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# Plasma chemical oxidation of phthalic anhydride: application to the treatment of Tunisian landfill leachate

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## Abstract

The performance of several catalysts (Fe (III), Fe (II) and TiO<sub>2</sub>) for the removal of phthalic anhydride by gliding arc plasma was studied, among which Fe (II) was the best catalyst (75 % of removal after 180 min). Indeed, the addition of Fe (II) into the reaction allows a better elimination of the organic matter through the production of additional .OH radicals. The oxidation of Persistent Organic Pollutants present in landfill leachate was studied by varying the loading of TiO<sub>2</sub>, and after 8h of treatment 51 % of removal was reached for 15 g L<sup>-1</sup> of TiO<sub>2</sub>.

## Keywords

Phthalic anhydride, landfill leachate, gliding arc plasma, catalyst, hydroxyl radicals.

## INTRODUCTION

The increase in industrial and agricultural activities in developing countries requires the use of increasingly high varieties and quantities of synthetic chemicals such as pesticides, insecticides, dyes and chemical additives. Most of these chemicals are Persistent organic Pollutants (POPs) and considered toxic when present in the aquatic environment. Among these pollutants, Phthalic acid esters (PAEs) are essentially used as plasticizers to increase the flexibility and durability of polyvinyl chloride “Alatrisme-Mondragon et al. (2003)”. Slightly associated to the polymer matrix, the phthalates (Fig. 1) can migrate from various articles on PVC “Marcilla et al. (2004)” to aquatic medium. Thus, the phthalic acid esters (PAEs) were identified in several kinds of environmental samples, like municipal solid waste composis “Gonzalez-Vila et al. (1985)”, river sediments and landfill lactates (Bauer and Herrmann. (1997)”.

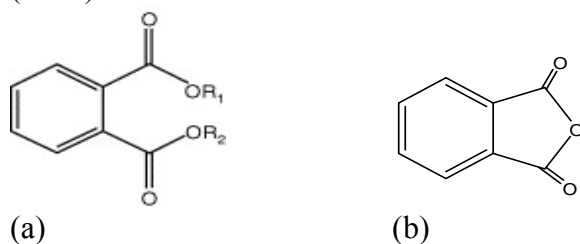
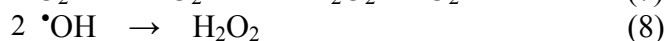
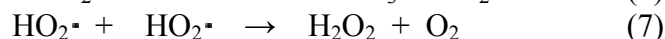
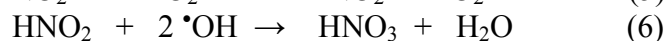
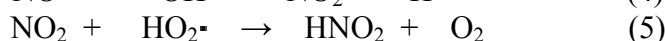
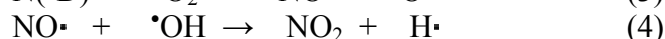
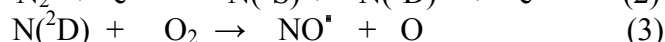
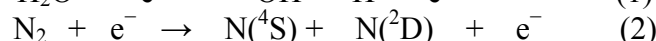
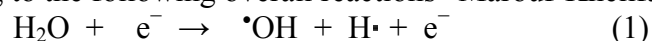


Figure 1: Chemical structure of: (a) phthalates and (b) phthalic anhydride.

PAEs were biorefractory compounds; the common treatment processes applied are inefficient. In this way, plasticizers can persist in the environment and contaminate the surface water and groundwater “Iraja do Nascimento et al. (2003)”.

The advanced oxidation processes (AOPs) have been significantly developed, which generate highly reactive intermediates (i.e.,  $\cdot\text{OH}$ ), able to oxidise even the persistent organic substances. The gliding arc or glidarc discharge is one of attractive emerging AOPs operating at atmospheric pressure and at low (close to ambient) temperature. It is well adapted to the pollution abatement from aqueous solutions “Abdelmalek et al. (2008)” “Ghezzar et al. (2009)” and gases “Kranczyk and Matek. (2001)”.

