

Short communication

## Gliding discharge-induced oxidation of a toxic alkaloid

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### Abstract

The gliding discharge is a quenched plasma source suitable for the plasma treatments of liquids since it is operated in quasi-normal  $T$  and  $P$  conditions. Discharges in wet air provide a flow of strongly oxidizing radicals, e.g.,  $\text{NO}^\bullet$  and  $\text{HO}^\bullet$ , able to oxidize and mineralize many organic pollutants in aqueous solution. The present paper reports on the destruction of nicotine, a toxic alkaloid from tobacco used as insecticide. Mineralization was monitored by total organic carbon (TOC) analysis and obeyed an overall first order kinetics mechanism. Carbon dioxide formation was followed by specific reactive Dräger tubes. The influence of the airflow rate was considered.  
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### 1. Introduction

Advanced oxidation processes have been a new part of ecological research for about two decades because they enable oxidation reactions called “cold combustion” by forming strongly oxidizing oxygenated species at atmospheric pressure and near room temperature. Among these techniques, the electric discharges, and more specifically the gliding discharge are among the cheapest ones to generate a non-thermal plasma. They require a cheap and easy to build device using commercial equipment and materials, with inexpensive operating cost, which makes it very attractive for industry and scientists.

This device involves an electric discharge generated by a HV transformer (5–10 kV; mean current intensity in working conditions: 160 mA) between at least two diverging electrodes. An arc forms at the shortest electrode gap (few mm): its feet move along the electrodes by a gas flow directed along the electrode axis. The arc length increases and the gas temperature falls accordingly, until the arc bursts in a plasma plume when short-circuited by a new arc. The thermal equilibrium between the electrons and the heavy species of the plasma is no more ver-

ified, since the temperature of the heavy species is drastically lowered with respect to the electrons. The liquid target exposed to the plasma plume at atmospheric pressure is then brought into contact with a quenched plasma at an overall mean temperature close to room temperature [1]. The electric energy is transferred to gas molecules which get excited or broken into radicals giving highly reactive species. For gliding discharge operated in wet air, the occurrence of  $\bullet\text{OH}$  and  $\text{NO}^\bullet$  radicals was evidenced by emission spectroscopy [2] as the main species in the plasma plume, additionally to  $\text{O}_2$ ,  $\text{N}_2$ , and  $\text{H}_2\text{O}$ . Surprisingly no oxygen-containing species, such as excited oxygen, atomic or ionic oxygen, ozone nor hydrogen peroxide or hydroperoxyl radical was identified [3] in the plume which is in contact with the target. The presence of  $\text{H}_2\text{O}_2$  in the liquid phase was checked in immersed and in gliding discharges [4,5]. The literature also reports that OH was quantified in immersed discharges [5].

These species are endowed with very strong oxidizing chemical properties (Table 1), and therefore able to oxidize organic solutes whose standard potential is not so far than 0.1 V/NHE and scarcely higher than 0.8 V.

The  $\text{NO}^\bullet$  radical whose standard oxidation potential is largely higher than 1 V is also involved in numerous oxidation/reduction systems, the NO readily reacts with oxygen to yield  $\text{NO}_2$  which is also the source of both oxidizing and acidic species [13,14].

The humid air plasma thus presents very interesting enhanced chemical properties. The device referred to as the “glidar” dis-

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Table 1  
Some selected pertinent oxidising systems [6–8]

