitrant pollutants and molecules as rapid as possible. Besides, the reduction product of OH (i.e., H₂O) has no harmful character, so its use is an important argument for industrial application.

However, when strongly reducing species are present in the target, then the Gibbs free energy (ΔG°) of the reaction may be too large and a risk exists for the reactor to explode. Two techniques may then be used to control this risk, and both are based on the control of the yielded OH formed in the discharge. This means either limiting the production of OH (and, consequently, the source H₂O of these radicals) or using oxidation reduction buffers.

Limiting humidity may result in tight control of the temperature and flow of the vector gas that can pass through a drying (or wetting) layer. The composition of the feeding gas may also be modified by adding a "neutral" gas to the input gas, to lower its activity by dilution, or oxygen, to strengthen the plasma treatment, according to the desired effect. One can at least control the current intensity and the resulting energy dissipated in the discharge, as discussed in section 7.

Gas mixtures with oxidizing and reducing properties is another reasonable solution, because the mixture acts as a buffer. Such a technique has been used for the treatment of solids: for example, etching silicon wafers was successfully performed with a mixture of oxygen and hydrogen fluoride (HF) (or carbon tetrafluoride, CF₄).

Table 7. Selected Values of Oxidation Potentials of Couples of Interest for Discharges in Humid Air^a

$Ox + ne^- = Red$	$E^{\circ}(Ox/Red)$ (V/NHE)	$Ox + ne^- = Red$	$E^{\circ}(Ox/Red)$ (V/NHE)
$F_2(g) + 2H^+ + 2e^- = 2HF(aq)$	3.06	$MnO_4^- + 8H^+ + 5e^- = Mn^{2+} + 4H_2O$	1.51
$F_2(g) + 2e^- = 2F^-$	2.87	$O_3 + 6H^+ + 6e^- = 3H_2O$	1.51
$OH + H^{+} + e^{-} = H_{2}O$	2.85	$HO_2 + H^+ + e^- = H_2O_2$	1.44
$ONOO^{-} + 2H^{+} + e^{-} = NO_{2} + H_{2}O$	2.44	$Cl_2 + 2e^- = 2Cl^-$	1.36
$O(g) + 2H^{+} + 2e^{-} = H_{2}O$	2.42	$Cr_2O_7^{2-} + 14H^+ + 6e^- = 2Cr^{3+} + 7H_2O$	1.33
$O_3 + 2H^+ + 2e^- = O_2 + H_2O$	2.07	$O_2 + 4H^+ + 4e^- = 2H_2O(l)$	1.23
$ONO_2H + H^+ + e^- = NO_2 + H_2O$	2.05	$NO^+ + e^- = NO$	1.21
$Cl_2O + 2H^+ + 2e^- = Cl_2 + H_2O$	1.71	$O_2 + 4 H^+ + 4e^- = 2H_2O(g)$	1.19
$HO_2 + 3H^+ + 3e^- = H_2O$	1.70	$NO_2 + H^+ + e^- = HNO_2$	1.09
$MnO_4^- + 4H^+ + 3e^- = MnO_2 + 2H_2O$	1.70	$NO_2 + 2H^+ + 2e^- = NO + H_2O$	1.05
$H_2O_2 + 2H^+ + 2e^- = 2H_2O$	1.68	$NO_3^- + 3H^+ + 2e^- = HNO_2 + H_2O$	0.96
$HCIO + H^{+} + e^{-} = \frac{1}{2}Cl_{2} + H_{2}O$	1.63	$NO_3^- + 4H^+ + 3e^- = NO + 2 H_2O$	0.94
$O(g) + e^- = O^-$	1.61	$ClO_{2 gas} + e^{-} = ClO_{2}^{-}$	0.93

^a Data taken from ref.⁷²

In the case of gliding discharges in humid air, the degradation of "pure" organic waste solvents such as tributylphosphate (TBP), 51,73 showed CO peaks in CO₂ exhaust gases at the beginning of the treatment and toward the end of the treatment. This suggests that formed CO₂ was reduced to CO by excess hydrocarbons. This feature is easily understood at the beginning of the treatment as a consequence of a partial vapor stripping; it is more puzzling at the end of the treatment, when there is no more organic solvent left. Hence, the control of the oxidizing power of the plasma species may be achieved by adding a reducing species, such as methane or propane (or CO), to avoid ammonia. For example, the removal of NO_x resulted from the addition of methane to air. 74,75

4.3.3. The Complex Formation Reactions. A well-known reaction between hydrogen peroxide (H_2O_2) and transition-metal ions such as Ti^{4+} or V^{5+} , occurs in acidic media: a colored complex forms. This reaction is used to identify⁷⁶ and occasionally quantify H_2O_2 . A violet solution of $TiCl_3$ exposed to the discharge readily changes to an orange color (absorption peak at $\lambda = 410$ nm): this illustrates both the oxidizing effect of the plasma treatment (because Ti^{3+} is oxidized to Ti^{4+}) and the peroxotitanyl complex formation reaction.

A matching example concerns NO or a derivative. A non-negligible part of the energy of a burning discharge is converted to UV light and may induce photochemical reactions. In particular, at wavelengths shorter than 134.3 nm, the absorption of light is followed by ionization:

$$NO + h\nu \rightarrow NO^{+} + e^{-} \tag{10}$$

The nitrosonium ion, NO⁺, reacts at primary or secondary amines and yields diazonium ions:

$$RNH_2 + NO^+ \rightarrow [RH_2N - N = O]^+$$
 (11)

Primary aliphatic amines lead to $R_1N=NOH_2^+$ and then to the poorly stable diazonium ion $(R_1N'N)^+$, whereas secondary amines may lead to colored nitrosamines,

$$R_1R_2NH + NO^+ \rightarrow [R_1R_2HN = NO]^+ \leftrightarrow R_1R_2N - N = O + H^+$$
(12)

and tertiary amines lead to quaternary ammonium ions,

$$R_1R_2R_3N + NO^+ \rightarrow [R_1R_2R_3N - N=O]^+ \rightarrow decomposition$$
 (13)

These reactions are well-known in classical organic chemistry. They are observed under plasma conditions, for example, in the case of the plasma-chemical degradation of amines or urea. ⁷⁷

It is also largely accepted⁷⁸ that the nitrosation of aromatic molecules may be performed using NO₂:

$$ArH + 2NO_2 \leftrightarrow [ArH, NO^+]NO_3^- \rightarrow ArNO + H^+ + NO_3^-$$
(14)

4.3.4. The Radical Reactions. First, H₂O molecules decompose in the discharge plasma and yield H and OH radicals as already mentioned:

$$H_2O + e^- \rightarrow H + OH + e^- \tag{15}$$

Apart from hydrogen abstraction on labile H atoms of hydrocarbon chains, OH participates in electrophilic addition to organic π systems, as in photochemical reactions. The radicals are able to add at double bonds:

Also, radical—radical or radical molecule reactions may occur, e.g.,

$$>=<+^{\circ}OH \rightarrow \nearrow^{\circ}OH$$
 (16)

$$OH + OH \rightarrow HO - OH \tag{17}$$

$$H_2O_2 + OH \rightarrow H_2O + HO_2$$
 (18)

The concentration of the yielded radical HO_2 is dependent on the acidity of the medium.