The exposure to humid air plasma generates the  $\text{NO}\cdot$  and  $\cdot\text{OH}$  « Mutaf-Yardinci et al. (2000) ». The  $\cdot\text{OH}$  species is the main responsible for strong oxidizing character of the discharge. On the other hand, the  $\text{NO}\cdot$  radical leads to the formation of  $\text{NO}_2$ , nitrite and nitrate ions according to the following overall reactions “Marouf-Khelifa et al. (2006)”:



A number of parameters such as solution composition, nature and concentration of catalyst, electrode material, and power supply voltage play important roles in the organic pollutant degradation.

The aim of this work is to investigate the influence of the nature and the concentration of some catalysts (Fe (III), Fe (II) and  $\text{TiO}_2$ ) to find the optimum condition of the oxidation of phthalic anhydride aqueous solution by glidarc discharges and to apply this process to a Tunisian landfill leachate from Jebel Chekir.

## MATERIAL & METHODS

The experimental apparatus of the glidarc plasma used is shown in Figure 2. An electric arc forms between two diverging electrodes rose to a convenient voltage difference at the minimum gap. A special generator (9000 V; 100 mA without charge) provides the electric power. The arc is pushed away from the ignition point by the feeding gas flow and sweeps along the maximum length of the electrode gap and forming a large plasma plume, so that it licks the liquid surface, and allows the chemical reactions to take place at the plasma–solution interface, thus generating highly reactive species.

A 200 mL solution is placed into the 1.0 L Pyrex reactor equipped with a cooling system to avoid evaporation. The treatment is done in open system fixing the functioning parameters. The gas flow is fixed at  $Q = 650 \text{ L h}^{-1}$ , the divergence between the electrodes  $e = 3.5 \text{ mm}$  and the distance between the electrodes and the target liquid surface  $d = 2.5 \text{ cm}$ .

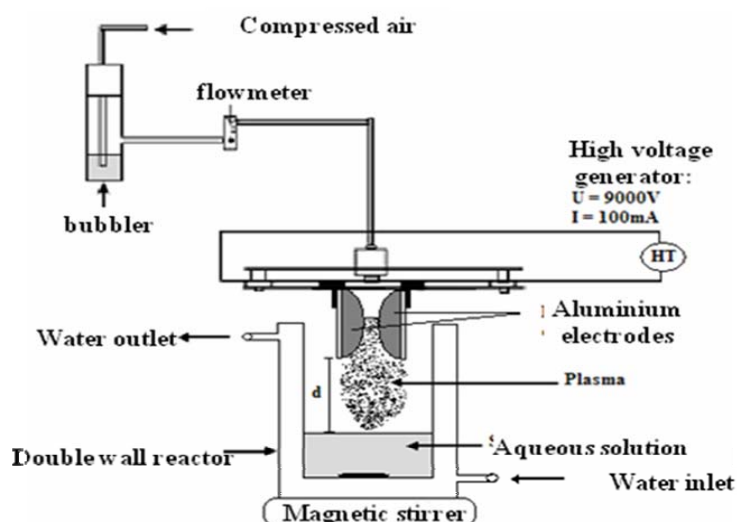
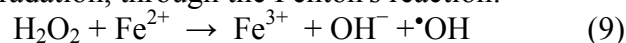


Figure 2: Experimental device of Glidarc

## RESULTS AND DISCUSSION

### Study of the phthalic anhydride removal by $GAD_{\text{humid air}}$ / iron ions

To promote the removal rate and removal efficiency of organic pollutants, and fully utilize excessive hydrogen peroxide, the introduction of catalyst (iron ions) into gliding arc discharge system is recommended. Indeed, the iron ions (ferrous and ferric ion) can react with residual hydrogen peroxide, and produce a large amount of  $\bullet\text{OH}$ , a powerful oxidizing agent for organic pollutants degradation, through the Fenton's reaction:



A phthalic anhydride aqueous solution ( $5 \times 10^{-2}$  mM) was exposed to a gliding arc discharge. The Fe (II) added range being from 0,1 to 1 mM, the evolution of the phthalic anhydride concentration in function of time was followed by HPLC. The results are summarized in Figure 3.