Ox + $ne^-$	$\leftrightarrow$	Red	$E^\circ$ (V/SHE)
$\text{OH} + \text{H}^+ + e^-$	$\leftrightarrow$	$\text{H}_2\text{O}$	2.85
$\text{O}_{\text{gas}} + 2\text{H}^+ + 2e^-$	$\leftrightarrow$	$\text{H}_2\text{O}$	2.42
$\text{O}_3 + 2\text{H}^+ + 2e^-$	$\leftrightarrow$	$\text{O}_2 + \text{H}_2\text{O}$	2.07
$\text{HO}_2 + 3\text{H}^+ + 3e^-$	$\leftrightarrow$	$2\text{H}_2\text{O}$	1.70
$\text{H}_2\text{O}_2 + 2\text{H}^+ + 2e^-$	$\leftrightarrow$	$2\text{H}_2\text{O}$	1.68
$\text{O} + e^-$	$\leftrightarrow$	$\text{O}^-$	1.61
$\text{O}_3 + 6\text{H}^+ + 6e^-$	$\leftrightarrow$	$3\text{H}_2\text{O}$	1.51
$\text{HO}_2 + \text{H}^+ + e^-$	$\leftrightarrow$	$\text{H}_2\text{O}_2$	1.50
$\text{O}_2 + 4\text{H}^+ + 4e^-$	$\leftrightarrow$	$2\text{H}_2\text{O}$ (liq./gas)	1.23 (liq)/1.19 (gas)
$\text{ONO}_2^- + 2\text{H}^+ + e^-$	$\leftrightarrow$	$\text{NO}_2 + \text{H}_2\text{O}$	2.05
$\text{NO}^+ + e^-$	$\leftrightarrow$	$\text{NO}$	1.21
$\text{NO}_2 + \text{H}^+ + e^-$	$\leftrightarrow$	$\text{HNO}_2$	1.09
$\text{NO}_2 + 2\text{H}^+ + 2e^-$	$\leftrightarrow$	$\text{NO} + \text{H}_2\text{O}$	1.05
$\text{NO}_3^- + 3\text{H}^+ + 2e^-$	$\leftrightarrow$	$\text{HNO}_2 + \text{H}_2\text{O}$	0.96
$\text{NO}_3^- + 4\text{H}^+ + 3e^-$	$\leftrightarrow$	$\text{NO} + 2\text{H}_2\text{O}$	0.92

charge [9] was successfully used for the treatments of gases [9,10] and more recently for that of spent solvents [11,12], for pollutant abatement in aqueous solutions [13–16] and for the solids surface properties modification [17]. This paper presents a direct application of the aqueous media treatment through the plasma-induced mineralization of nicotine, which is a highly toxic alkaloid used as insecticide and also present in tobacco industry wastes. It allows us to complete our experience on the plasma treatment of N-containing molecules (e.g., amines and amides [12,16], diazoic dyes [15], or proteins [18].

The reaction between the activated species formed in the discharge and nicotine molecules takes place at the liquid surface in contact with the impinging plasma species.

## 2. Experimental

A scheme of the gliding discharge reactor is presented in Fig. 1. It involves a glass cylinder fitted with water-cooling jacket and magnetic stirring. The gliding discharge takes place between two diverging aluminium electrodes symmetrically disposed in the vessel around a blowing nozzle that allows the gas input. In the present study, the nozzle is fed with wet air obtained by bubbling air provided by a compressor through a water-filled Durand flask. The electrodes are raised to a 10 kV potential fall provided by an Aupem Sefli HV (ac, 50 Hz) transformer. Two wet airflow rates, i.e.,  $540 \text{ L h}^{-1}$  and  $730 \text{ L h}^{-1}$ , were studied. In both cases a standard volume of 200 mL of  $7.47 \times 10^{-4} \text{ M}$  aqueous solution of L-nicotine was exposed to the plasma flow. The remaining total organic carbon (TOC) was measured every hour with a Shimadzu TOC-VE analyser. The sampling was immediately performed after switching off the discharge and analysed by TOC-meter. The formation of carbon dioxide was also shown by specific reactive Dräger tubes disposed in a T-shaped derivation disposed on the exhaust gas pipe before the condenser.

Nicotine is purchased from Aldrich and used without further purification. The target solutions are prepared with distilled water.

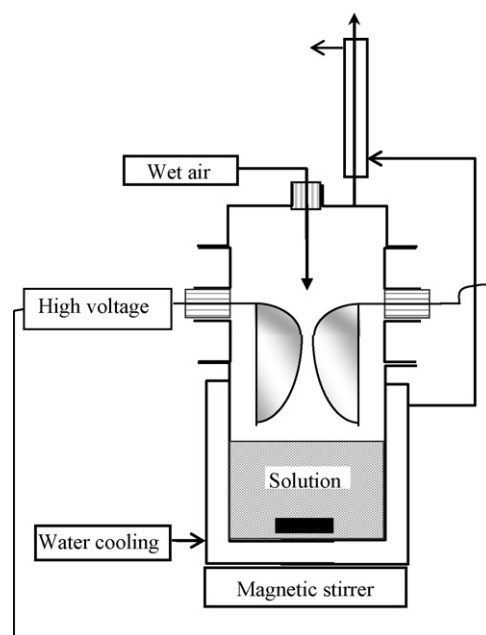


Fig. 1. Scheme of the experimental device.