Matching examples relevant to NO are developed in the work of Alfassi. 81

- **4.4.** Modification of the Plasma-Induced Reactions. A large part of the forthcoming application of the gliding discharges lies in the pollutant abatement of wastewaters and air, apart from the surface treatments of materials, which will not be considered hereafter. Therefore, it is essential for industrial application of the discharges to optimize the discharge working parameters, and among them are the following: (i) the amount of energy transferred from the discharge to the gas (or the efficiency of the energy transfer), (ii) the nature and the population of the reactive species formed in the discharge, and (iii) the chemical effects (the oxidation reactions that involve organic compounds often are dependent on the local acidity).
- **4.4.1.** The Nature of the Active Species. The nature of the active species is dependent on the chemical properties required for the considered treatment. In the case of pollutant abatement, the chemical reactions are oxidization/degradation of the pollutant and, therefore, very strong oxidizing species are required. The OH radicals are excellent candidates (e.g., $E^{\circ}(OH/H_2O) = 2.85 \text{ V/NHE}$, from Table 7); however, other systems can be helpful. Briefly, oxygen- and nitrogen-containing species (i.e., N_xO_y species) might present some interest for the task. The strong oxidizing character of these active species required for pollutant abatement purposes will be a key argument for the selection of the feeding gas and the parent molecules.
- **4.4.2.** The Nature of the Plasma Gas. An inexpensive and efficient source of OH radicals and relevant species is humid air, because the discharge favors the dissociation of water molecules. It is well-known now that the occurrence of water molecules in the fed gas largely enhances the oxidizing power of the plasma species. This oxidizing character is attributed to OH, but also to the secondary species, such as H_2O_2 , as well as nitrogen-containing species (see Table 7).
- **4.4.3.** The Nature of the Electrodes. The nature of the electrodes may control the formed species. For example, the use of iron electrodes induces the formation of Fe^{2+} and Fe^{3+} cations, which results from metal etching, and they are then able to react with H_2O_2 and increase the OH yield, as suggested by Fenton's reaction in an acidic medium:

$$Fe^{2+} + H_2O_2 + H^+ \rightarrow Fe^{3+} + H_2O + OH$$
 (19a)

However, we tend to consider this reaction as a side reaction, because of the limited etching effect and the energy required to ionize iron.

Also, copper pieces in the reactor reduce the concentration of nitric oxide formed and, therefore, the matching acidic effect. Although copper is readily oxidized to Cu²⁺ in concentrated nitric acid and forms cupric nitrate, other phenomena probably occurs in the discharge and limits the formation of nitric oxide. In dilute acid, copper is not attacked and no hydrogen forms, because of the high value of the standard potential: this may explain why the decrease in pH is limited under discharge conditions.

In the presence of oxygen (or air) at high temperature, which is realized when copper is the metal electrode, various copper oxides 82 (e.g., precursor oxides Cu , with x > 4, Cu (I) oxides

(Cu₂O and Cu₃O₂), and Cu(II) oxide (CuO)) form at the electrode surface as a dielectric barrier, which make further oxidation processes more difficult. This feature also limits the quantity of oxygen available. Then competitive reactions occur for oxygen, which may react both with copper and with formed NO, so that the formation of nitrite, and, subsequently, that of HNO₃, become limited, which matches a more limited pH drop.

4.4.4. The Local Acidity. As a direct consequence of the previously developed features, the acidity level of the target solution must be considered. First, and as mentioned, the formal potential of an organic system usually decreases as pH increases. This means that the difference $\Delta E^{\prime \circ} = -\Delta G^{\prime \circ}/nF$ between the systems has a tendency to decrease in alkaline medium. Hence, the reaction rate gets slower and slower.

Therefore, it is desirable to operate in an acidic medium, or at least in a neutral medium. However, this general feature may be adjusted by taking into account the stability of organic compounds, which may be deeply modified when ionized functions are present: for example, the basic form of phenol (i.e., phenate) is more reactive than the associated acidic form, because the electron lability of the π bonds is enhanced.

A series of buffers, the pH of which did not vary by more than 0.4 pH units within 1 h of plasma treatment, were proposed, 70 as mentioned, and covered a large acidity range (see Figure 8 and Table 6). The base and the matching acid were selected because they were unaffected by the oxidizing power of the discharge.

4.4.5. The Energy Transfer. The number of active species formed in a discharge is directly correlated with the energy transferred to the discharge. This first suggests using a powerful energy source that can provide the needed energy, and transferring the largest amount possible to the gas. Because energy involves the square of the current intensity i, the key factor should then be i and the most suitable domain in the plot of ivs U should be the arc-forming zone.

From this point of view, the arc domain should be preferred.

However, the high thermal effect that is associated with arcs prevents their use for the treatment of heat-sensitive materials and organic liquids. Besides, the high voltage required implies an important cost for isolation and operation. It presents also the risk of synthesizing hazardous species that might be more harmful than the parent species. The risk of forming dangerous species, such as dioxins that appear in incinerated smokes, must then be carefully considered.

These features tend to discourage the use of thermal plasmas and prefer a quenched plasma. This plasma may be poorer in active species, and, consequently, are less efficient than a thermal plasma that allows incineration, but it is largely more interesting for investment and operating costs. Preparing suitable energy sources would provide enhanced energy and deliver high current intensities.

Several examples have shown that an increasing current intensity induced an improved zero-order kinetic rate (k_0). Until now, experiments have led us to limit i to 0.8 A, because the required chemical effects do not increase anymore for higher intensities: this feature is probably related to the formation of other species or the occurrence of other mechanisms. An illustrative example of the needed control of the input energy is relevant to the already-presented titration of standard sodium hydroxide (NaOH) solutions by gliding discharge in humid air. 69,70 The treatment time (t_{eq}) required to exactly neutralize the number of OH⁻ in excess in the target solution (and obtain pH 7) is dependent on the input energy, i.e., the current intensity

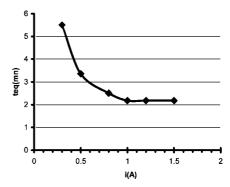


Figure 9. Typical variation of the treatment time $t_{\rm eq}$ needed to neutralize a given quantity of OH added to the aqueous solution with the current intensity of the discharge.

of the discharge. Figure 9 shows that t_{eq} decreases to a plateau when the current intensity increases.

This feature shows that t_{eq} is dependent on the current intensity i and, hence, on the energy involved in the discharge (i.e., the fed energy and the energy transferred to the discharge and to the gas). It suggests the following interpretation based on the production of activated species.

The repartition scheme of the population of active species versus energy usually presents a maximum, which means that (i) several different active species are present in the discharge, and their nature is mainly dependent on the fed gas and the electrodes metal; (ii) each type of species is involved in a given specific chemical reaction; (iii) therefore, one specific reaction induced by exposure to the discharge can hardly be expected for a given input energy; (iv) the population repartition of the active species is dependent on the input energy; and (v) a toohigh input energy should lead to a decrease in the population of the selected active species implied in a given reaction, and, thus, the yield should be lowered.

To summarize, the quantity of energy delivered to the discharge to achieve an expected reaction should be optimized. The building of suitable power sources with a tight control of the energy delivered to the discharge must be developed by electrotechnical engineers and high-voltage (HV) specialists in close connection with chemists to optimize the yield of the discharges.

4.5. Plasma—Target Interaction. As underlined in section 4.4. the target exposed to the discharge is subjected to a large variety of reacting species. A scheme limited to the noncharged species is presented in Figure 10. It must be completed with a similar sketch involving ions. However, the influence of anions remains hypothetical in the scope of chemical effects, because species present in large quantities are only concerned with the main reactions.

Some pertinent kinetic constants reported in the work by Herron and Green⁸³ are listed in Table 8.

4.6. Plasma-Target Kinetics. Exposure of numerous organic solutes to the discharge induces a quite general behavior: the concentration of the solutes decreases as the exposure time t* increases. This feature is evidence that degradation phenomena of the solute occur as the target is exposed to the flux of the impinging activated species of the discharge.

