

Atmospheric Plasma-Catalytic Treatment of Methyl Orange

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Abstract: Atmospheric gliding arc discharges in humid air are used for the treatment of Methyl Orange (MO) solutions for depollution purposes. Highly reactive neutral hydroxyl radicals OH[•] and NO[•] are produced in the plasma. Their interaction with the solution is investigated using UV/Visible spectroscopy. The plasma treatment shows the creation of intermediate species systematically followed by their degradation leading to one end product. The presence of hydrogen peroxide (H₂O₂) and titanium oxide (TiO₂) as catalysts differently influences the plasma treatment of the MO solution. H₂O₂ influences further the direct chemical reactions due its straightforward decomposition under UV radiations while TiO₂ has to be activated before releasing species that contribute to the highly oxidant HO[•] radicals production.

Keywords: Gliding discharge; humid air, non thermal plasma; atmospheric pressure; Plasma-chemical degradation, Methyl Orange; Hydrogen peroxide.

1. Introduction

Advanced oxidation process (AOP) reactors are commonly used nowadays for their enhanced performance and better selectivity using catalysts (ozone (O₃), hydrogen peroxide (H₂O₂), titanium oxide (TiO₂), etc) compared to normal reactors whether treating liquid or gaseous products. A hybrid non-thermal plasma reactor packed with nanometer titanium dioxide catalyst shows a better selectivity of carbon dioxide when used for benzene removal in the air to give a benzene removal efficiency of nearly 99% for low benzene concentration (600 mg/m³) and 90% for high benzene concentration (1500 mg/m³) [1]. Dielectric barrier discharge (DBD) reactor was used to investigate the efficiency of the treatment of Orange II dye at different conditions using: O₃, O₃+ UV, O₃ + UV +TiO₂ [2]. The rate of degradation of the azo dye increases with the previous conditions order. Comparative analysis of degradation of Methyl Orange (MO) or Orange III using non thermal plasma of gliding arc discharge (GAD) in humid air and photocatalytic UV reactor was carried out using H₂O₂ catalyst. The presence of H₂O₂ catalyst accelerates the degradation of MO leading to the same final end product obtained without catalyst in GAD while UV reactor degrades totally MO [3].

The purpose of this paper is to present the results of the interaction of neutral radicals' species produced by non thermal GAD of humid air and their chemical reaction effects on MO in presence of H₂O₂ and TiO₂ catalysts. Predominant HO[•] and relatively less abundant •NO radicals have been identified in previous spectroscopic investigations [4,5]. The plasma interaction with the MO solution and the reaction kinetics are followed by UV/Vis molecular absorbance spectroscopy. Atmospheric plasma produced HO[•] and •NO radicals were identified through their UV emission spectra starting at 306 nm for HO[•] and

237 nm for •NO radicals. The presence of UV photosensitive catalysts H₂O₂ and TiO₂ differently enhance the degradation of MO at different degradation rates leading to the same end products.

2. Materials and Methods

2. 1 The plasma source

The non thermal plasma source was initially developed by Czernichowski *et al.* [6] and detailed for its use in liquid solutions treatment in previous paper [7]. Pressurised bubbling air crosses a distilled water flask and gets water vapour saturated before entering the GAD reactor through a nozzle. It spreads in the diverging limited space between two electrically 220V/10kV high voltage supplied semi elliptic electrodes that an alternative potential difference of 10kV and a current intensity of 100-150mA. The electric arc generated ignites at the electrode minimum gap (2.5 mm wide) and is being pushed to the top lengthening. The arc voltage increases until it reaches the breakdown voltage of the starting gap. A new arc reappears at the top of the reactor, short-circuiting the first one that extinguishes at the arc length threshold. The gas flow rate Q_v, which can be adjusted from 0 to 25L.mn⁻¹, is measured by a Show Rate Brooks flow meter.

2. 2 Solution preparation and treatment conditions

Methyl Orange (MO) with molecular structure C₁₄H₁₄N₃NaO₃S and molecular weight 327.34 g/mol was supplied by Aldrich prepared. The initial solution prepared solution of 10⁻² Mol/L is red and turns to orange when diluted to a concentration of 7.8125 x 10⁻⁵ Mol/L. MO solutions containing H₂O₂ with concentration 1.14 x 10⁻² mol L⁻¹ were also prepared. Another mixture of equal concentration of 7.8125 x 10⁻⁵ Mol/L of MO and TiO₂ of

molecular weight 79.90 g/mol (supplied by Sigma-Aldrich) was prepared. The magnetically stirred 80 mL sample solution was exposed at a distance of $d = 7.5$ cm from the ignition point of the GAD and treated by non thermal plasma of humid air at a flow rate $Q = 10$ L/min. Each treatment period of $T = 30$ s was monitored by measurements of absorbance using a double beam UV-Vis Shimadzu spectrometer 1601 model with 900 lines/mm holographic grating.