## 3. Results and discussion

The gliding degradation of a large number of organic pollutants [7–10] dispersed in solution showed an overall zero-order mechanism (for concentrated targets, with constant  $k_0$ ) followed by a first order mechanism for dilute solutions (constant  $k_1$ ). The concentration of the organic solute decreases with increasing exposure time for given working parameters. After reminding the main lines of an already published model, which emphasizes the influence of the plasma/liquid contact surface, we plan to focus on the influence of the gas flow rate. Fig. 2 illustrates the TOC decrease kinetics for both airflows.

The transfer of active species (i.e., both primary species such as NO or OH which were spectrophotometrically observed and measured, and secondary species that result from the interaction of the primary species with the ambient gas, e.g.,  $\text{NO}_2$ ,  $\text{H}_2\text{O}_2$ ) is probably the rate-limiting step of the overall process. For concentrate solutions, the key parameter is likely the flux of primary species which varies in the same way as the energy provided to the discharge in a given energy range. This flux provides less numerous active species than the target molecules present at the surface of the concentrate solute. Then the zero-order kinetic rate  $k_0$  accounts for the very beginning of the process. The situation is illustrated in the present study by Fig. 2A and for  $t < 60 \text{ min}$ :  $k_0$  increases as the delivered energy and the gas flow rate increase.

A second kinetic step (constant  $k_1$ ) is first ordered and observed for dilute solutions: it has been attributed to diffusion phenomena of the solute molecules to the surface. This is probably the situation considered in the present study: Fig. 2B shows a linear correlation between  $\text{Ln}(\text{TOC})$  and long exposure times for both gas flow rates.

However, if diffusion of the solute target was the only parameter that governs the second (diffusion) step, the  $k_1$  values should then be constant and should not depend on the gas flow. This

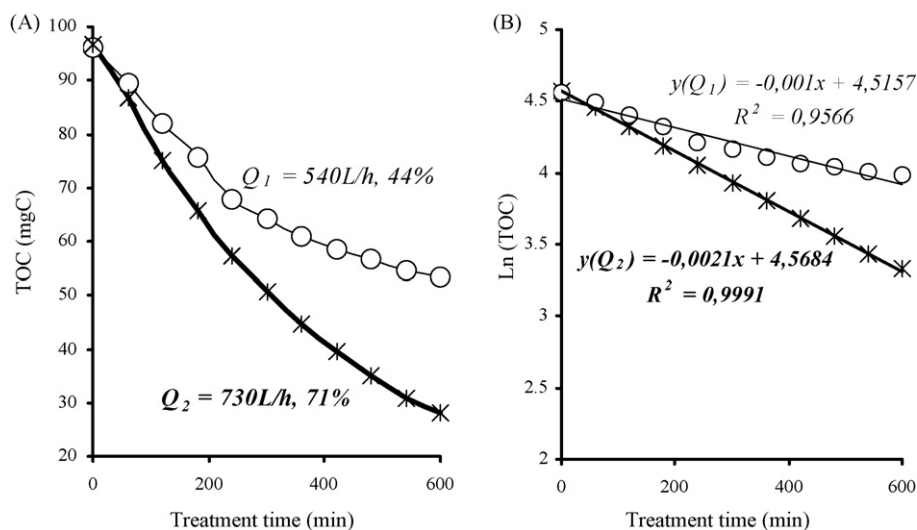


Fig. 2. TOC monitoring of the solution: (A) plot of the kinetics and (B) plot of  $\text{Ln}(\text{TOC})$  vs. exposure time showing an overall first order reaction.

feature is not observed (Fig. 2B). The working conditions have then to be considered. The wet airflow falls normally to the liquid surface and causes vigorous agitation and important changes in the treated surface. The more important the flow is, the stronger the agitation and the larger the liquid surfaces are. The gas to liquid exchange is favoured and the resulting kinetics enhanced. However, the input gas flow rate cannot be carelessly increased in our batch reactor because a too high flux should blow out the arc as soon as forming and create such an instability of the liquid phase that the kinetic results should be poorly reproducible.