This result is provided by various analytical measurements, e.g., specific titration, total organic carbon measurements, evolution of the absorbance spectrum of the target at the absorbance peak, high-performance liquid chromatography (HPLC) or gas-phase chromatography measurements, and voltammetry.

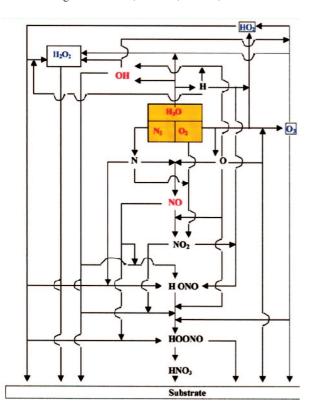


Figure 10. Sketch of the interaction with the target (referred to as the "substrate") of the parent, primary, and secondary species present in the discharge. Only molecular species are considered.

The reaction occurs at the liquid surface, as easily illustrated by the color change. For example, the upper layer of a nonstirred solution of an acid-base indicator in its basic form readily turns to the acid color (blue and yellow, respectively, in the case of Bromothymol Blue, BTB). Stirring the solution with a magnetic stirrer enables one to homogenize the target and prevents a color gradient from forming. If the nonstirred solution is exposed for a long time to the discharge, then diffusion phenomena occur and the solution changes to the acidic form.

Two typical situations account for the overall evolution of the concentration of the solute under discharge conditions, according to the concentration of the solute (see Figure 11):

(1) For concentrated solutes (and also for nonaqueous waste organic solvents), the surface concentration of target molecules is high. A given ratio of the impinging plasma species reacts at the surface molecules, so that the reaction rate is controlled by the impinging active species flux falling at the surface. A zeroorder reaction results; that is, the remaining concentration in the target molecules in the solution $C(t^*)$ is a linear decreasing function of the exposure time t^* to the discharge; C_0 is the solute concentration for $t^* = 0$.

$$\frac{\mathrm{d}C}{\mathrm{d}t^*} = -k_0$$

or the matching integer form

$$C(t^*) = -k_0 t^* + C_0$$

Incidentally, the function $ln(C(t^*))$ barely varies with t^* as far as this limit kinetic law is observed. This means that a plateau occurs when $ln(C(t^*))$ is plotted against t^* .

(2) For dilute solutions (or when the concentration in the target molecules becomes low), none of the impinging species participate in the abatement anymore, and the process is governed by diffusion phenomena of the target molecules from the bulk solution to the surface. Diffusion then controls the abatement kinetics, and a first-order mechanism occurs, in agreement with Fick's laws:

$$\frac{\mathrm{d}C}{\mathrm{d}t^*} = -k_1C$$

and

$$C(t^*) = C_0 \exp(-k_1 t^*)$$

The usual log plot, i.e., $\ln(C(t^*))/C_0 = -k_1t^*$ vs t^* , shows a line with a negative slope $(-k_1)$.

These two limit situations account for all the examples we had to consider until now, including the inactivation of bacteria, provided the considered kinetics is the determining step. Microbiologists have focused better on the total inactivation of bacteria and, therefore, on the second step (first-order reaction), which is concerned with very low bacteria concentrations. For the inactivation of *Hafnia alvei*, 86 a free add-in for the Microsoft Excel software program (GinaFiT) intends to account for a plateau of ln C, followed by a linearly decreasing function of the exposure time t^* . This is a kinetic profile that is rather popular among biologists, for the general behavior of $ln(C(t^*))$ = $f(t^*)$. According to the program, the general kinetic equation

$$N = N_0 e^{-k_{\text{max}}t} \left[\frac{e^{k_{\text{max}}SL}}{1 + (e^{k_{\text{max}}SL} - 1)e^{-k_{\text{max}}t}} \right]$$

where N is the cell concentration (CFU/mL) after the overall treatment time t (given in minutes; i.e., $t = t^* + t_{\text{postdischarge}}$. N_0 is the initial cell concentration (CFU/mL), k_{max} the maximum inactivation rate (in units of min⁻¹), and SL the shoulder length (i.e., the duration of the zero-order step of the reaction, also given in minutes).

A detailed analysis of the kinetic equation easily allows one to evidence the couple of kinetic steps.

4.7. Model for Surface Reaction. A model relevant to the discharge-induced reaction has already been proposed, 51,72 based on the rate-determining reaction. It involves a couple of diffusion layers, each one on both sides of the aqueous surface.

The upper layer corresponds to the plasma phase with a given concentration of active species A (e.g., $C^{\circ}g(A)$) in the bulk plasma phase, which lowers in the plasma diffusion layer and decreases to $C_g(A)$ at the liquid surface.

The lower phase is relevant to the liquid (i.e., usually water). It involves an upper diffusion phase with a surface concentration C° w(A) decreasing to the value $C_{\rm w}(A) = 0$ at a depth $z = \delta_{\rm w}$ (i.e., at the end of the diffusion layer). The lower phase is identified as bulk water for $z > \delta_w$.

- **4.8. Influence of the Working Parameters.** The nature of the input gas and the electrodes metal was considered previously, as were examined the "target parameters" (i.e., concentration and volume). The other usual working parameters are gathered in Table 9 and mainly concern the reactor geometry, the energy provided to the discharge, and time (e.g., exposure time of the target). The reported results are relevant to batch treatments of a standard solution disposed in front of the fed gas flow (see Figure 4).
- **4.8.1. Geometry Parameters.** Some of them have already been examined (section 4.4.4) for given knifeblade-shaped electrodes (see Figure 3). The general shape was selected by Czernichowski et al. for gas treatment and later optimized to liquid treatment. The influence of the electrode gap and that of the electrode to target distance were considered.^{69,74} The thickness of the electrodes was considered more recently⁵⁹ and

Table 8. Kinetic Constants of Reactions Selected from the Work of Herron and Green⁸³ Involving Neutral Species^a

				Kinetic Cons	stant, k	
	reagents		products	(cm ³ /s)	(cm ⁶ /s)	ref
1	$N + O_2$	→	NO + O	8.9×10^{-17}		83
2	N + NO	\rightarrow	$N_2 + O$	3×10^{-11}		83
3	N + OH	\rightarrow	NO + H	4.9×10^{-11}		83
4	$N + HO_2$	\rightarrow	NO + OH	2.2×10^{-11}		83
5	N + O + M	\rightarrow	NO + M		$1.76 \times 10^{-31} T^{-0.5}$	83
6	$NO + O + O_2$	\rightarrow	$NO_2 + O_2$		8.6×10^{-32}	83
7	$NO + O + N_2$	\rightarrow	$NO_2 + N_2$		1×10^{-31}	83
8	$O + O_2 + O_2$	\rightarrow	$O_3 + O_2$		6.9×10^{-34}	83
9	$OH + O_3$	\rightarrow	$HO_2 + O_2$	6.5×10^{-14}		83
10	$OH + HO_2$	\rightarrow	$H_2O + O_2$	1.1×10^{-10}		83
11	$O_3 + NO$	\rightarrow	$O_2 + NO_2$	4.6×10^{-14}		83
12	$HO_2 + NO$	\rightarrow	$NO_2 + OH(?)$	1.1×10^{-11}		83
13	$NO_2 + OH + M$	\rightarrow	$HNO_3 + M(?)$		2.2×10^{-30}	83
14	$NO_2 + H$	\rightarrow	NO + OH(?)	$5.8 \times 10^{-10} \exp(-740/T)$		81
15	OH + NO + M	\rightarrow	HONO + M	$7.4 \times 10^{-31} (T/300)^{24}$		81

a Reaction 12 is involved in ozone removal in high atmosphere, although the formation of OH as a reaction product is thermodynamically unlikely (because of the values of the standard potentials), and the formation of nitric acid from nitrogen dioxide (reaction 13) involves the transposition of an intermediate.80,84,85

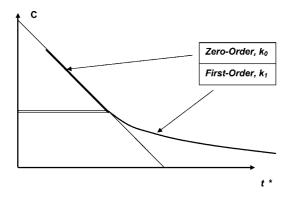


Figure 11. General evolution of the concentration of an organic solute exposed to a gliding discharge.

