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Decoloration of Methyl Red by gliding arc discharge

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ABSTRACT

The degradation of an azo dye, the Methyl Red, has been studied by gliding arc discharge. The main advantage of this process is due to the large production of reactive species, specially the hydroxyl radicals ($OH^{\cdot}$). These radicals are able to oxidize organic pollutants and treat dye wastewater. The coupling of this process with Fenton reagent (Fe^{2+}), with Titanium oxide (TiO_2) and with TiO_2 and Fe^{2+} simultaneously was investigated in order to enhance the decoloration rate. The results show that the decoloration of Methyl Red was more efficient in the presence of Titanium oxide than Fe^{2+}. Moreover, the presence of TiO_2 has the same effect as Fe^{2+} and TiO_2 simultaneously. Under optimal condition, the degradation of Methyl Red was around 97.8%. This implies that the majority molecules of Methyl Red are destroyed. In other hand, the hydroxylation reaction of Methyl Red can be treated as a kinetic pseudo-first order.

Keywords: Humid air plasma; Gliding arc; Methyl Red; Decoloration

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1. Introduction

Dyes production industries and many others industries which used dyes and pigments generated wastewater, characteristically high in color and organic content. Some of these dyes cause health hazards [1]. These are also a dramatic source of aesthetic pollution, eutrophication and perturbations in aquatic life [2].

The toxicity and mass production of dyes leads to the necessity of treatment. There are several studies on the physical, chemical and biological treatment of dye containing effluents. For the Methyl Red, used as a model of an azo dye in this study, we can mention the biodegradation (microbiological decoloration) [3], the oxidative degradation using H_2O_2 [4], photocatalytic degradation under UV irradiation using Ag^+ doped TiO_2 [5] or in the presence of ZnO and TiO_2 [6], dye removal from aqueous solution by using adsorption [7].

However, biodegradation suffers from optimization problems, while physical adsorption is not efficient enough, due to the fact that the compounds are only transferred from wastewater to solid waste and consequently the residue needs further processing. Recently, the advanced oxidation processes (AOPs), such as humid air plasma degradation, significantly developed.

This kind of plasma allow to work on a quasi-ambient temperature and on an atmospheric pressure. The chemical composition of the plasma depends on the nature of

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used gas. When we used humid air, species formed in the discharge may react in the gas phase with the feeding gas molecules nitrogen (N_2), oxygen (O_2) and water (H_2O). Considering the various reactions occurring in the plasma, there is formation of $OH^{\cdot}$, H_2O_2, O_3, NO_x, $NO^{\cdot}$ [8]. These active species are able to degrade pollutant molecule [9–11]. The $OH^{\cdot}$ radicals are responsible for the strong oxidizing properties [12]. Several other species with high normal oxidation potential confer also marked oxidizing character on the plasma.

Plasma treatment prove their efficiency to organic pollutant degradation as in the destruction of nicotine used as pesticide [13], the oxidation of H_2S and CH_3SH diluted in air [14], the organic pollutants abatement of a brewery effluents [15], the phosphorous-containing warfare agents stimulants [16], the anthraquinonic acid green 25 [17], the destruction of thio-urea and urea [18], the mineralization of spent solvent as tributylphosphate and trilaurylamine [19,20] and also the degradation of dyes [21–27].

Among techniques to generate non-thermal plasma, gliding discharge is the cheapest. In fact, it requires a cheap and easy to build device with an inexpensive operating cost. This paper reports on using non-thermal plasma provided by an electric gliding discharge in humid air to the treatment of Methyl Red.

2. Experimental

2.1. Experimental apparatus

The original device was first suggested in 1988 by Lesueur et al. [28]. In 1994, Czernichowski developed this device for the treatment of volatile organic compounds in gaseous effluents [29]. This kind of device was conceived around the principle of the gliding electric arc, characterized by high tensions (kV) and the relatively weak currents (mA) [30].

The gas used is the air provided by a compressor (Fig. 1). The air passes in a bubbling water flask before passing in a flow meter. The humid air is then injected in the reactor through a nozzle of 1 mm diameter. The reactor is fitted with two aluminium electrodes which are arranged vertically and symmetrically with a narrowest fixed at 3.5 mm. These electrodes, having the profile of a half-ellipse, have approximately 2 mm in thickness. The used transformer (9000 V; 100 mA) provides the electric power.

The magnetically stirred batch reactor used for this study is thermostatted by water circulation, so that the temperature of the sample never exceeds 30°C.