The overall kinetics observed in this study obey typical first order laws, as confirmed by the plots of  $\text{Ln}(\text{TOC})$  vs. the exposure time  $t$  (Fig. 2B). The limiting factor is the diffusion flow  $f$  of the solute molecules from the bulk solution to the gas–liquid interface:

$$f = KS(C - C_{\text{lim}}) \quad (1)$$

where  $K$  is the diffusion coefficient,  $S$  the effective process occurring interface between the plasma and the liquid,  $C$  and  $C_{\text{lim}}$  the respective nicotine concentration in the bulk solution and at the interface.

Assuming that  $C_{\text{lim}}$  is very low compared with  $C$ , Eq. (1) becomes Eq. (2):

$$f = KSC \quad (2)$$

The resulting reaction rate  $V$  is proportional to the diffusion flux  $f$  by means of the proportionality constant  $r$  and can be written as

$$V = rf = rKSC \quad (3)$$

$$V = r'SC = kC \quad (4)$$

If the effective interface is assumed to have a nearly constant area  $S$  during the experiment, then

$$-\frac{dC}{dt} = kC \quad (5)$$

The associated integral form, i.e.,

$$C = C_0 e^{-kt} \quad (6)$$

(with  $C_0$  referring to the initial concentration in carbon), agrees with a first order kinetics. It is worth to point out that the monitored variable accounts for the total organic carbon concentration and not only for the nicotine concentration. The relevant variables may slightly differ, due to occurrence of partial degradation products. The degradation rate is not very rapid in batch conditions and an abatement of 50% of the starting concentration requires 300 min.

The plots illustrated in Fig. 2 show that the overall rate constant  $k$  obtained with the greatest airflow ( $Q_2 = 730 \text{ L h}^{-1}$ ) is twice as great as that associated with  $Q_1 = 540 \text{ L h}^{-1}$ . The linearity of  $\text{Ln}(\text{TOC})$  vs.  $t$  is also improved when the gas flow rate increases, as illustrated by the plot relevant to  $Q_2$  (Fig. 2B). A greater airflow reduces the time of flight of the active species between the electrodes and the liquid interface. By that way more active species are still present at the interface and drift to the solution. Such effect of the airflow was already observed [13,14]. A matching argument is that an increased flow of the activated species prevents any accumulation of partial degradation products at the target surface, which might otherwise behave as a passive layer. This means that such compounds are less stable than nicotine toward active species and are degraded prior to nicotine as soon as they are formed, so that the monitored TOC is mainly given by nicotine. In the case of  $Q_1$  ( $540 \text{ L h}^{-1}$ ) airflow, a low concentration of active species induces a slight accumulation of the degradation products, so the monitored TOC concentration slightly differs from the nicotine concentration in the bulk solution, and causes a slight discrepancy with a “true” first order plot. The complete degradation was confirmed by carbon dioxide detection with Dräger-specific reagent tubes.

Increasing the degradation rate may result from a vigorous stirring, and one can guess that increasing the rotation rate of the stirrer would improve the plasma/liquid surface and facilitate the reaction. It would actually result in an increase in the

exchange surface but also in splashing the reactor walls with the electric risk of short-circuiting the arc and increase instability of the device. Other solutions have then to be developed and a promising one is operating with a circulating reactor equipped with a modified input gas nozzle.

#### 4. Conclusion

Aqueous solutions of nicotine, a toxic compound used as an insecticide, were exposed to gliding electric discharges. As expected a noticeable abatement of the pollutant concentration resulted, as already shown by other experiments [11–14]. The degradation depended on the input gas flow rate: 50% of the initial pollutant concentration was mineralized within 5 h treatment when operating with  $Q=730\text{ L h}^{-1}$  while a longer treatment time was required for a weaker flow rate. The purpose of this study was not to optimise the reaction rate, and in this event a recycling mode would have been preferred, but to confirm the influence of the feeding flow rate. Arguments are proposed to account for this feature, which are based on the accumulation of a “passivating” layer at the target surface which is not dissipated when operating at a low flow rate. With a greater airflow partial degradation products do not accumulate in the solution and the monitored TOC is related to nicotine. By that way the TOC plot of nicotine disappearance follows more tightly a first order kinetic model, which agrees with other experiments on the plasmachemical degradation of organic pollutants. Work is in progress to improve kinetics and especially to improve the plasma–liquid exchange surface, e.g. by using circulation reactor with modified gas input, and to extend gliding discharge to the treatment of other pesticides.

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