Table 9. Overview of the Main Working Parameters That Control the Discharge Effects

energy parameters	geometry parameters	time parameters
electricpower	electrode gap, d	exposure time, t^*
U	electrode-to- target distance, D	gas flow Q
i	electrode thickness	circulating flow rate
t*	exchange surface	

found to be slightly more efficient for thick blades than for thin sharpened ones.

- **4.8.2. Time.** the treatment or exposure time t^* of the target to the flux of active species is the primary easy-to-determine parameter in the case of batch reactors. As mentioned, t^* is affected by the geometry of the reactor, the energy delivered to the discharge, and the gas flow rate. When using circulating reactors, the flux of the circulating liquid target must be considered: therefore, it is better to refer to the treatment time as the contact time.
- **4.8.3.** Energy. Electrical parameters are dependent on the energy transferred from the power source to the discharge, and this energy is the key parameter, because it is the origin of the gaseous species activation and, thus, the origin of the population of the impinging flux.

The energy term, $E = Uit^*$, is the product of the potential drop involved between the electrodes when the discharge is switched on (U), the mean current intensity that passes through the working electrodes (i), and the time of the burning discharge (t^*) . The gliding discharge conditions are found in the FG region (see Figure 2) where the potential drop U is not so high as that for corona discharges. The energy term varies as the square of the current intensity, so that the main term in the expression of E is actually the current intensity, which is higher than for corona discharges, and, hence, the device is more favorable to the formation of an activated species.

It clearly appears that an improved reactor yield requires a high electric power to be transferred to the discharge: the supply source should preferably have characteristics typical for the current, rather than for the voltage source. However, the input energy must remain in a certain energy range to favor the formation of activated species with useful chemical properties and the range limits obviously are dependent on the nature of the required species.

4.9. Examples of Pollutant Degradation. We are not yet in a position to list all the applications of the gliding discharge, even in the field of waste treatment, because more and more numerous studies are developed and published in Far Eastern and African laboratories. We only intend to gather examples to cover a large spectrum of forthcoming industrial applications, with an emphasis on the chemical function: Table 10 gives selected illustrative examples of gas and VOC abatement.

Table 11 is specially devoted to the published works that involve bacterial inactivation through the use of a gliding discharge. 124-132

Intentionally, Tables 10 and 11 focus on examples of pollution abatement and do not report side studies in connection with the gliding discharge, for instance, the energy savings allowed by the conversion of hydrocarbons, the preparation of syngas from hydrocarbons assisted by electric discharges, developed by Czernichowski et al.;87 improving the efficiency of gliding arc device for gas treatment by Khacef and Cormier³⁰ in France, developing suitable electric sources by Stryczevska and Janowski³⁷ in Poland, diagnostics of the plasma, and surface modification (from the work of Kamgang et al. 46 and Benstaali et al.⁴⁷), because these topics should require special attention.

5. Post-Discharge Reactions

5.1. Immediate Observation. A striking consequence of exposing a solution to the discharge is a newly observed phenomenon called "temporal post discharge reaction" (TPDR). TPDR is observed when the discharge is switched off, and the target solution isolated from both reactor and any extra energy source. For example, the treated solution is stored in a sealed vessel, outside the reactor, in darkness, without stirring and far from heat or any other energy source. TPDR differs from the

Table 10. Examples of Published Studies Relevant to Pollution Abatement in Liquid Targets (Solutions or Pure Organic Solvents) with Matching References by Gliding Discharges; Selected Matching Examples of VOC or Gas Degradation Are Also Reported

			Characteristics					
compound	example	recalc ^a	E/C agent ^b	solvent	solute	very harmful	VOC or gas	ref(s)
			Hydro	carbons				
aliphatic	methane						×	29, 33, 64, 65, 87
	N. heptane hexane		×	•			×	73 88
	cyclohexane						^	89
aromatic	toluene		×	•		•	×	63, 88, 89, 90, 91
halogenated	chloroform, CHCl ₃			•			×	60, 92, 93
	carbon tetrachloride, CCl ₄		×	•		•	×	93 94
	111-trichloroethane		•				×	94
			Alco	ohols				
aliphatic	2-propanol						×	95
	ethylene glycol							96
			Phe	enols				
	phenol				•			59, 97
substituted	4-chlorophenol				•			59, 96
	pentachlorophenol Bisphenol-A				•	•		98
dyes	(aza) Heliantine	•			•	×		96, 97 53, 54
ay cs	Bromothymol Blue				•			61
	Alizarine				•			99
	Oxazine Yellow and Blue				•			100, 101
	(aza) Blue 137				•			57, 58 102
	Orange G Orange II				•			55
	Malachite Green				•			55
	Indigo				•			104
	Acid Green 25				•			56, 103
	industrial dyes				•			54, 104
			Ket	ones				
	acetone			•			×	95
			Es	ters				
	ethyl acetate			•			×	88, 90
	diethyl malonate				•			106
	methyl salicylate				•			105
	EDTA				•			106
			S-containing	Compound	ds			
	$\mathrm{SO_2}^c$						×	108, 109, 110
	H ₂ S						×	111, 112
	thio-urea sodium lauryl sulfate	×			•			113 114
	sodium fauryi suffate	X		~				114
			P-containing	g Compound	ds			
	tributyl phosphate	×	×	•		×		51, 73
	triethyl phosphate dimethyl methyl phophonate	•			•			116 116
	hexamethyl phosphoramide				•			117
	RNA				•			117, 118
			N-containing	Compoun	ds			
	NO_x			, .			×	49
amines	nicotine				×	•	^	121, 122
	trilauryl amine	×	×	•		×		52
amides	urea				•			77, 113
	thio-urea				•			77, 113 118
	protein				•			110
			Surfa	ctants				
	trilauryl amine	×	×	•		×		52
	lauryl sulfate	×	•					114
			Recalcitra	ant Wastes				
nuclear wastes	tributyl phosphate	×				×		51
	trilauryl amine	×				×		52
			Highly To	xic Wastes				
alk. cyanides	CN ⁻				×	•		62
-	nicotine				×	•		121, 122
			Industri	al Wastes				
niscellaneous	dyes		×		•			54, 56, 104
occinaneous	atrazine		^		•			123
	CFC					•	×	124

^a Recalcitrant. ^b Extractant/complexing agent. ^c No study of gliding discharge removal of SO_2 is reported as far as we know. However, de- SO_x effects by e-beam, corona, or DBD discharge are well-known.

