

Cold Atmospheric Pressure Argon Plasma Jet Assisted Degradation of Malachite Green (MG) Aqueous Solution

D. Vasu ^a, M.C. Ramkumar ^b, A. Arunkumar ^a, K. Navaneetha Pandiyaraj ^{a,*}

^a Research Division of Plasma Processing (RDPP), Department of Physics, Sri Shakthi Institute of Engineering and Technology, L&T by pass, Chinniyam Palayam (post), Coimbatore-641062, Tamil Nadu, India.

^b Department of Physics, School of Basic Sciences, Vels Institute of Science, Technology & Advanced Studies, Chennai-600117, Tamil Nadu, India.

* Corresponding Author; navaneetharaj@siet.ac.in

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Abstract: The oxidative degradation of cold atmospheric pressure plasma assisted degradation of malachite Green (MG) was investigated in this study. Cold atmospheric pressure plasma assisted MG degradation process was carried out as a function various plasma treatment time (05, 10, and 15 mins). The % of degradation and presence carbon content in the plasma treated MG was examined by UV-Visible spectroscopy (UV-Vis) and total organic carbon (TOC) analyzer. Optical emission spectrometer was used to identify formation of various reactive species during *in situ* plasma treatment. The higher degradation percentage of 90% was obtained after plasma treatment time of 15 min and value of TOC also found to decreased significantly with increasing plasma treatment time. Toxicity of the plasma-treated MG aqueous solution samples was also examined by Staphylococcus aureus (S.aureus) bacteria.

Keywords: Cold atmospheric pressure plasma jet, Malachite Green (MG), Optical Emission spectrum, TOC

1. Introduction

Water is considered as the elixir of all living organisms and water consumption is increased day-by-day because of increase in the population. Water is most important in our life, however the living organisms needed fresh water quantity and quality are insufficient [1]. Indeed, only a few amounts of (2.5%) freshwater is available for domestic and agriculture usage. With the rapid growth of industrialization, the amount of water consumption is increased. Therefore, the amount of wastewater is increased yearly more than six times of freshwater. Furthermore, textile,

leather, plastic, paper and cosmetic industries has consumed large quantity of freshwater which depends on their requirements [2]. Textile industries are one of the largest sectors in water consumption compared to the others sectors because it consumed a very large amount of fresh water about 25 to 250 m³ per ton, which depends on their process [3]. Moreover, textile industries are using major classes of synthetic colorants such as azo, anthraquinone and reactive dyes. Those dyes are difficult to degrade, which is stable in aerobic and anaerobic conditions. About, 10-15% dyes containing wastewater are directly disposed into the environment after the dyeing process. The disposed dye wastewater is directly mixed with water resources like rivers, ponds, and streams, etc. Thus, the textile effluent creates a major impact on environmental pollution issues. Therefore, wastewater treatment should be a major concern for researchers and scientists. Moreover, the elimination of pollutants from the wastewater can be involved in several methods such as ultrafiltration, coagulation, membrane separation and biological methods. Conventional treatment methods are not suitable in those dyes because of dye intermediates and harmful by-products are produced after the treatment. Hopeful results and higher removal rate have been achieved using advanced oxidation process (AOPs) [4-5]. AOPs process is based on the in-situ generation of various reactive nitrogen (RNS) and oxygen species (ROS) such as hydroxyl radicals (OH[•]), singlet oxygen (O), nitrogen (N), nitrate (NO³), nitrite (NO²), ozone (O₃), hydrogen peroxide (H₂O₂). Those, radicals are facilitated to degrade the organic molecules in the effluents. In this context, the cold atmospheric pressure plasma process is one of the AOPs, which leads to chemical and physical effects in a liquid phase by generation of various reactive oxygen and nitrogen species (ROS and RNS). [5-7]. Malachite Green (MG) dyes represent the most important class of dyes in textile, paper and acrylic industries. This manuscript studies the degradation of MG using cold atmospheric pressure plasma jet under various plasma parameters. After the plasma treatment the physical and chemical change of MG aqueous solution was studied using UV-Visible spectrometer (UV-Vis), and total organic carbon (TOC) analyzer. During the MG degradation various ROS and RNS reactive species formation were identified using an optical emission spectrometer (OES). Toxicity nature of before and after plasma treated MG aqueous solution was examined by antibacterial activity using against *Staphylococcus aureus* (S.aureus) bacteria.

