

# Simulation of the degradation of methyl red by gliding arc plasma

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## Abstract:

The use of plasmas for the treatment industrial effluents provides a new alternative to the decontamination of wastewater. The strong oxidizing species ( $O$ ,  $O_3$ ,  $OH$ ) generated by the plasma, at room temperature, can oxidize organic pollutants present in the water. A GliArc reactor used for the treatment of an organic pollutant dissolved in industrial effluents (Methyl Red) is simulated with the CFD code COMSOL®. Our simulation deals with the degradation of methyl red by a Glidarc humid air plasma producing active species, mainly  $OH$ , that can diffuse in the liquid phase and react with the pollutant until his oxidation. The degradation of the methyl red, performed in a horizontal laminar film reactor, was simulated in 3 steps. In the first step with a 2D configuration using a Navier Stokes incompressible model (ns) was simulated the flow in the reactor. Then with an 1D pseudo 2D convection diffusion model were simulated, the diffusion of  $OH^\circ$ , produced by the GlidArc, in the liquid, its reaction with the methyl red giving  $CO_2$ . In the 3rd step with a 2D convection diffusion model were simulated the diffusion and the reactions of species along the reactor and especially the diffusion of  $CO_2$ , issued from the depletion of methyl red. Preliminary calculations show that the total penetration depth of  $OH^\circ$  is between 0.5 and 1 mm.

**Keywords:** GlidArc reactor, waste water treatment, 2D reactor simulation

## 1. Introduction

Nowadays, the industrial effluents are an important source of environmental contamination. Indeed these effluents are often toxic. This risk and the more stringent international environmental standards lead to

limit harmful emission and the necessity of treatment. So that several decontamination processes were adopted to reduce noxious emissions such as biological, chemical or physical process. However, in spite of their success they remain limited by their cost and efficiency. The use of plasma provides a new alternative to the decontamination of wastewater, gas and soil. This kind of plasma allow to work on a quasi-ambient temperature and on atmospheric pressure. His advantage is the strong oxidizing species generated. These active species, mainly  $O^\circ$ ,  $O_3$ ,  $NO_x$  and  $OH^\circ$  with an humid air plasma, can totally or partially oxidize the organic pollutant, methyl red in our case. The used reactor is an horizontal two phase flow one (liquid and gas.) The gas phase contains the active species ( $O^\circ$ ,  $O_3$ ,  $NO_x$  and  $OH^\circ$ ) and the liquid phase the pollutant (methyl red). (fig.1).

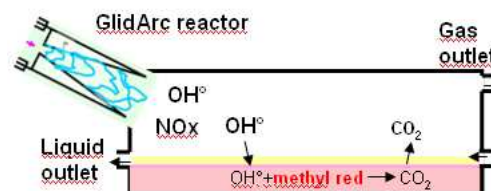


Fig.1: GlidArc reactor for waste water treatment

In the case of a dry air plasma the main species are  $NO_x$ , while in the case of a humid air the major species are  $OH^\circ$  and  $NO_x$ . These last species react with  $H_2O_2$  forming nitrate ions. In order to simplify our model we have considered only the action of hydroxyl radicals. As the reactions of  $OH^\circ$  with most of organic species are very fast [1] the limiting step should be the diffusion of  $OH^\circ$  in the liquid phase. The 1D model dealing with the diffusion-reaction of  $OH^\circ$  is based on the tutorial of COMSOL “Absorption in a falling film” [2].

## 2. Modelling of the flow field flow

The 2D model used for the simulation of the non-reactive flow, is shown in fig. 2. Humid air plasma enters in the upper left side of the reactor. The inlet velocity is 0.26m/s. The water is introduced in the right side with a velocity of 0.0033m/s. The liquid film is 5 mm thick. The flow in this two-phase media is calculated using the Navier-Stokes incompressible model chns.

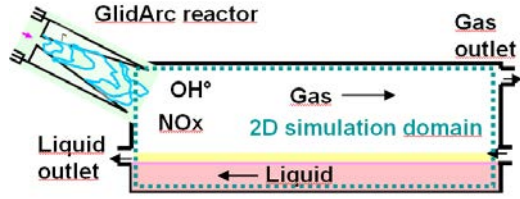


Fig.2 Domain for the calculation of the Velocity field in the reactor

The velocity field (fig.3) shows the highest velocity for the gas in the in the inlet and the outlet. In the liquid film the velocity in the x direction is low and there no convective flow the y direction.