3. Results and discussions

3. a. MO plasma treatment

Initial MO solution of concentration of 7.8×10^{-5} mol L^{-1} (pH=6) shows a broad absorption peak at the wavelength 464.5 nm with an absorbance value 1.83 (molar absorption coefficient $\epsilon_{464.5nm} = 2.34 \times 10^4$ L mol $^{-1}$ cm $^{-1}$) and a shoulder at a lower wavelength 415 nm. The molecular coefficient at the shoulder is calculated $\epsilon_{415nm} = 1.64 \times 10^4$ L mol $^{-1}$ cm $^{-1}$. The visible spectrum of MO solution is shown in Figures 1 and 2. Exposed during fixed treatment periods of 0.5 min to the humid air plasma, MO solution shows a shift of the absorption band initially centred at $\lambda_{max} = 464.5$ nm to higher wavelength and higher absorbance of the absorption peak with treatment time. The absorbance at the shoulder 415 nm on the other hand decreases with time. Longer exposure to humid air plasma shows variation of the absorption band with the treatment time which suggests that the treated MO solution is undergoing a set of complex reactions involving acid transform and oxidation processes as a result of chemical reactions with non thermal plasma produced neutral reactive species HO^{\bullet} and $^{\bullet}NO$. The presence of less dominant neutral radicals $^{\bullet}NO$ creates acidic medium encouraging chemical reactions to take place. The decrease of the absorbance of MO at 464.5 nm accompanied by a shift in the absorption band at higher wavelength 495 nm and color changes may suggest that some molecules at the interface of the plasma liquid solution are degraded into small fragments that recombine with oxidized non-degraded molecules to form another type of dyes. It is therefore clear that the structure of MO has been changed and the maximum peak shifts from 464.5 nm to 495 nm after plasma treatment of MO solution, while the absorbance values at these peaks are more or less equal, indicates that the MO in the presence of plasma produced reactive species is undergoing direct chemical oxidation (DCO) by oxidizing hydroxyl radicals HO^{\bullet} .

3. b. MO plasma treatment with H_2O_2 catalyst

$MO+H_2O_2$ ($c_{MO}=7.8 \times 10^{-5}$ mol L^{-1} , $c_{H_2O_2}=1.14 \times 10^{-2}$ mol L^{-1}) were also exposed to plasma species. The visible spectrum of $MO+H_2O_2$ solution is shown in Figure 1. The absorbance of $MO+H_2O_2$ solution at 464.5 nm is slightly

higher (2.17) compared to (1.83) of MO alone. It seems that the presence of H_2O_2 accelerates the rate of direct chemical reactions occurring in the plasma treated MO solution. It reduces the treatment time to reach the maximum absorption peak at 495 nm. This effect is largely observed for the maximum absorption peak at 415 nm for $MO+H_2O_2$ and MO where four minutes of plasma treatment for $MO+H_2O_2$ solution to reach the appearance of supposed final product. Over four minutes of exposure to the humid air plasma, the absorbance spectra show a decrease of the absorbance at 415 nm followed with a shift of the absorption peak at 390 nm in the UV band. Therefore adding H_2O_2 to the MO solution reduces the treatment time to nearly 50% of that of MO alone.

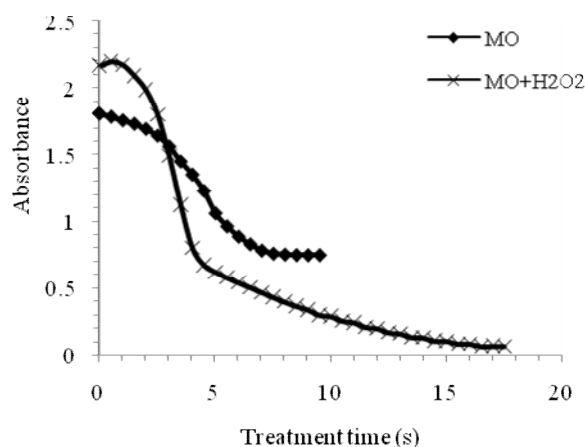


Fig.1: Variation of the maximum absorption peak at 465 nm vs. treatment time during non thermal plasma treatment of MO and $MO+H_2O_2$.

3. c. MO Plasma Treatment with TiO_2 catalyst

$MO+TiO_2$ solutions are also exposed to humid air plasma. The pH of the solution was initially at 5.95. Visible spectra of MO and $MO+TiO_2$ solutions are shown in Figure 2. The absorbance of the two solutions undergo a similar behavior with a little difference in absorbance amplitude, the $MO+TiO_2$ amplitude being higher than that of MO. The absorbance intensity is somewhat higher (1.92) than that (1.83) obtained without the catalyst. Also the maximum absorption peak does not change; the absorbance of $MO+TiO_2$ solution raises the absorbance to 4.5% more than that of MO alone. The increase of the absorbance is observed during the whole plasma treatment. The presence of the catalyst TiO_2 enhances the presence of more hydroxyl radicals in the plasma. The medium becomes more populated with hydroxyl radicals and the oxidation of MO is more effective. Therefore an increase in direct chemical oxidation is taking place and the absorbance of MO in presence of TiO_2 catalyst could be related to an MO oxidation effect induced by TiO_2 .