2.0 Materials & Methods

2.1 Material

Malachite Green (MG) dye was obtained from the textile industry from Tirupur, India. The nutrient agar and nutrient broth were purchased from HiMedia. The bacterial cultural plates purchased from the Biotek laboratory, Coimbatore, India. The plasma forming gas Argon was supplied from Jayam SPL Gases, Coimbatore, India. All the required solutions were prepared to double Deionized (DI) water.

2.2 Cold Atmospheric pressure plasma jet

The detail description of cold atmospheric pressure plasma reactor has reported in our previous publications [8-9]. Cold atmospheric pressure plasma jet consists of a rod and ring-type electrodes made of copper, which is shown in figure-1. The rod type electrode was acting as a live electrode and ring-type was acting as a ground electrode. Furthermore, the two electrodes were covered by a quartz tube to avoid arc formation. The distance between the two electrodes was approximately 2.2 cm. In addition, the whole setup was covered by Teflon enclosure, in order to prevent electric induction (Figure-1). The cold atmospheric pressure plasma was generated by a high voltage (40 kV) and high frequency (30 kHz) power supply. The noble gas like argon was used as a plasma forming gas. The degradation process was carried out at various treatment time of 5, 10 and 15 mins with a fixed applied potential of 32 kV and argon gas flow rate of 9 lpm.

2.3 Analytical analysis of plasma-treated samples

The plasma-treated MG aqueous solution was analysed by various analytical methods. The plasma-treated MG aqueous solution percentage of degradation was observed using a UV-Visible spectrometer (Ocean Optics HR4000). Plasma treated MG aqueous solution carbon content was analysed using total organic carbon (TOC) analyser (SHIMADZU (TOC/L CPH/CSN). The toxicity of plasma treated MG aqueous solution was examined by Agar Well Diffusion Method against *Staphylococcus aureus* (Gram Positive Cocci).

3.0 Results and Discussion

3.1 Measurement of relative intensities of plasma species

It is important to investigate what are the reactive species involved in degradation of MG molecules in aqueous solution was examined by OES. Figure-2 clearly shows the emission spectrum of argon plasma before and plasma during the degradation processes. It was observed that the OES spectra of Ar plasma exhibited strong intense peaks in the range of 690-900 nm due to presence of various excited states of argon atoms [8-9]. In spite of Ar emission line, we have found additional peaks due to hydroxyl radicals (309 nm), nitrogen second positive system (334, 354 and 376 nm) and the atomic oxygen species (772 and 842 nm) (Figure-2a) [9-10] due to interaction of plasma species with nitrogen and oxygen content in the surrounding atmosphere [8-10]. In contrast, the OES spectra of Ar plasma during the processes exhibited various new peaks at 656, 486 and 430 nm due to H_{α} , H_{β} , and H_{γ} (Balmer series H spectral lines) and 206 and 236 nm due to NO lines (Figure-2b) [9-11]. Moreover, the intensity of the peak due to OH^{\bullet} and N_2 SPS was found to be increased than the spectral line of Ar plasma jet alone, may be attributed to the formation of higher concentration of OH^{\bullet} radicals during the processes. The increase in N_2 SPS may be attributed to dissociation and excitation of dye molecules in the aqueous solution. Moreover, there was no significant variation in intensity of the Ar spectral line during the processes. The generation of OH^{\bullet} and H species during the plasma treatment may

be attributed due to fragmentation/dissociation of water molecules ($\text{H}_2\text{O} + e^- \rightarrow \text{OH}^\bullet + \text{H}^\bullet + e^-$) and the formation of NO spectral lines may be due to interaction of N_2 with O^\bullet radicals [11-12]. The OES results clearly confirms the formation of various ROS and RNS during the plasma treatment are aided to the molecules of MG.