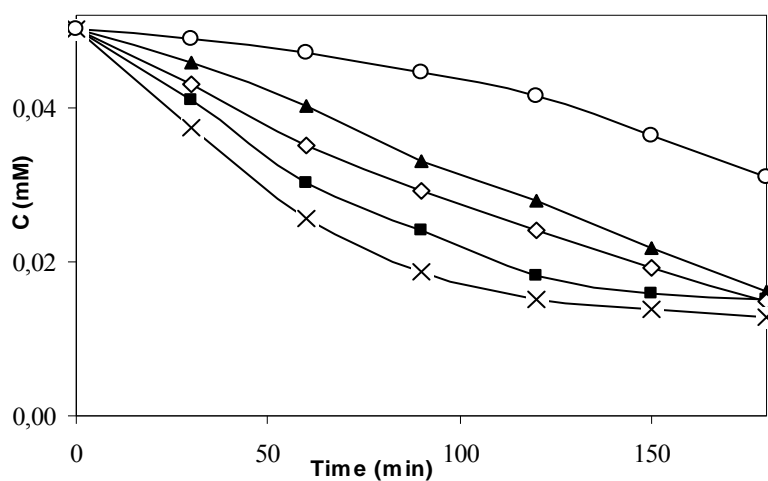
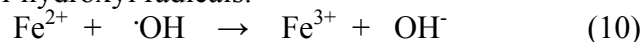
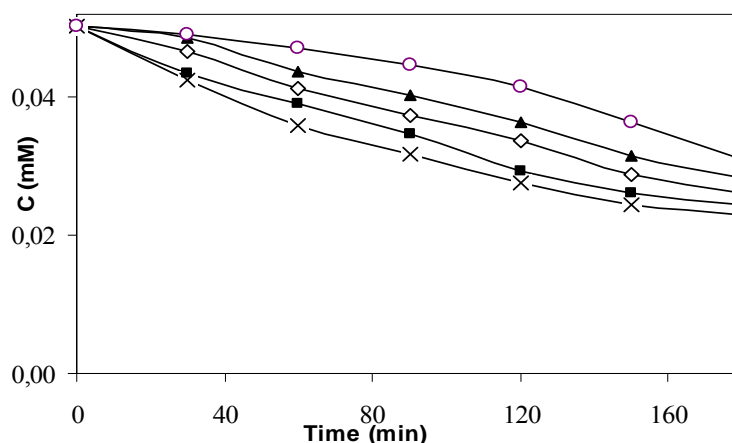


Figure 3: Effect of catalyst (FeII) initial concentration on phthalic anhydride decay as a function of time during gliding arc discharge treatment.  $[\text{FeII}]$ : 0 (○); 0,1 (▲); 0,2 (◇); 0,5 (×) and 1 (■) mM.  $[\text{phthalic anhydride}]_0 = 0,05$  mM,  $V = 200$  mL,  $\Phi = 650$  L  $\text{h}^{-1}$ ,  $d = 2,5$  cm.

As can be seen in this figure, the phthalic anhydride removal rate depends on the ferrous ions initial concentration. Indeed, the increase of the catalyst concentration from 0,1 to 0,5 mM allows the increase of the removal rate from 38,8 to 75,4%, after 180 min of treatment. However, in the presence of high catalyst concentration, the removal kinetic of anhydride becomes slower. This can be explained by the increase of the rate of parasites reactions (Eq. 10) which compete for hydroxyl radicals.



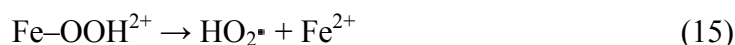
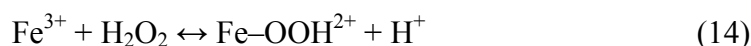
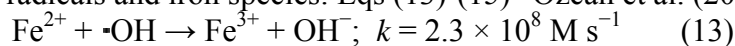
The removal of phthalic anhydride in the presence of Fe(III) as catalyst was also conducted under operating conditions cited in the previously. We have varied the Fe (III) initial concentration from 0,1 to 1,0 mM. The results are shown in Figure 3.



**Figure 4: Effect of Fe (III) initial concentration as catalyst on phthalic anhydride decay as a function of time during gliding arc discharge treatment. [Fe (III)]: 0 (○); 0,1 (▲); 0,2 (◇); 0,5 (×) and 1 (■) mM. [phthalic anhydride]<sub>0</sub> = 0,05 mM, V = 200 mL, Φ = 650 L h<sup>-1</sup>, d = 2,5 cm.**

As can be seen from this figure, the removal rate increases with increasing Fe (III) concentration from 0,1 to 0,5 mM. After this value, the removal becomes slow.