When switched on, an electric arc takes place between two diverging aluminum electrodes. Under the influence of the gas flow, the electric arc slides along the electrodes, before extinguishing at the largest electrode gap. After extinguishing, a new arc forms and the cycle resumes. The plasma plume carries away reactive species and sweeps the liquid surface, so that reactions can take place at the plasma-solution interface.

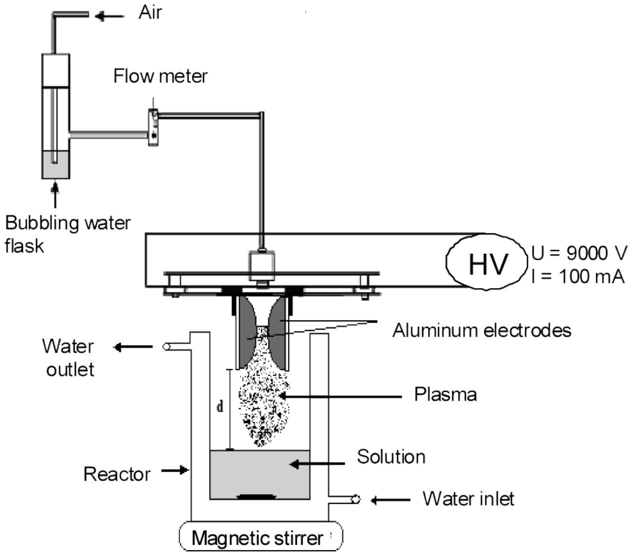

Fig. 1. Gliding discharge device.

2.2. Materials and methods

The synthetic wastewater was prepared with distilled water and azo dye Methyl Red (20 $mg.L^{-1}$) as the model organic compound. Methyl Red was purchased from R.A.L. The molecular structure of Methyl Red ($C_{15}H_{15}N_3O_2$, formula weight 269.2985 $g.mol^{-1}$) is given in Fig. 2.

Wastewater (V = 200 mL) was treated for 5 h with an airflow Q = 650 $L.h^{-1}$ and a distance electrode-solution d = 2.5 cm. Samples were taken from the reactor vessel at appropriate time intervals and analyzed by an UV/Vis spectrophotometer (BEKMAN) at 240–600 nm. Methyl Red present a maximal absorption at 530 nm which is attributed to the function N=N of the dye.

The Fenton reagent Fe^{2+} was purchased from Riedel-De Haën, iron(II) sulphate heptahydrate, puriss. The photocatalyst, titanium dioxide, was purchased from Riedel-De Haën, puriss, rutile grade. It is well known that TiO_2 can adsorb some amount of organic compounds, so

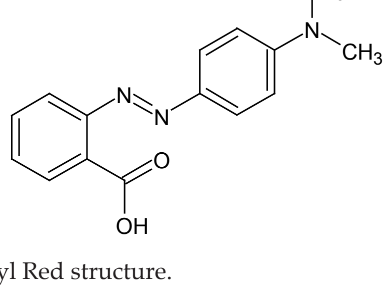

Fig. 2. Methyl Red structure.

before exposing the Methyl Red solution + TiO_2 to the plasma, it was stirred for 30 min in the dark in order to achieve the adsorption equilibrium. Finally, before UV-Vis analysis, samples were centrifuged and filtered through milliporous filter of 0.45 μm in order to eliminate TiO_2 particles. The concentration of the dye after adsorption saturation was adopted as the initial concentration.

In other words, in all experiences, the pH value is stabilized after a few minutes of treatment around 2.9 due to the production in plasma of HNO_3 and HNO_2 acids.

3. Results and discussion

3.1. *Effect of ferrous ions*

In order to improve the efficiency of degradation, ferrous II ions were added in the solution. Indeed, in advanced oxidative processes, the Fenton reagent provides an available explanation, that is, the Fe^{2+} ion can catalyze the degradation of organic compounds because they favor the formation in situ of additional $OH^{\cdot}$ which have the higher potential, so plasma becomes more oxidative [31].