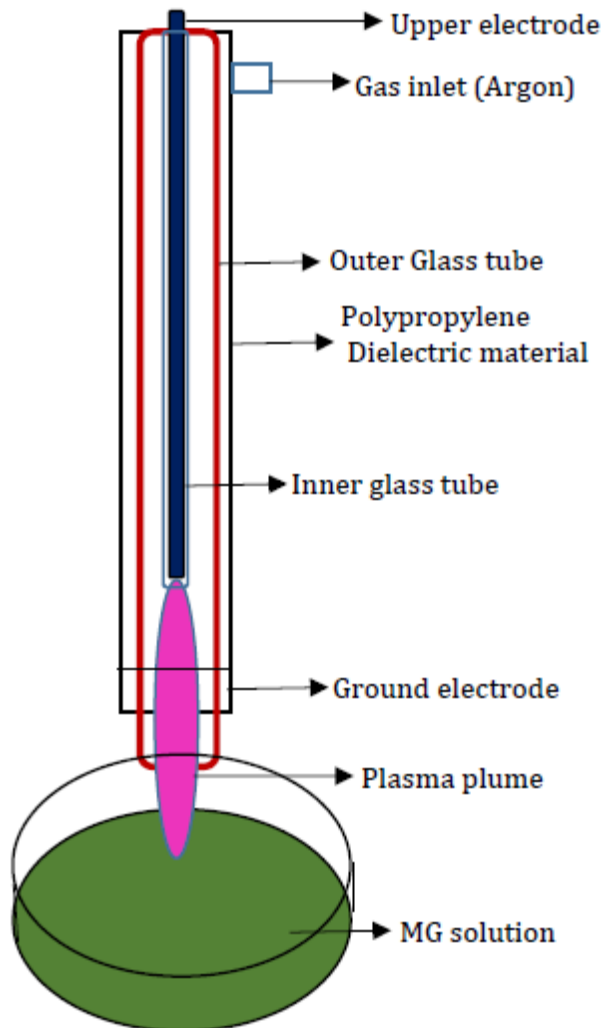


Figure-1. Cold atmospheric pressure plasma jet

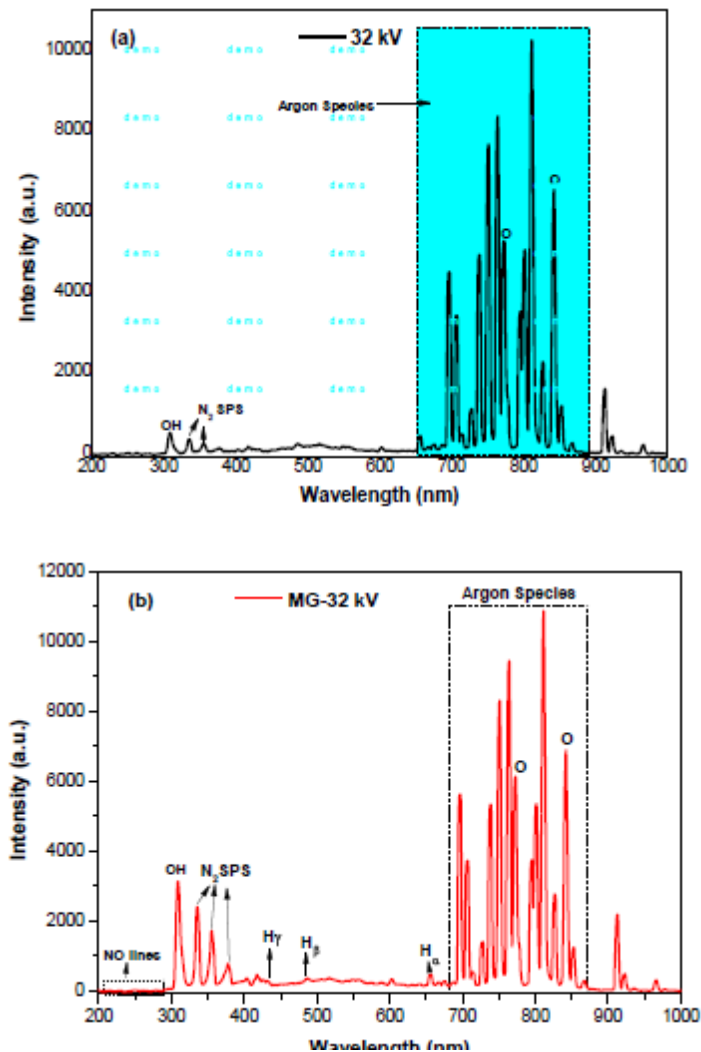


Figure-2. Optical emission spectra (OES) of (a) normal plasma jet and (b) during the treatment