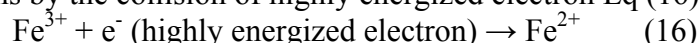
The negative influence of the higher catalyst concentration on oxidation kinetics can be explained by the increase of the rate of parasitic reactions occurred during the process between hydroxyl radicals and iron species: Eqs (13)-(15) “Ozcan et al. (2009)”



Similar observations were already reported by some publications “Trabelsi et al. (2009)”.

In this word, we found that the optimal concentration of Fe (II) and Fe (III) for the removal of phthalic anhydride is about 0,5 mM. Subsequently, we compared the results obtained for the two catalysts.

It can be note that the ferric ions have a promoting effect on phthalic anhydride degradation in the GAD<sub>humid air</sub> processes, although the promoting effect of ferric ions is somewhat weaker than that of ferrous ions. It may be explained that ferric ions are converted to ferrous ions for Fenton-like reactions by the collision of highly energized electron Eq (16).

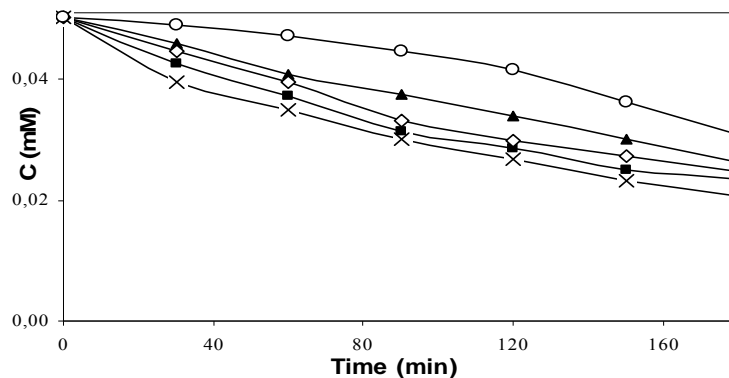


This result is in agreement with that obtained by “Hao et al. (2007)”.

## Plasmacatalysis treatment with TiO<sub>2</sub>

The photocatalysis of organic compounds using  $\text{TiO}_2$  particles presents many advantages, so  $\text{TiO}_2$  has been extensively used in the mineralization of toxic organic contaminants present in wastewater. Hence, combined plasmachemical treatment and  $\text{TiO}_2$ -mediated heterogeneous process may be efficient for the oxidation of the organic pollutants. The photogenerated electrons react with adsorbed molecular  $\text{O}_2$ , reducing it to superoxide radical anion  $\text{O}_2^{\cdot-}$ , and the photogenerated holes either can oxidise the organic molecules directly, or can oxidise  $\text{OH}^-$  ions and water molecules adsorbed on the  $\text{TiO}_2$  surface to form  $\cdot\text{OH}$  radicals “Ghezzer et al. (2007)”. These will act as strong oxidizing agents that can easily attack any organic molecules adsorbed on, or located close to the surface of the catalyst, thus leading to their degradation into small inorganic species.

The determination of the optimal concentration of catalyst was made regarding oxidation of the phthalic anhydride as a function of time. We varied the catalyst concentration from 0 to  $4 \text{ g L}^{-1}$ . The results (Figure 5) show that the kinetic of oxidation increase by the increase of the catalyst concentration until reaching the concentration of  $2 \text{ g L}^{-1}$ . Beyond this optimal catalyst concentration, a reduction in the treatment efficiency was observed.