Table 11. Inactivation of Bacteria Exposed to the Gliding Discharge

bacteria	origin of strain	abatement (log ₁₀ units)	exposure time, t (min)	state	ref(s)
Escherichia coli	MG 1655	8	6	planktonic	125
Staphylococcus epidermidis	ATTC 12228	7	15-30	planktonic	126
Staphylococcus epidermidis	ATTC 12228	6^a	20	adherent	124
Staphylococcus epidermidis	ATTC 12228	7^a	90	biofilm	127, 128
spores of Bacillus subtilis, var. niger	ATTC 9372	4.5^{b}	30	adherent	129
Erwinia carotovora atroseptica, Eca	CFBP 1526	10.5	7.5	planktonic	130, 131
Erwinia carotovora atroseptica, Eca	CFBP 1526	10.5	3.5^{c}	•	
Erwinia carotovora carotovora, Ecc	CFBP 2808	10.3	6.5	planktonic	130, 131
Erwinia carotovora chrysanthemi, Ech	CFBP 2408	10.3	7	planktonic	130, 131
Hafnia alvei	CIP 5731	7	12	planktonic	132

^a Results are dependent on the working conditions and, therefore, comparisons are risky. Small-sized cover glasses (area of 4.2 cm²) were contaminated with 10^6 (adherent) and 10^7 (biofilm) bacteria. A 30-min plasma treatment at an electrode-target distance of D=22 cm induced the complete destruction of all cells. ^b Contaminated (4 \times 10⁵ spores per 4.2 cm² coverglass exposed to the discharge for 30 min at D=5 cm. ^c Experiments performed with an improved reactor device. Eca is slightly more difficult to inactivate than Ech and Ecc.

largely considered "post-discharge phenomena", which are observed when the samples are disposed out of the discharge but in a part of the reactor in contact with the discharge zone and with the gas species formed in the discharge. In this case, a part of the primary or secondary species continuously formed in the plasma may be in permanent contact with the target and react at its surface.

The two candidates of concern as TPDR sources are H₂O₂ and NO (and their derivatives), among which peroxonitrite (OONO) is probably the key reagent involved in the oxidation processes. The previously reported oxidizing power of OH is a feature that conceals the matching properties of peroxonitrite [OONO] and peroxonitrous acid [HOONO] (p $K_a = 6.8$). Apart from oxidation, NO and the derived species are concerned with the nitration reaction of aromatic species. NO is considered to be an important source of stress for living material 128 and in the destruction of DNA. It has a large role in physiology and is probably implied in some human pathologies.

5.2. Examples. Several examples of temporal postdischarge reactions that are available in the literature present some general character. 53,61,77,132,136 Only five illustrative examples will be considered hereafter, because they are valid for several situations that involve discharges in contact with aqueous targets, such as contact glow discharge electrolysis, and glidarc and electrohydraulic discharges.

We now must consider two different evolutions and, therefore, two kinetics. The first one is directly related to the discharge and occurs when the target is exposed to the discharge for time t*: this has been considered in section 4.6. The relevant kinetic constants are k_i^* (where i = 0 or 1). The second one develops under post-discharge conditions, after the discharge has been switched off, and the relevant time scale is referred to as t and the relevant kinetic constants are referenced as k_i (i = 0 or 1).

5.2.1. Nitrate Formation. It is well-known now that the acidity of an aqueous target exposed to an electric discharge in air increases (pH decreases) and that matching ions (i.e., mainly NO₂⁻ and NO₃⁻) enter the liquid phase, so that they induce an enhanced conductivity of the solution. The formation of nitrous/ nitric acids is not limited to the treatment of solutions, because a DBD treatment of polyethylene in humid air reports⁷¹ indicates their presence. Those authors⁷¹ suggested the occurrence of an equilibrium. Therefore, their model involves a three-body reaction as an elementary step and the occurrence of N_2O_5 , which has not been proven experimentally.

The analytical techniques involve chemical analysis and ion chromatography. They are performed in acidified solutions, so that previous authors ⁷⁵ could conclude with the formation of nitrous and nitric acids in the gas phase. However, they did not take into account the disproportionation of nitrous acid in an acidic medium: HNO2 is not thermodynamically stable at pH < 2.6 and slowly disproportionates to NO and NO₃⁻. Therefore, the evolution with time of NO₂⁻ to NO₃⁻ may be considered as a TPDR.

The absorbance spectra of gliding-discharge-treated aqueous solutions for time t^* (in minutes) shows characteristic absorption bands in the 350-400 nm range that account for nitrite ions in an acidic medium $(pK_a(HNO_2/NO_2^-) = 3.3)$. The nitrite concentration increases with t^* and presents a flat maximum, according to the working parameters of the discharge, before it slowly decreases. This behavior shows that the nitrite concentration results from a synthesis step and a degradation step. At the same time, the nitrate concentration continuously increases.

We then must consider the transformation of NO to nitric acid: $NO_3^- + H^+$. The overall evolution of nitrogen to be considered is described by the sequence

$$NO \rightarrow NO_2 \rightarrow NO_2^- \leftrightarrow ONO_2^- \leftrightarrow NO_3^-$$
 (19b)

It is acknowledged that NO rapidly reacts with oxygen from air and yields NO2. Other reaction paths may be considered, for example,

$$H_2O + e^- \rightarrow H + OH + e^-$$
 (20)

$$H + O_2 + M \rightarrow HO_2 + M$$
 ($k =$

$$7.5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$
) (21)

$$NO + HO_2 \rightarrow HO + NO_2$$
 ($k =$

$$8.3 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$
) (22)

$$HO + NO + M \rightarrow HONO + M$$
 ($k =$

$$3.3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$
) (23)

$$HO + HONO \rightarrow NO_2 + H_2O$$
 (k =

$$5.6 \times 10^{-12} \,\mathrm{cm}^3 \,\mathrm{molecule}^{-1} \,\mathrm{s}^{-1}$$
) (24)

The kinetic constant values listed for these reactions were reported by Herron and Green.83

The formation of the nitrite ion results from either an electron capture by NO2 or the oxidation of nitric oxide NO, or both:

$$NO + HO \rightarrow NO_2^- + H^+ \tag{25}$$

The pH of the solution then is reduced, which favors the disproportionation of NO₂⁻ to NO and NO₃⁻. However, the formation of nitrate may also proceed via the fixation of OH at NO_2 to form peroxonitrous acid (p $K_a = 6.5$), which can hardly be identified, or, even better, the matching base peroxonitrite ONOO in a neutral or basic medium. This unstable moiety then isomerizes to the nitrate anion (NO₃⁻), which can be

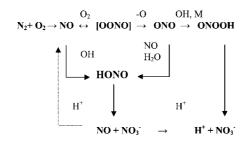


Figure 12. General scheme for the reaction of N₂ with O₂, involving the formation of NO₂, the disproportionation of HONO, the formation of peroxonitrous acid (ONOOH), and its isomerization to nitric acid.

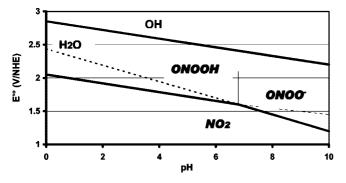


Figure 13. Formal standard potentials E'° of relevant systems (V/NHE): (a) for pH <6.8: ONOOH + H⁺ + e⁻ = NO₂ + H₂O, E'° = 2.05 - 0.06pH; (b) for pH >6.8: ONOO⁻ + 2H⁺ + e⁻ = NO₂ + H₂O, E'° = 2.44 - 0.12pH; (c) OH $^{\circ}$ + H⁺ + e⁻ = H₂O, E'° = 2.85 - 0.06pH. The lines E'° = f(pH) separate the domains where each species is prominent. The sketch shows that OH can easily oxidize NO₂.

identified by its absorbance spectrum (absorbance peak at $\lambda = 302$ nm, with $\varepsilon = 1670 \text{ mol}^{-1} \text{ L cm}^{-1}$).

$$OH + NO_2 \rightarrow [ONOOH] \rightarrow ONOO^- + H^+$$
 (26)

$$ONOO^{-} \rightarrow NO_{3}^{-} \tag{27}$$

The intermediate peroxonitrite was identified⁵³ when aqueous solutions were exposed to the discharge in a medium of suitable acidity. This set of reactions clearly shows that post-discharge phenomena occur in the solution, because the formation of nitrites/nitrates can be easily followed under such conditions. It is pertinent to remember that, several decades ago, Taube et al.¹³³ studied the interaction between nitrous acid and hydrogen peroxide and reported on the formation of intermediates such as activated ONOOH.