3.2 Cold atmospheric pressure plasma-assisted degradation of Malachite Green (MG)

Figure-3a shows the changes in absorption spectra of MG during the plasma treatment process at constant applied potential with various treatment times. The absorption spectra of MG show maximum absorption at 617 nm [13-15]. After degradation, the intensity of absorption spectra decreased with increasing treatment time. The maximum degradation was obtained at higher treatment time of 15 min which was found to be similar to the UV-Vis spectra of distilled water (Figure-3).

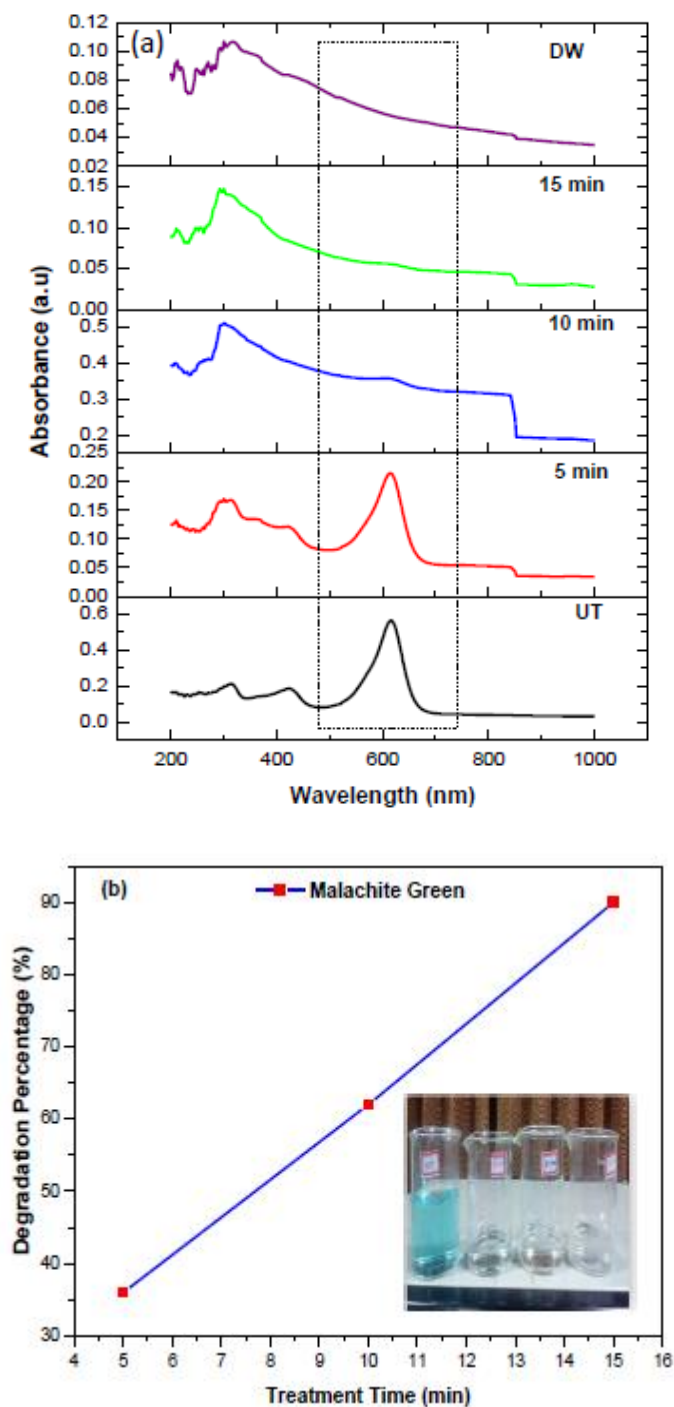


Figure-3. (a) UV-Visible absorption spectrum of plasma-treated MG as a function of treatment time and (b) percentage of degradation.