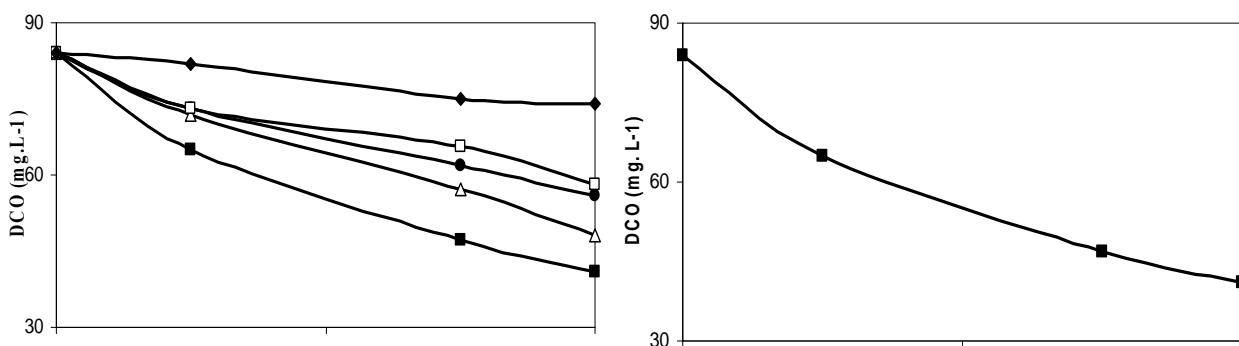
**Figure 5: Effect of catalyst ( $\text{TiO}_2$ ) initial concentration on phthalic anhydride decay as a function of time during Gliding arc discharge treatment.  $[\text{TiO}_2]$ : 0 ( $\circ$ ); 1 ( $\blacktriangle$ ); 2 ( $\times$ ); 3 ( $\blacksquare$ ) and  $4 \text{ g L}^{-1}$  ( $\diamond$ ).  $[\text{phthalic anhydride}]_0 = 0.05 \text{ mM}$ ,  $V = 200 \text{ mL}$ ,  $\Phi = 650 \text{ L h}^{-1}$ ,  $d = 2.5 \text{ cm}$ .**

These results show that a concentration higher than  $2 \text{ g L}^{-1}$ , can affects negatively the degradation efficiency. Thus, in the case of high  $\text{TiO}_2$  concentrations, the aggregation of the particles reduces the contact surface between the solution and catalyst, decreases the number of active sites on the surface rendering difficult light infiltration resulting in a loss of catalyst efficiency “Ghezzer et al.(2007)” and “Sequib et al. (2003)”.

Finally, Figure 2, 3 and 4 show that the  $\text{GAD}_{\text{humid air/ FeII}}$  process is more efficient than the  $\text{GAD}_{\text{humid air/ FeIII}}$  and photooxidation process.

### Plasmacatalysis depollution of landfill leachate with $\text{TiO}_2$

The determination of the optimal concentration of  $\text{TiO}_2$  was made regarding oxidation of persistent organic pollutants present in the landfill leachate as a function of time. We varied the catalyst concentration from 0 to  $35 \text{ g L}^{-1}$ . The results (Figure 6) show that the oxidation increase by the increase of the catalyst concentration until reaching the concentration of  $15 \text{ g L}^{-1}$  (51 % of removal). Beyond this optimal catalyst concentration, a reduction in the treatment efficiency was observed “Sequib et al. (2003)”.



**Figure 6: Effect of catalyst (TiO<sub>2</sub>) initial concentration on Tunisian landfill leachate treatment as a function of time during gliding arc discharge treatment. [TiO<sub>2</sub>] en g L<sup>-1</sup>: 35 (◆); 25 (□); 0 (●); 10 (△) and 15 g L<sup>-1</sup> (■). [phthalic anhydride]<sub>0</sub> = 0,05 mM, V = 200 mL, Φ = 650 L/ h, d = 2,5 cm.**

## CONCLUSIONS

The glidarc is a non-thermal source of plasma, which generates very reactive species such as OH radicals. These species exhibit powerful oxidizing properties that capable of mineralizing organic compounds. In this study, we used the plasma in humid air for the degradation of phthalic anhydride solution. Effect of nature and concentration of catalyst was studied. It is found that phthalic anhydride decay rate was enhanced when [Fe<sup>2+</sup>] = 0.5 mM is used as catalyst. Indeed, after 8h, 65% of phthalic anhydride was oxidized.

Tunisian landfill leachate was also treated by gliding arc plasma. The use of TiO<sub>2</sub> photocatalyst has produced a promoting effect with plasma in humid air. Indeed after 8 h of treatment using [TiO<sub>2</sub>] = 15 g.L<sup>-1</sup>, 51% of COD was removed. This non satisfactory mineralization efficiency can be enhanced by using of closed system.

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