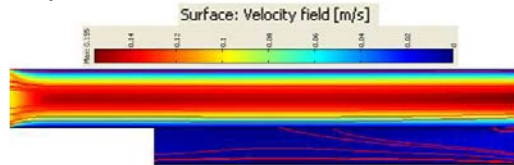
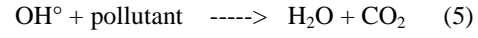
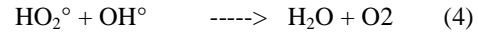
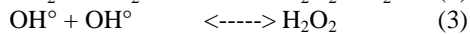
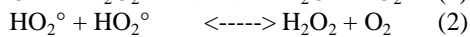
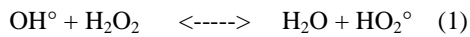


Fig.3. Velocity field in the GlidArc reactor

## 3. 1D Diffusion model (Pseudo 2D model)

In this model (fig.4) the formation of active species and especially of  $\text{OH}^\circ$  is performed by by electron-molecule collisions in the GlidArc interelectrode region. Then  $\text{OH}^\circ$  radicals diffuse in the liquid phase, react with the pollutant forming carbon dioxide. In this model is assumed that the reactions take place only in the liquid phase and there is no diffusion of the formed species in the gas phase . The kinetic model for the interaction of active species with the pollutant includes 6 species and 5 reactions: Species:  $\text{OH}^\circ$ ,  $\text{H}_2\text{O}_2$ ,  $\text{HO}_2^\circ$ ,  $\text{O}_2$ , pollutant and  $\text{CO}_2$ .

Reactions:



The first three reactions are reversible while reactions 4 and 5 are irreversible.

Constants of forward reactions are denoted  $k_{di}$  and for the reverses ones  $k_{ri}$ .

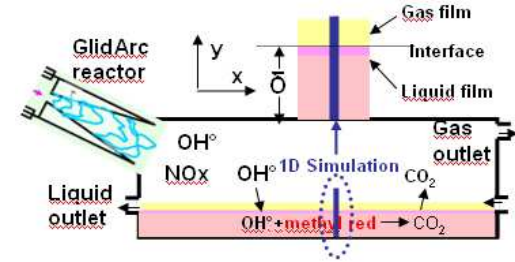


Fig.4 1D model domain

The first reaction consumes  $\text{OH}^\circ$  (formed in the GlidArc) and  $\text{H}_2\text{O}_2$ . But  $\text{H}_2\text{O}_2$  is formed again from  $\text{OH}^\circ$  or/and  $\text{HO}_2^\circ$  recombination. Reaction 4 produces  $\text{O}_2$  that can be consumed by the reverse second reaction, but the  $\text{CO}_2$  formed in the reaction 5 is accumulated.

The mass balance for the 6 species can be written as follows [2]:

$$-D_i \frac{\partial^2 c_i}{\partial y^2} + v_x \frac{\partial c_i}{\partial x} - \sum R_j = 0 \quad \text{in } \Omega$$

The first term accounts for the diffusion flux, the second for the convective one and the third  $R_j$  ( $\text{mol}/(\text{m}^3/\text{s})$ ) represents the reaction rate for each of the reactions. As in the liquid film there is velocity gradient  $dv_x/dy$ ,  $v_x$  can be written as follows:

$$v_x = 1.5v_{av} \left(1 - \left(\frac{y}{\delta}\right)^2\right)$$

where  $v_{av}$  represents the average relative velocity and  $\delta$  the thickness of the film. The space coordinate  $y$  is 0 at the gas phase boundary and  $\delta$  at the wall of the reactor. The coordinate  $x$ , is 0 at the inlet and equal to the length of the reactor, at the outlet. The concentration at the inlet of each involved species is 0 except for those of the  $\text{OH}^\circ$  in the gas phase and the pollutant at the liquid film. The transformation from horizontal coordinate  $x$  to time implies that the boundary conditions at  $x = 0$  become initial conditions at  $t = 0$  [2]. The boundary conditions for the system at the gas phase boundary is:

$$-D_i \frac{\partial c_i}{\partial x}(0, t) = 0 \quad \text{except for}$$

$$\text{OH}^\circ: -D_i \frac{\partial c_i}{\partial x}(0, t) = k_{g, \text{OH}}(p_{\text{OH}} - c_{\text{OH}} H_{\text{OH}}) \quad \text{and}$$

$$\text{CO}_2: -D_i \frac{\partial c_i}{\partial x}(0, t) = k_{g, \text{CO}_2}(p_{\text{CO}_2} - c_{\text{CO}_2} H_{\text{CO}_2})$$

where  $k_g$  ( $\text{mol}/(\text{m}^2 \cdot \text{s} \cdot \text{Pa})$ ) denotes the mass transport coefficient in the gas phase,  $p$  (Pa) is the partial pressure, and  $H$  ( $\text{Pa}/\text{m}^3/\text{mol}$ ) refers to the Henry constant.

As already mentioned there are no calculations in the gas phase, so  $\text{CO}_2$  remains in the liquid film.

As length of the reactor is 0.3 m and the average velocity is 0.0033 m/s the final time for the calculation is 100 s. However calculations were performed also for 1 and 10 seconds. The results show that hydroxyl radical is consumed immediately ( fig 5) in all cases (1, 10 or 100 seconds)

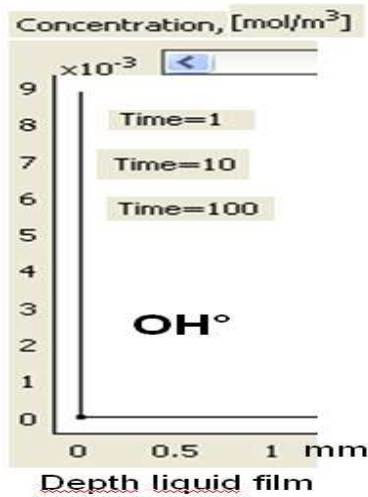


Fig. 5 Concentration of  $\text{OH}^\circ$  as a function of the depth of liquid film.

The diffuse-reactive length  $l_D = \sqrt{\frac{D}{k'}}$

Where  $D$  is the diffusion coefficient (typically  $\sim 10^{-9} \text{m}^2 \text{s}^{-1}$  in liquids) and  $k'$  is the first order rate constant ( $\text{s}^{-1}$ ) for the reaction of  $\text{OH}^\circ$ , is a measure of the distance from the interface in which the reaction occurs [3]. For a rapid reaction at the surface, one can consider  $l=1$  nm. Then  $k' \sim 10^9 \text{s}^{-1} = k[\text{species}]$  where  $k$  is a second order rate constant for the reaction between  $\text{OH}^\circ$  and a species. The reaction of  $\text{OH}^\circ$  with most organic compounds is very fast with  $k$  approaching  $10^{10} \text{l}/\text{mole} \cdot \text{s}$ . Thus for a diffuse-reactive length of 1 nm the concentration of the organic species must be of the order of 0.1 mole/l in the interface layer, which corresponds to a surface coverage of  $\sim 1\%$  of a monolayer [4]. The concentration of methyl red decreases near the interface as a consequence of the reaction

with  $\text{OH}^\circ$  (fig. 6). Its depletion increases with the residence time. At a residence time of 10s the depletion is complete at 0.5mm depth. At 100s the concentration of methyl is zero at 1.5 mm.

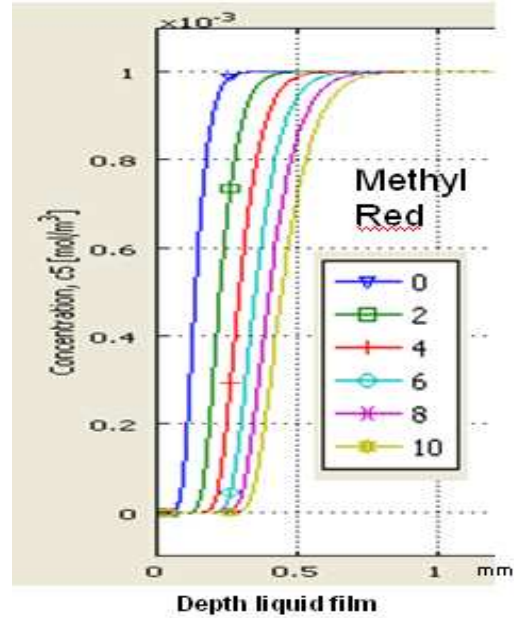


Fig 6. Depletion of methyl red for various residence times as a function of the depth of liquid film.