Figure-3b shows the percentage of degradation of MG with respect to treatment time. It was perceived that the maximum degradation percentage of 90 % was obtained at higher treatment time of 15 min due to reactive species in plasma react very longer duration in air-liquid interface that leads to produce higher concentration of reactive species which are facilitate to increase the degradation of MG molecules in aqueous solution.

3.3 Kinetic studies of MG degradation

The pseudo-first-order kinetic studies of MG degradation using cold atmospheric pressure plasma performed at various treatment times and constant applied potential was shown in Figure-4. The plasma-assisted MG degradation with various treatment times was followed by Pseudo-First order kinetics. The MG aqueous solution degradation rate constant was calculated by following expression [16-17].

$$\ln \frac{C}{C_0} = -kt$$

Where, C_0 and C represent the MG dye concentration of before and after plasma treatment at t time (min), and k is the pseudo-first-order kinetic rate constant. It was observed that k was gradually decreased with increasing the plasma treatment time which indicate the degradation of MG molecules in aqueous solution with respect to plasma treatment.

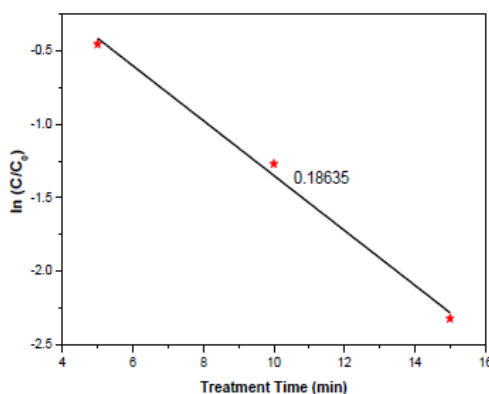


Figure-4 Pseudo-First order kinetic studies of MG degradation with respect to treatment time

3.4 Total Organic Carbon (TOC) Analysis of MG aqueous solution

In order to determine the amount of mineralization of the plasma-treated MG aqueous solution was examined by measuring total organic carbon (TOC). It was found that the TOC of untreated MG solution was 58 mg/L and the same was reduced significantly to 45 mg/L due to fragmentation of dye molecules in the aqueous solution by plasma treatment which confirms the degradation of MG molecules in aqueous solution.

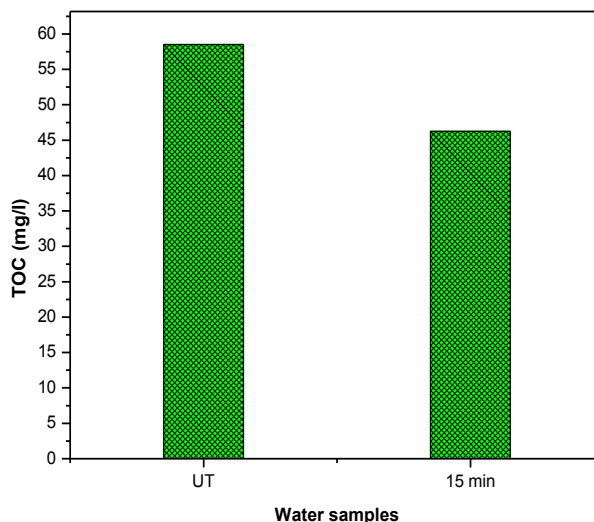


Figure-5. TOC analysis of before and after plasma-treated MG aqueous solution

3.5 Toxicity analysis of plasma-treated MG aqueous solution.

An additional important goal of this process was to study the plasma-treated MG aqueous solution was toxic or not. Thus, the plasma-treated MG aqueous solution was evaluated against *S. aureus* microorganisms [8-9, 18] (Figure-5). It was observed that clear zone of inhibition around untreated MG solution and diameter of the zone was 13 mm. After plasma treatment, the zone of inhabitation and its diameter was found to be decreased with increasing the treatment time (Figure-6 a and b). There was no zone inhibition around at the 15 min treated MG aqueous solution which indicates plasma treated MG solution exhibited non-toxicity against micro-organism due to complete degradation of toxic MG molecules in aqueous solution.