The Fe^{2+} reacts with H_2O_2 produced in situ in plasma to form additional hydroxyl radicals $OH^{\cdot}$ as in reactions (1), (2) and (3) [31]. The hydroxyl radical has an oxidation potential of 2.85 V, which is greater than 1.78 V of hydrogen peroxide [32] so it enhances the degradation.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + \mathbf{OH^{\bullet}} \tag{1}$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\bullet} + H^+ \tag{2}$$

$$HO_2^{\bullet} + H_2O_2 \rightarrow O_2 + H_2O + \mathbf{OH^{\bullet}} \tag{3}$$

Fig. 3 shows the variations of the decoloration rate for the samples taken from the wastewater after 5 h of treatment. The results in Fig. 3 were obtained at different ferrous concentrations (0.2×10^{-3} mol.L^{-1}, 0.5×10^{-3} mol.L^{-1}, 0.8×10^{-3} mol.L^{-1}, 1.2×10^{-3} mol.L^{-1}). The decoloration efficiency of Methyl Red increased from 90.6% without ferrous ions to 95.5% and 97.4% for 0.2×10^{-3} mol.L^{-1} and 0.5×10^{-3} mol.L^{-1} respectively, implying that most of Methyl Red molecules were destroyed. This proves the catalytic effect of Fe^{2+}.

However for a higher amount of Fe^{2+} decoloration rate decreased. This is shown in Fig. 3 for 0.8×10^{-3} mol.L^{-1} and 1.2×10^{-3} mol.L^{-1} of Fe^{2+}. Indeed the hydroxyl radicals can react with Fe^{2+} according to Reaction (4) implying a decrease of the decoloration rate [33]:

$$Fe^{2+} + OH^{\bullet} \rightarrow Fe^{3+} + OH^- \tag{4}$$

So when Fe^{2+} concentration is raised, the reaction enters in competition with the oxidation of Methyl Red and thus decreases the degradation efficiency. Fe^{3+} formed also could react with H_2O_2 resulting in decrease of the decoloration rate [33].

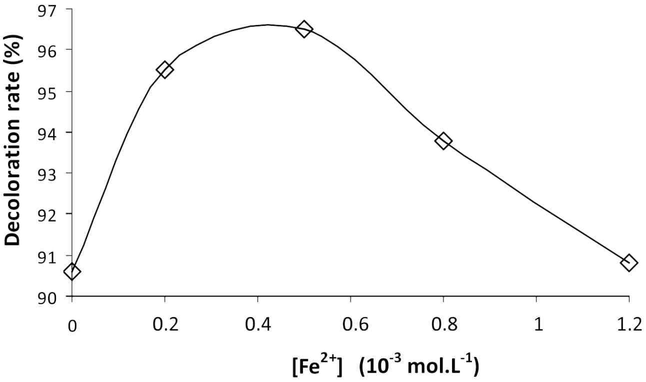

Fig. 3. Decoloration efficiency in presence of several amount of Fe(II) after 5 h of treatment (V = 200 mL, Q = 650 L.h^{-1}, d = 2.5 cm, C_i = 20 mg.L^{-1}).

$$Fe^{3+} + H_2O_2 \rightarrow Fe - OOH^{2+} + H^+ \tag{5}$$

3.2. *Effect of titanium oxide*

The coupling of the non-thermal plasma of glidarc type with TiO_2 in aqueous solution for depollution purposes provides an alternative to improve the efficiency of treatment of organic pollutant [17,24,34]. The titanium oxide photocatalyst absorbs the UV photons to produce additional hydroxyl radicals as follows [35]:

$$TiO_2 + h\nu \rightarrow e^- + h^+ \tag{6}$$

$$h^+ + H_2O \rightarrow H^+ + OH^{\bullet} \tag{7}$$

where e^- is the electron in the conduction band and h^+ is the electron vacancy in the valence band. The effect of TiO_2 is shown in Fig. 4. The optimal amount of TiO_2 is around 4 mg.L^{-1}. Under this value the decoloration rate increased with the increase of the TiO_2 additive amount. This can be explained by the fact that TiO_2 produce additional $OH^{\cdot}$ implying that their number increases in solution. So the probability of reaction between hydroxyl radicals and Methyl Red molecules increases. Thus, the dye will be degraded more quickly and efficiently and consequently the decoloration rate increases with the concentration of titanium oxide. Above 4 mg.L^{-1}, it decreased. In fact, at a high concentration of titanium oxide, the aggregation of the particles reduces the contact surface between the solution and catalyst, decreases the number of active sites on the surface and rendering difficult light infiltration resulting in a loss of number of additional hydroxyl radicals which are responsible for the strong oxidizing character of the discharge [17].

3.3. *Effect of ferrous ions and titanium oxide simultaneously*

In Fig. 5 we compare the efficiency of the degradation in presence of optimal amount of Fe^{2+}, TiO_2 and Fe^{2+} + TiO_2.