The formation of peroxonitrite is an overall first-order reaction that involves NO and ${\rm O_2}^-$, with a kinetic constant that indicates that a diffusion process occurs. Briefly, two rather inactive species result in a more reactive form. Figure 12 summarizes the formation of NO₂ and the transformation to nitrous acid, to peroxonitrous acid, and, ultimately, to nitric acid.

In addition, the oxidation properties of peroxonitrite and peroxonitrous acid must be considered in the solution as another TPDR, because the standard potential of the ONOOH/ NO₂ system is reported to be 2.05 V/NHE (see Figure 13).⁸³ Therefore, this species may have a determining role in the oxidation—degradation processes of pollutant abatement. This feature is detailed by Squadrito and Pryor,⁸⁵ who suggested the occurrence of several partners: the base peroxonitrie [¬OONO], an activated form of peroxonitrous acid [HOONO*] that is more selective and less reactive than the ground-state peroxonitrous acid (which undergoes a slow conversion to this species),^{85,134,135} and peroxonitrous acid [HOONO] itself. All these species present noticeable oxidizing power (see Figure 13).

Moreover, peroxonitrite has powerful nucleophilic character. Squadrito and Pryor⁸⁵ are particularly concerned with the interaction of peroxonitrite with biotargets.

All these features may easily explain the TPDR that occur, and they also suggest that peroxonitrite is mainly responsible for this particular reactivity.

In addition, reactions performed with ambient air involve the presence of carbon dioxide (CO₂): the process should then be concerned with the reactivity of NO derivatives with CO₂, although with less interest than in biological studies. The literature 84,85,132,134,135 mentions the reaction of peroxonitrite with CO₂ in a two-step mechanism, where the first step involves the formation of nitrosoperoxycarbonate (O=NOO-CO₂⁻), i.e., an intermediate that rapidly degrades to CO₂ and NO₃⁻.

It has also been proposed that heterolysis of the intermediate yields NO_2^+ and CO_3^{2-} after a new transposition to nitrocarbonate ($O_2NO-CO_2^-$): this explains the nitration of aromatic compounds being ascribed to NO_2^+ , in accordance with the classical nitration reaction.⁷⁷ This feature would match the previously described nitrating character of peroxonitrite:¹³² it may be involved among the TPDR, because only reactions in solution are then concerned in the plasmachemical abatement of organic pollutants.

5.2.2. Degradation of Nitrogen-Containing Compounds. This section will be devoted to the TPDR observed for the plasma-chemical treatment of nitrogen-containing molecules, and it is organized according to the type of chemical functions (i.e., amines and amides).

5.2.2.1. Amines. Trilaurylamine is used in nuclear recovery processes as a complex forming agent and extracting solvent: thus, the wastewaters cannot be degraded by classical solutions. An extensive study has shown that the molecule degrades when exposed to the discharge. However, the plasma processing is rather long and complicated, so that it masks possible TPDRs.

The plasma treatment of urea leads to its degradation: it involves two parallel kinetic schemes, with the slow acid-catalyzed hydrolysis of the amide, and the matching formation of a diazoic compound, which results from the nitrosing power of a secondary species (NO^+ or $\mathrm{NO_2}^+$). Because of the fact that the reported kinetic constants are different for hydrolysis and nitrosation, a TPDR can be observed.⁷⁶

5.2.2.2. Amides. The treatment of urea has just been mentioned. Another example is provided by the destruction of the membrane proteins of a bacterial cell. Moreau et al. ^{130,131} showed that a bacterial membrane was severely damaged by exposure to a gliding discharge. The analytical procedure did not allow us to evidence TPDR in this case. However, both the Bradford and the biuret titration of proteins showed the occurrence of two successive reactions. The first reaction is a linear increase in the protein concentration delivered by the external membrane, in a fashion similar to the evolution of the nitrite concentration, and the second reaction is a decrease in the extracted protein. Although no unquestionable evidence is available yet for the occurrence of a TPDR, one can guess that such a feature may happen again.

5.2.3. Degradation of Dyes. A very spectacular and efficient use of the gliding discharge consists of removing organic dyes dispersed in wastewaters, as mentioned previously.^{54–56} A detailed study of the plasmachemical treatment of an azoic dye, Methyl Orange (also called Heliantine), provides an excellent illustration of the post-discharge kinetics.⁵³ The dye, which is usually used as an acid—base indicator, was taken in the acid form, to prevent any color change in association with the acid effect of the treatment. Exposing the solution to the discharge

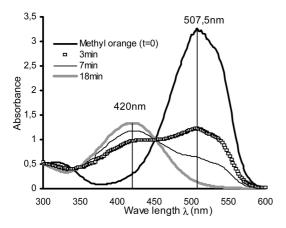


Figure 14. Post-discharge evolution of 25 mg/L Methyl Orange solutions exposed for 2 min to the discharge (air flow = 595 L/h). Spectral evolution after 3–7 min and 18 min under post-discharge conditions is also shown.⁵³

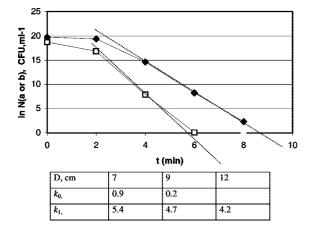


Figure 15. Inactivation of *E. coli* (MG1655) by gliding discharge ¹²⁵ in an open reactor with an air flow of Q = 440 L/h and electrode-to-target distances of D = (•) 7 cm, (□) 9 cm, and 12 cm (not shown). N_i refers to the bacterial population after experiments performed at a distance d_i between the target surface and the tip of the electrode (given in centimeters). Kinetic constant values k_0 (mol L⁻¹ min⁻¹) and k_1 (min⁻¹) for zero- and first-order steps, respectively, may be derived as rough estimate values, as suggested by a similar behavior of other bacterial inactivations.

for 2 min only and following the post-discharge self-evolving kinetics afterward showed a decrease in the absorbance at the initial molecular peak which matched a new growing peak, so that the spectra organize according to an isobestic system (see Figure 14). The absorbance measurements were performed at the initial (molecular) peaks and at the growing peaks. Their respective evolution with time t indicated kinetics that both obeyed an overall first-order law (which was expected from the low concentration of the starting solute) with the same kinetic constant: $k = 9 \times 10^{-2} \, \mathrm{min}^{-1}$. The reaction product was identified as N,N-dimethyl-4-nitroaniline (DMNA), using the absorbance spectrum and HPLC identification. The guessed matching 4-nitrobenzene sulfonate resulted from the oxidative cleavage of the diazoic bond by nitrous acid or peroxonitrite (or ozone traces) formed in the discharge.

A series of experiments with various exposure times to the discharge verified that the degradation of the dye was complete.

Examples of post-discharge evolution were also observed for the plasma treatment of other dyes (e.g., Bromothymol Blue). ⁶¹

5.2.4. Oxidation and Complex Formation. Another example of TPDR was observed with the oxidation of iron(II) complexes exposed to the gliding discharge. ¹³⁴ The basic experiment was performed on exposing an equimolecular

mixture of Fe²⁺ and SCN⁻ in nonbuffered aqueous solution to the plasma. The parent ions do not react, but the oxidized form of iron (Fe³⁺) readily combines with the thiocyanate anion to form a colored (absorbance peak at $\lambda = 450$ nm) 1:1 complex that is well-known in analytical chemistry.