The depletion is obtained from the reaction of methyl red with  $\text{OH}^\circ$ , probably with formation of  $\text{H}_2\text{O}_2$  (reaction 3d) as in intermediate species at the interface, its diffusion in the liquid film and its decomposition (reaction 3r. ).

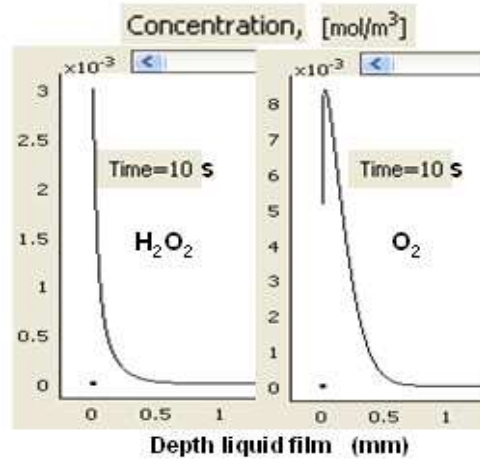


Fig. 7 Concentration of  $\text{H}_2\text{O}_2$  and  $\text{O}_2$  as function the depth of liquid film for a residence time of 10s.

Carbon dioxide formed by the reaction 6 should be released in the gas phase. Is not consumed since there is no reaction for this (fig. 8).

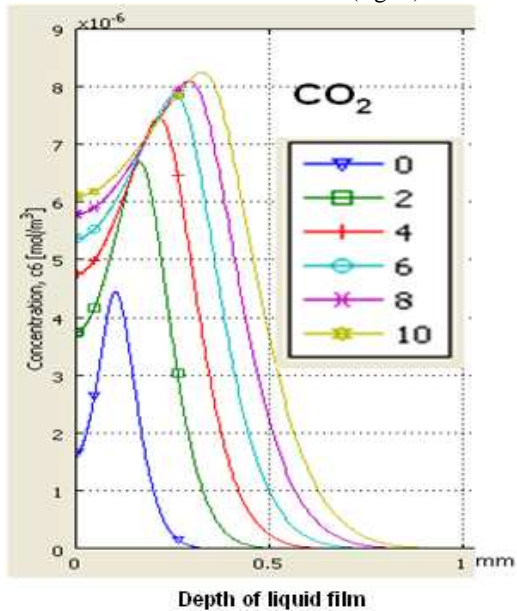


Fig. 8 Concentration of  $\text{CO}_2$  as function the depth of liquid film for a residence time of 10s.

So, it diffuses in the interface and in the bulk. At 10s,  $\text{CO}_2$  reaches a depth of 0.5 mm All the species are formed or consumed at depths less than 1 mm.

## 5. 2D model

The diffusion of OH and  $\text{CO}_2$  in the gas phase, and the convection were taken into account in a 2D configuration with a Navier Stokes (chns) and a convection-diffusion model (chcd) model. The calculated flow field with the Navier Stokes model were already presented in figure 3. For the convection-diffusion model the species occurring in both phases are introduced twice. So for  $\text{OH}^\circ$  are counted two species, one for each phase, that means  $\text{OH}^\circ_{\text{g}}$  and  $\text{OH}^\circ_{\text{l}}$ , with different diffusion coefficients. These species in the interface are in equilibrium and their concentrations in the two phases are linked with the Henry constant. It is the same for  $\text{HO}_2^\circ$ ,  $\text{O}_2$  and  $\text{CO}_2$ . Gas phase species are inactive in the liquid domain and vice-versa. Hydroxyl radicals enters from the upper left side of the domain. Its concentration

decreases from the left to the right and from the top to the interface (fig. 9).