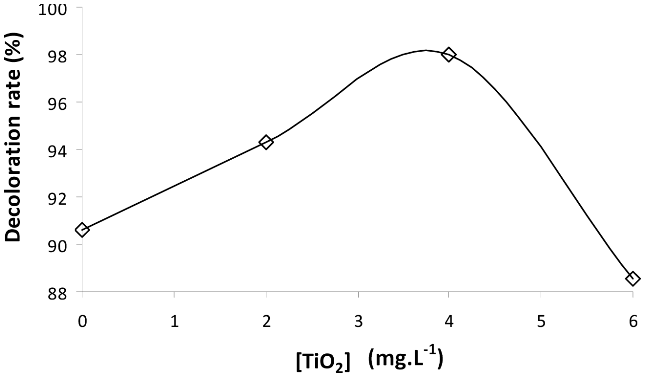

Fig. 4. Decoloration rate with several amount of titanium dioxide (V = 200 mL, Q = 650 L.h^{-1}, d = 2.5 cm, C_i = 20 mg.L^{-1}).

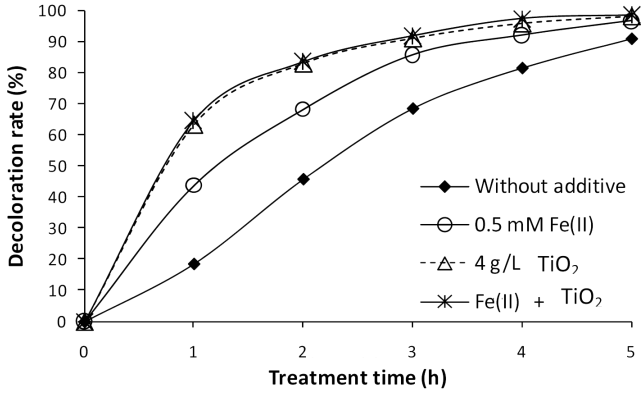

Fig. 5. Decoloration rate without additives and in the presence of 0.5×10^{-3} mol.L^{-1} of Fe^{2+}, 4 mg.L^{-1} of TiO$_2$ and 0.5×10^{-3} mol.L^{-1} of Fe^{2+} + 4 mg.L^{-1}of TiO$_2$ (V = 200 mL, Q = 650 L.h^{-1}, d = 2.5 cm, C_i = 20 mg.L^{-1}).

Experiments show that the degradation when using TiO$_2$ or Fe^{2+} + TiO$_2$ is more efficient and faster than when using only Fe^{2+}. This would be due to a larger amount of chemically active species produced by photocatalystic action of TiO$_2$, resulting from the redox reactions of electrons vacancy (h^+) in the valence band and photogenerated electrons (e^-) in the conduction band produced on the surface of TiO$_2$ particles by UV light [36]. However TiO$_2$ lonely has around the same decoloration rate than the one in presence of Fe^{2+} and TiO$_2$ together. As conclusion it is recommended to work with 4 mg.L^{-1} of titanium oxide.

Fig. 6 shows the UV/visible spectra of the samples taken from the wastewater after being treated for 5 h with addition of 4 mg.L^{-1} of titanium oxide. The 530 nm peak intensity of treated solutions decreases as treatment time increases implying that the majority of Methyl Red molecules are destroyed. This proves the efficiency of the gliding arc treatment to the decoloration of dyes. In an other hand, it also shows that the 300 nm absorption bands keeps increasing and may thus be assigned to the products of degradation as ketones, aldehydes, carboxylic acid and p-dimethylaminoaniline [4,37,38].

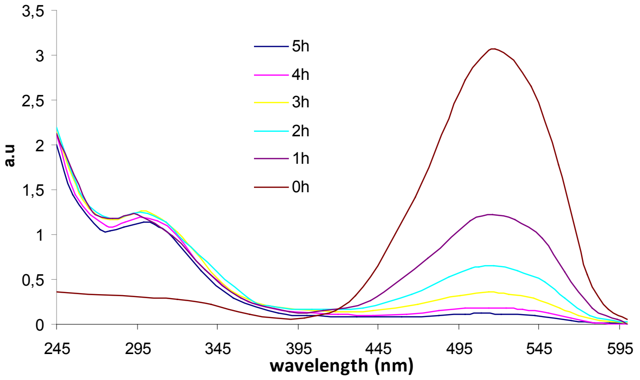

Fig. 6. UV/visible spectra of Methyl Red (V = 200 mL, Q = 650 L.h^{-1}, d = 2.5 cm, C_i = 20 mg.L^{-1}, [TiO$_2$] = 4 mg.L^{-1}).