4.0 Conclusion

In this work, we have presented cold atmospheric pressure plasma assisted degradation of MG aqueous solution. The degradation processes were carried out as a function of various plasma treatment time with the constant applied potential. It was found that the higher degradation or removal percentage of MG was observed at higher plasma treatment time due to formation of various ROS and RNS which conformed by OES. The degradation of the MG aqueous solution has followed Pseudo-First order kinetics. degradation of MG aqueous solution.

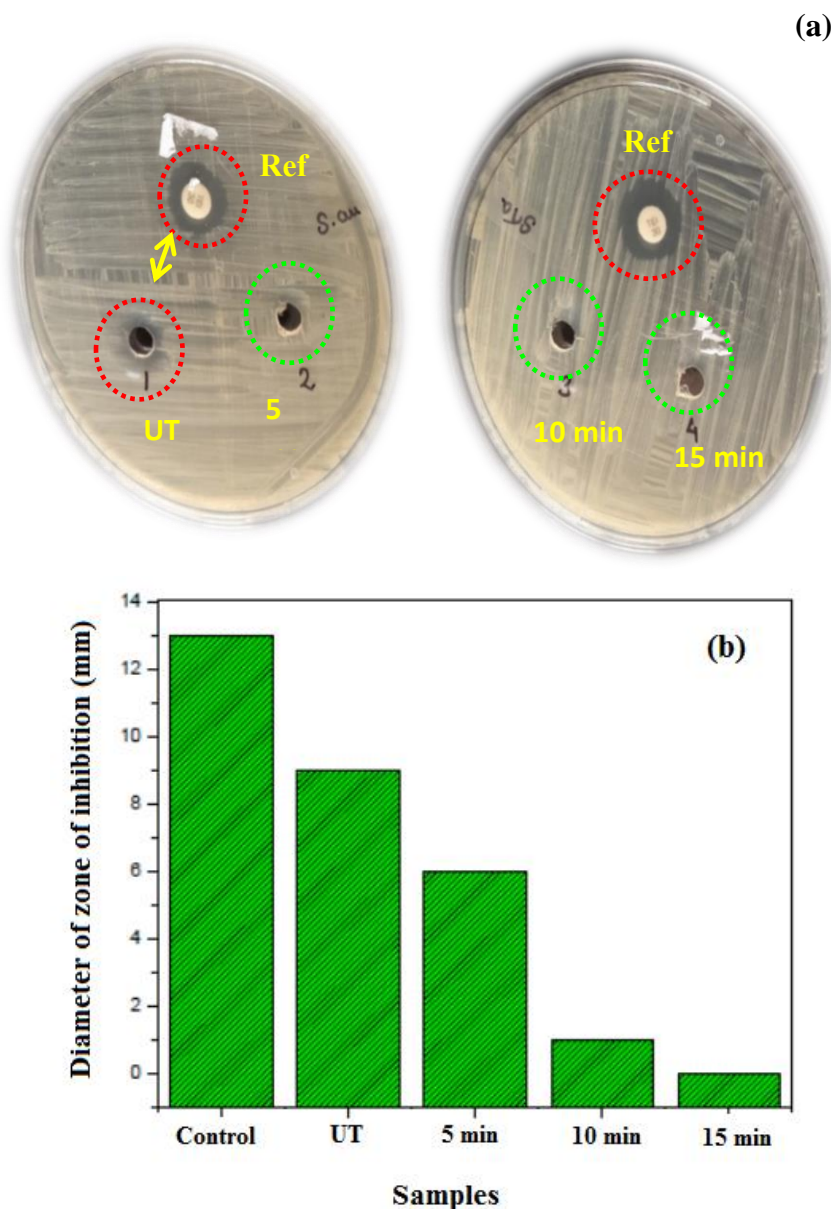


Figure-6. (a) Toxicity analysis of MG aqueous solution using *Staphylococcus aureus*

(b) diameter of zone

In addition, the plasma-treated MG aqueous solution exhibited non-toxic nature against *Staphylococcus aureus*. Indeed, the results indicated that the atmospheric pressure plasma

assisted effluent treatment is efficient and influences the removal of the organic compound in aqueous solution which could be beneficial for various industrial effluents.

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Conflict of interest: NIL

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