Exposure of the target solution to the discharge induced a change in the color that rapidly became reddish, which accounts for the formation of [Fe.SCN]²⁺ and, hence, the expected oxidation of Fe²⁺ to Fe³⁺. The absorption peak at $\lambda = 450$ nm increases with the exposure time t^* .

$$\frac{\mathrm{d}C_{\text{FeSCN}}}{\mathrm{d}t^*} = k_0^*$$

This zero-order kinetics step ($k_0^* = 8.3 \times 10^{-5}$ mol/s) was attributed to the impact of OH radicals at the liquid surface, where the radicals oxidize the ferrous (Fe²⁺) ions to ferric (Fe³⁺) ions (according to Fenton's reaction), which are then able to enter the complex formation reaction.

$$Fe^{2+} + OH + H^{+} \rightarrow Fe^{3+} + H_{2}O$$
 (28)

$$Fe^{3+} + SCN^{-} \rightarrow [FeSCN]^{2+}$$
 (29)

This set of reactions requires protons, and, therefore, limits the pH decrease of the target.

Under post-discharge conditions, two situations occur, according to the exposure time t^* to the discharge:

(1) For 0 min $< t^* < 30$ min, the red complex continues to form, according to pseudo-first-order kinetics, with the relevant kinetic constants (k_1) , and this is consistent with a diffusion control process. It was proposed that H_2O_2 that had formed in the discharge and dissolved in the aqueous target was the oxidizing agent for Fe ions and therefore is responsible for the post-discharge steps.

$$H_2O_2 + 2Fe^{2+} + 2H^+ \rightarrow 2Fe^{3+} + 2H_2O$$
 (30)

$$Fe^{3+} + SCN^{-} \rightarrow [FeSCN]^{2+}$$
 (29)

where

$$\frac{\mathrm{d}C_{\mathrm{FeSCN}}}{\mathrm{d}t} = k_1 C_{\mathrm{FeSCN}} \qquad C_{\mathrm{FeSCN}} = C_{\mathrm{FeSCN}}^{t*} \exp(k_1 t)$$

with

$$C_{\text{FeSCN}}^{t*} = k_0 t^*$$

The overall-first-order step may be related to the pH stabilization, because protons are used again, which has a tendency to make the reaction slower.

For $t^* > 30$ min, the absorbance at the complex absorption peak decreases with time t, and this shows that the concentration in formed complex decreases. This feature may be ascribed either to (i) the acid effect on the complex, according to

$$FeSCN^{2+} + H^{+} \rightarrow HSCN + Fe^{3+}$$
 (31)

because the conditions of a very acid medium are achieved (an argument favors this point of view: the pH is not high enough to enable the formation of iron hydroxide precipitates or that of the yellowish μ -dihydroxo compound $(H_2O)_4$ -Fe³⁺- $(OH)_2$ -Fe³⁺- $(H_2O)_4$), or (ii) the oxidation of SCN⁻ by OH into the unstable (SCN)₂,

$$2SCN^{-} \rightarrow (SCN)_2 + 2e^{-}$$
 ($E^{\circ} = 0.77 \text{ V/NHE}$) (32)

followed by (SCN)2 disproportionation in aqueous solution:

$$3(SCN)_2 + 4H_2O \rightarrow 5SCN^- + SO_4^{2-} + HCN + 7H^+$$
 (33)

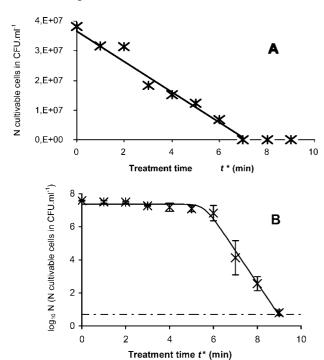


Figure 16. Survival population of *Hafnia alvei* for various exposure times t^* (min) to the gliding discharge without TPDR. ¹³² Data were plotted (A) in direct scale and (B) in semilogarithmic scale, to illustrate the zero- and first-order kinetics, respectively. In panel B, log N is preferred to $\ln N$, because it more closely fits with the microbiologists' use for bacterial population abatement (the dotted line indicates the determination threshold).

(this reaction is probably secondary, because neither cyanhydric acid nor sulfate were detected in noticeable concentration).

This example illustrates the situation where TPDR may act either in the direction of the desired initiated reaction or in the opposite way. Acidity is also considered to be responsible for this evolution, which confirms the need of a sharp control.

5.2.5. Inactivation of Bacterial Materials. It is known that electric discharges are an efficient tool for microbiological inactivation (see Figure 15). The gliding discharge was shown to allow abatements larger than 6 logarithmic colony forming units in the case of *Escherichia coli*, ¹²⁵ *Staphylococcus epidermidis*, ^{128,137} or *Erwinia spp*. ¹³⁰

The gliding discharge was also determined to be efficient against *Hafnia alvei* cells. Suspensions of planktonic *H. alvei* cells were exposed to the discharge for a given time *t** before sampling and stopping the lethal effect by neutralizing, according to known procedure, and determining the survival population by plating. Experiments confirmed that the bacteria were effectively killed by direct exposure to the discharge. The relevant inactivation kinetics presents two steps: the first one obeys a zero-order reaction (Figure 16A) and the population decay is thus proportional to the exposure time; the second step is a first-order reaction (Figure 16B), as already observed. ^{125,128,130,132,137}

TPDR were also observed¹³² after the plasma treatment of *Hafnia alvei* at temperatures not exceeding 30 °C. The post-discharge phenomena were evidenced¹³² by exposing the bacteria to the discharge for t^* again, then left in the treated medium for the postdischarge time t before neutralizing the medium. The relevant population vs. time plots (Figure 17) presented similar shapes to those obtained for standard direct treatment.

The first kinetic step clearly is a linear decreasing function of the exposure time t^* (Figure 17A), which confirms that the

first kinetic step is zero-ordered, and is consistent with most gliding discharge treatments of concentrated solutes or suspensions.

5.2.6. Post-Discharge Kinetics. Thereafter, the concentration of Hafnia alvei132 dispersed in a target solution exposed to the discharge for t^* and abandoned for a time t under post-discharge conditions decreases and provides evidence of TPDR. Relevant overall-first-order kinetics were then observed. This feature suggests diffusion-controlled kinetics as a first approximation. This assumption is supported by the feature that no primary plasma species are in contact with the target solution anymore. This means that the post-discharge reaction involves secondary species that form or are already dispersed in the liquid phase. They are then able to react with other solute species. For example, H₂O₂ results from the discharge and is readily soluble in the aqueous target. It usually reacts rather slowly, and it must then be involved in sustained oxidation processes. Ozone may also form, but the presence of water vapor does not favor its synthesis, so it may be present as a secondary species in a trace amount and will not be a determining factor in post-discharge processes.

However, the feature that the rate constants k_1 for the overall-first-order kinetics step linearly increase with t^* (see Figure 18) is more tricky. The following can be assumed:

- (1) Active species that are able to kill the bacteria are formed in the discharge,
- (2) The number of these species directly increases as the treatment time t^* increases,
- (3) Mass transfer occurs between the gas phase and the condensed phase, and
- (4) These active species react at the surface of the planktonic bacteria in the liquid phase.

These assumptions may account for a first-order step for the bacterial inactivation, because diffusion phenomena are concerned. However, no serious argument is available yet to explain the inner mechanism for inactivating bacteria.

A simple approximate calculation accounts for the linear relationship between the TPDR kinetic constant and t^* . At time t^* , the concentration in living bacteria (i.e., $C_{t^*} = C_0 - k_0^* t^*$, where C_0 refers to the starting concentration (at $t^* = 0$) of TPDR in the case of a zero-order kinetic law, and C_{t^*} is the starting concentration for the first-order reaction. Hence,

$$C_t = C_{t^*} \exp(-kt) = (C_0 - k_0^* t^*) \exp(-kt)$$

Approximating the exponential terms leads to

$$C_t = (C_0 - k_0^* t^*)(1 - kt) = (C_0 - k_0^* t^*) - (C_0 - k_0^* t^*)kt$$

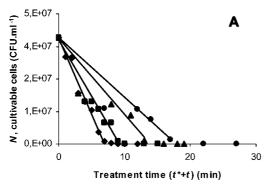
which means that the rate coefficient k_1 of t,

$$k_1 = (C_0 - k_0^* t^*)k$$

is dependent on t^* , as observed experimentally.