3.4. *Kinetic order of the decoloration*

Our interest is turned to study the kinetic order of the degradation of Methyl Red. In this way, we can write the reaction of degradation like that:

$$\mathrm{C_{15}H_{15}N_3O_2} + 86\,\mathrm{OH^{\bullet}} \rightarrow 15\,\mathrm{CO_2} + 49\,\mathrm{H_2O} + 3\,\mathrm{NO_3^-} + 3\,\mathrm{H^+} \tag{8}$$

So

$$\nu = \frac{d[\mathrm{C_{15}H_{15}H_3O_2}]}{dt} = k_{\mathrm{app}} \times [\mathrm{C_{15}H_{15}H_3O_2}]^{\alpha}$$
$$\Rightarrow \int_{[\mathrm{C_{15}H_{15}H_3O_2}]_o}^{[\mathrm{C_{15}H_{15}H_3O_2}]} \frac{d[\mathrm{C_{15}H_{15}H_3O_2}]}{[\mathrm{C_{15}H_{15}H_3O_2}]^{\alpha}} = \int_0^t k_{\mathrm{app}}\,dt \tag{9}$$

If α = 1 (first kinetic order)

$$\ln\frac{[\mathrm{C_{15}H_{15}H_3O_2}]}{[\mathrm{C_{15}H_{15}H_3O_2}]_o} = k_{\mathrm{app}}t \tag{10}$$

As shown in Fig. 7, all curves corresponding to

$$\ln\frac{[\mathrm{C_{15}H_{15}H_3O_2}]}{[\mathrm{C_{15}H_{15}H_3O_2}]_o} = f(t)$$

are linear (R^2 near the unit), also as hydroxyl radicals are not cumulative because their half life is very short (a few nanoseconds) so the quasi-stationary state can be applied to the concentration of hydroxyl radicals consequently the hydroxylation reaction of Methyl Red can then be treated as a kinetic pseudo-first order which agrees with other experiments on the plasmachemical degradation of organic pollutants [13,17,23,34].

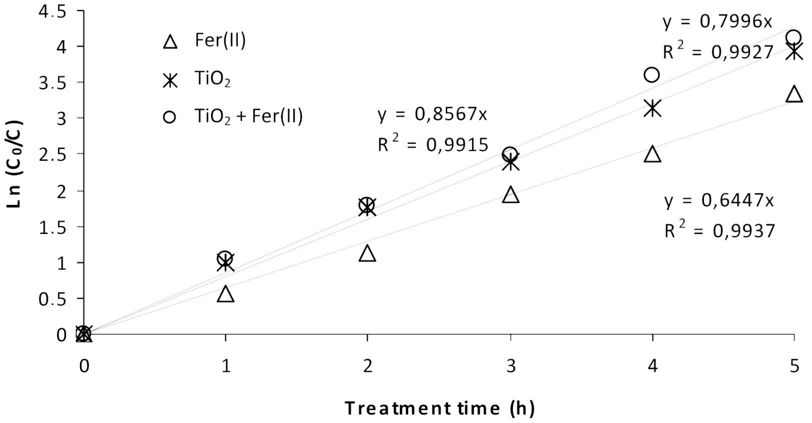

Fig. 7. Kinetic order of the decoloration of Methyl Red (V = 200 mL, Q = 650 L.h^{-1}, d = 2.5 cm, C_i = 20 mg.L^{-1}).

4. Conclusion

This study shows that the gliding arc technique could decolour Methyl Red dye wastewater. The decoloration rate without additives is around 90.6%. When ferrous ions were added, the decoloration efficiency increased by nearly 6.8% and it increased by 8.2% when titanium oxide was added. This proves the efficiency of plasma to decolour Methyl Red. The experiments show that titanium oxide is more efficient than ferrous ions.

The UV/visible spectra of the samples taken from the treated wastewater after being treated for 5 h with the addition of 4 mg.L^{-1} of titanium oxide show that the 530 nm peak intensity decreases. At the end of treatment this peak disappeared, implying that most of Methyl Red molecules were destroyed.

On the other hand, the hydroxylation reaction of Methyl Red can be treated as a kinetic pseudo-first order.

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