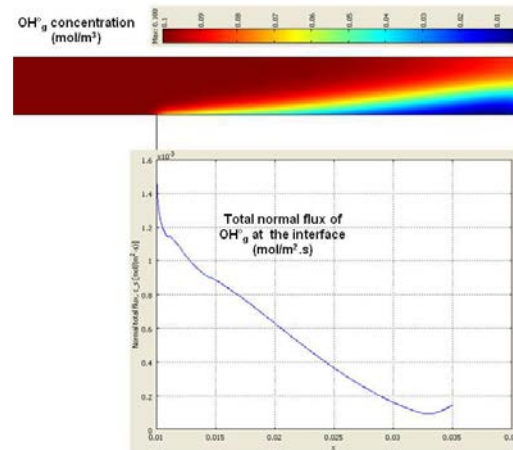


Fig. 9  $\text{OH}^\circ_{\text{g}}$  concentration in the gas phase and total normal flux at the interface

As  $\text{OH}^\circ_{\text{g}}$  has a high Henry constant value 83% of the radicals are absorbed, converted at  $\text{OH}^\circ_{\text{l}}$ .  $\text{OH}^\circ_{\text{l}}$  diffuses in the bulk and reacts with the methyl red producing  $\text{CO}_{2\text{l}}$  (fig. 10).

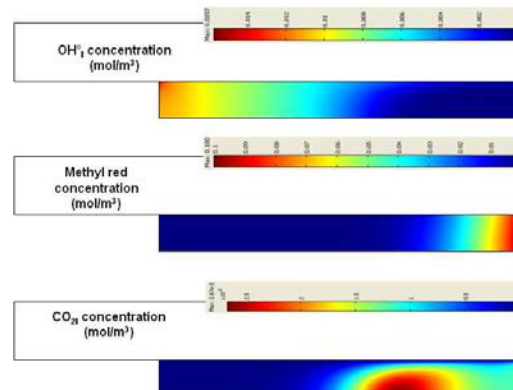


Fig. 10  $\text{OH}^\circ_{\text{l}}$ , methyl red and  $\text{CO}_{2\text{l}}$  concentration in the liquid phase.

Carbon dioxide produced only from the reaction of the depletion of the methyl red in the liquid phase, diffuses at the interface. The concentration of gas phase  $\text{CO}_{2\text{g}}$  in the interface (fig 11), in equilibrium with the liquid phase  $\text{CO}_{2\text{l}}$ , is considered as boundary limit for the resolution of convection diffusion in the gas phase domain.

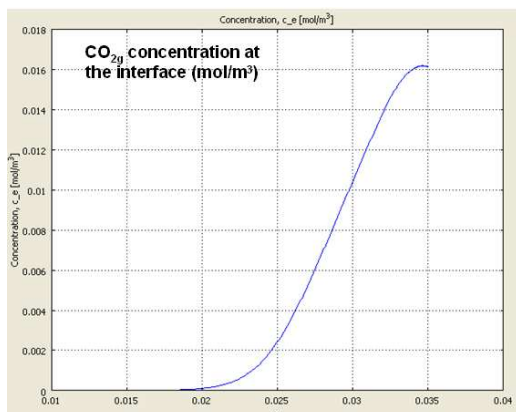


Fig. 11 CO<sub>2g</sub> concentration in the interface gas-liquid.

Carbon dioxide enter in the gas phase domain mainly from the right end of the reactor. Under the action of the convection, the concentration increases near the outlet.

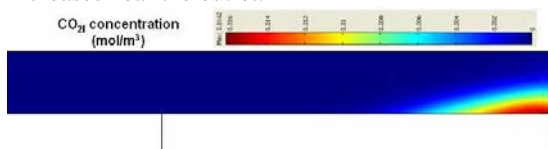


Fig. 12 CO<sub>2</sub> concentration in the gas phase

A material balance of OH at the inlet and the outlet shows that only half of the hydroxyl entered the domain is absorbed in the liquid phase and can react with a pollutant.

## 5. Conclusion

The depletion of an organic compound in waste water, treated by GlidArc plasma, can be simulated using COMSOL® code. By using a simple kinetic model for the formation of active species and their interaction with the pollutant, it is possible to obtain semi qualitative results. A relation between the residence time and the depth of the treatment is established. Only half of OH entering in the domain is used for the reaction with the methyl red in the liquid phase. Simulation shows that the absorption of OH takes place in the first tenths of mm from the interface gas-liquid. However the contact area between gas and liquid phases are still low and should improved with another reactor configuration as a bubble or three phases reactors. Obtaining more accurate and

representative results depends on the performance of the computer as it is necessary to use complex kinetic schemes including several species and reactions.

## 8. References

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