Complementary experiments bring decisive arguments in favor of the previously mentioned assumptions. Because the plasma-treated medium is suspected to be responsible for the lethal effect, an effort was made to put unexposed bacteria in contact with so-called "activated water" (i.e., a 0.15 M NaCl solution exposed to the discharge for 5 min). An abatement in the *Hafnia alvei* population resulted, which roughly follows the "usual" kinetic plots and no detectable cell was found for t = 10 or 20 min. This lethal effect may be ascribed to the occurrence of H_2O_2 , $ONOO^-$, or even to chlorine-containing species (e.g., dissolved Cl_2 or HClO) that form in the treated chloride solution and are known for their bactericidal properties.

The efficiency of this post-discharge effect toward bacterial cells is a key parameter for cleaning techniques. Therefore, it



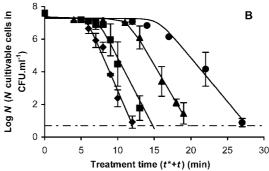


Figure 17. Survival population of Hafnia alvei¹³² for various exposure times (t^*) to the gliding discharge followed by TPDR (during t): (\bullet) $t^* = 2$ min, (\blacktriangle) $t^* = 3 \text{ min}$, (\blacksquare) $t^* = 4 \text{ min}$, and (\spadesuit) $t^* = 5 \text{ min}$. As in Figure 16, data were plotted (A) in direct scale and (B) in semilogarithmic scale, to illustrate the zero- and first-order kinetics, respectively.

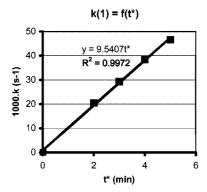


Figure 18. Variation of the first-order kinetic constant k_1 , relative to the exposure time to the discharge t^* (given in minutes).¹³²

is essential to examine how long this lethal effect lasts: experiments have shown that it fades with time but is persistent up to 24 h.127

We are not yet in a position to model the discharge or the associate lethal effect for many bacteria. However, chemical effects have been identified and may be tentatively transposed to living matter, even when keeping its specificity in mind.

As mentioned, the discharge in humid air is the source of strong oxidizing species, but short-life radicals must be discarded and only those with a rather moderate overall reaction rate should be considered. Among the candidates, peroxonitrite may be considered with special care, because the species is concerned with oxidation reaction and reactions with nitrogen-containing moieties. Therefore, one can assume that peroxonitrite attacks at the transmembrane proteins and largely weakens the structure of the cell, so that inner proteins are liberated. 130 An etchinglike process then occur, as suggested by Lerouge et al., ¹³⁸ and accounts for the death of the bacterial cell.

5.3. Consequences. The various examples presented in this survey concern the plasma treatments of liquid phases: this might suggest that post-discharge phenomena are exclusively limited to the case of solution treatments. The feature actually covers a wide range of applications, in particular, for pollution abatement in wastewater, because a recent study on the gliding discharge treatment of brewery wastewaters showed the efficiency of the technique and demonstrated that TPDR also occurred in the case of industrial wastewater treatment. 139

A matching example of TPDR is developed in a completely different field relevant to the plasma treatment of organic polymers. Exposure of a polymer sample to the gliding discharge in humid air induces a large modification of the surface properties. In particular, the contact angle with a water droplet is affected and accounts for a change in the surface energy of the treated material. The effect is not very important for PTFE (e.g., an abatement by 10°), but it is much larger and more spectacular for polyethylene, where the contact angle decreases by more than 60° in the first seconds of exposure, 140 which accounts for a large increase in wetting. Storage in natural air of the treated materials showed an aging effect and a very slow increase in the contact angle, which may result from two antagonistic effects: the adsorption of dust, which has a tendency to decrease wetting, and TPDR, which has an opposite effect.

These arguments let us consider that TPDR presents some general character, which, however, must be systematically checked.

A side consequence of the occurring TPDR concerns the reliability of the results for a given treatment: the longer the required time to achieve a suitable analysis, the longer the time allowed for potential TPDR to develop and the more efficient the "overall" plasma treatment. It is then necessary to examine the exact time elapsed after switching off the discharge, to compare the analysis data and derive a reliable kinetic evolution of the system, and such essential details are rarely given in published papers.

6. Technical Trends and Conclusion

6.1. Specific Reactions. The dream of every chemist is to achieve a chemical reaction with 100% yield. This dream is definitely out of reach in plasma chemistry, because electric discharges generate a large number of species, most of them being reactive. An increase in the energy available in the reactor should then be a key parameter, because it is related to the formation of activated species: one must remember that the specific energy delivered to the discharge falls in the following ranges: 10 J/L for standard corona discharge, 10-30 J/L for DBDs, and 500–700 J/L for gliding discharges. Therefore, the gliding discharges seem to be more favorable for getting faster reactions than other plasma systems that are operated at atmospheric pressure.

However, having too much available energy may allow unexpected species to form, react with the target molecules, and yield unexpected products.

The only reasonable way to improve the yield of the desired reaction results in a sharp limiting of the number of the activated species that are formed in the discharge and are able to interfere with the considered reaction. We then can guess that a steep filtering might allow one to discard most of the undesirable species. It could involve either a chemical method (by introducing molecules able to enter specific reactions with the discarded species) or, more likely, an energy filter with a thin energy range that would allow the expected species to form.

6.2. Increasing the Reactor Efficiency. The standard gliding discharge reactors developed for pollution abatement present various interesting characteristics, compared with other systems. For example, the size of the reactor and the energy source is small and the setup can be disposed in a classical decontamination line or, even better, gather and process the wastewater taken from a given plant. The pollutant abatement rate is obviously dependent on the nature of the pollutant and cannot be predicted, although it falls in the range of the industrially acceptable rate values. In addition, examples of recalcitrant pollutants that have been degraded by gliding discharges are numerous, which shows that the technique is ready to be developed for industrial applications.

A less-ambitious aim up to now is to improve the reactor efficiency. Several working parameters were identified, and their influence was carefully checked by several workers. The nature of the gas and the flow rate were considered. The possibilities remain limited within a given flow rate range.

All the investigated parameters concern the interface between the plasma gas and the target that must be enlarged, and various systems were examined. One of them concerns using several electrodes (e.g., a couple of main electrodes and a couple of controlled electrodes that allow one to lower the required potential drop and increase the current intensity. This setup also enables one to increase the gap between the main electrodes and then dispose of an enlarged plasma-treated area). The use of a multielectrode device was proposed and determined to be more efficient.²

Circulation reactors revealed themselves to be more efficient than batch reactors.

Several injection devices were compared, and the nozzle for the liquid input was positioned along the axis of the reactor or perpendicular to the gas flow, which seems to be the moreefficient system, and increased the reaction rate significantly.

6.3. Economical Interest of Post-Discharges. The economical aspect of temporal post-discharge reactions (TPDRs) is easily demonstrated by the fact that the discharge is only used to start the desired reactions. Then, leaving the target liquid out of the discharge allows the TPDR to develop without expending further energy. This feature suggests that the exposure time to the discharge t^* might be drastically shortened, even down to a series of short pulses, so that the gliding discharge could join the group of pulsed electric discharges or any other technique that involves pulse energy.

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