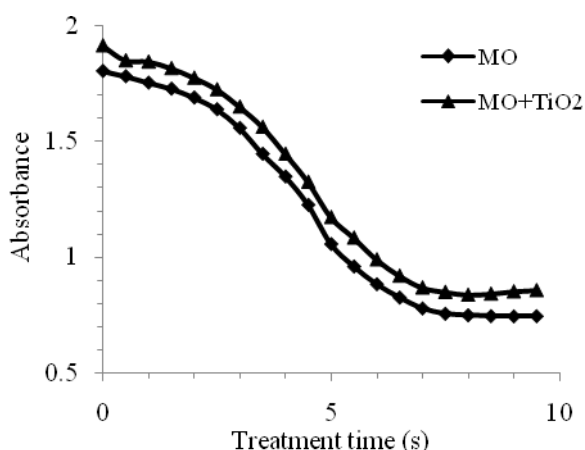


Fig.2: Variation of the maximum absorption peak at 465 nm vs. treatment time during non thermal plasma treatment of MO and MO+TiO₂.

When exposing TiO₂ suspensions in aqueous solutions to UV radiations, they increase HO• radicals which should oxidize dissolved organic materials responsible for coloring solutions. Since the atmospheric plasma produced HO• and •NO radicals are identified through their UV emission spectra [4], the presence of UV photosensitive catalyst such as TiO₂ may enhance the plasma treatment. UV radiations interact with TiO₂ to produce additional HO• radicals in the solution. The final product obtained is stable within several days after treatment. The addition of few drops of H₂O₂ to the final product and its exposure to UV radiations make it lose its yellow color within five minutes of treatment.

4. Discussions

The slight increase of the solution absorbance before the treatment has been observed for all solutions MO, MO+TiO₂ and MO+H₂O₂. The absorbance of MO + H₂O₂ solution at 464.5 nm is slightly higher (2.17) compared to MO+TiO₂ (1.92) and MO (1.83) alone. Similar behavior of spectra is observed for MO, MO+H₂O₂ and MO+TiO₂. Adding catalysts to MO solutions has increased the initial absorbance of the solution and also reduces the treatment time to reach the maximum absorption peak at 495 nm. One and half minutes are needed for MO+H₂O₂ to reach the first maximum at 495 nm while it takes 2 minutes for MO+TiO₂ and more for MO as shown in Table 1.

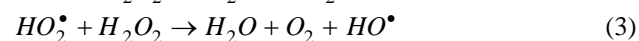
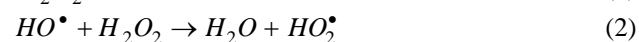
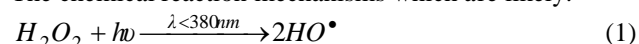
The influence of H₂O₂ on MO plasma treatment is largely observed for the maximum absorption peak at 415 nm appearance at four minutes of plasma treatment while nine and half minutes treatment time were not enough for MO+TiO₂ and more for MO. Over four minutes of exposure to the humid air plasma, the absorbance spectra show a decrease of the absorbance at 415 nm followed with a shift of the absorption peak at 390 nm in the UV band. Therefore adding H₂O₂ to the MO solution reduces the

treatment time to nearly 50% of that of MO alone.

Table 1. Absorbance values at absorption peak 464.5 nm and minimum time to reach absorption peak at 495 nm.

	A (at 464.5 nm)	t (at 495 nm)
MO	1.8	> 2 min
MO + TiO ₂	1.9	2 min
MO+H ₂ O ₂	2.2	1.5 min

The reason for such a rapid acceleration effect is due to the production of HO• radicals produced through the interaction of UV radiations emitted by NO• (237 nm) and HO• (306 nm) radicals with H₂O₂. These two values correspond to photonic energies 5.23 eV (NO•) and 4.05 eV (HO•) that are higher than the threshold value 3.26 eV that triggers the degradation of H₂O₂ into HO• radicals by UV radiations as expressed by equations (1), (2) and (3). The chemical reaction mechanisms which are likely:



The production phenomenon of HO• radicals is a primary product of the interaction of H₂O₂ with UV radiations. H₂O₂ molecules are straightforward decomposed to HO• radicals. This is why it is quicker than when TiO₂ catalyst is used.

With titanium oxide, HO• radicals are secondary products obtained through the activation of TiO₂ molecules by UV radiations followed by the release of electrons through (4) and (5).



Therefore TiO₂ catalyst is a slower process than direct H₂O₂ since it involve other reaction mechanisms to produce HO• radicals.

5. Conclusion

A comparative approach to the use of TiO₂ and H₂O₂ catalysts has been investigated during the treatment of MO by non thermal humid air plasma of gliding arc discharge. H₂O₂ reduces the treatment time to nearly 50% of that of MO alone. The degradation rate of MO is enhanced by the increasing generation of HO• radicals created through the interaction of UV radiations emitted by non thermal plasma produced NO• and HO• radicals with H₂O₂. H₂O₂ influences further the direct chemical reactions due its straightforward decomposition under UV radiations while TiO₂ has to be activated to release species before contributing to the highly oxidant HO• radicals.

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