INTRODUCTION

Organic dyes in aqueous solution are widely used in many manufacturing techniques, especially in the textile industry. After the dyeing processes, the effluents used can contain high levels of unfixed dyes with intensive colour and toxicity, [Kant 2012, Yassen et al. 2019]. This can be considered as an environmental risk if infiltration of wastewater occurs toward main water resources in rivers and ground water [Lellis et al. 2019]. As organic dyes show high solubility in water, making them difficult to remove by conventional methods, the treatment of industrial dyeing effluents should be performed before being discharging in waste streams [Anjaneyulu et al. 2005]. Different techniques of advanced oxidation processes (AOP) can be used for the degradation of organic dyes in the effluent water. Many authors have considered the treatment of wastewater using AOP. Cesaro et al. [2013] have examined the combination of AOP with conventional biological processes; they used main standard tests and parameters for wastewater biodegradability assessment and found that the action mechanism of AOPs relies on the formation of high reactive oxidant species, mainly hydroxyl radicals. Oturan et al. [2014] describe AOPs as promising, efficient, and environmental-friendly methods developed to principally remove persistent organic pollutants (POPs) from waters and wastewaters, and they consider the performances of various types of AOPs, based on the chemical, photochemical, sonochemical, and electrochemical reactions in degradation and destruction of toxic and/or POPs in aquatic media. Garrido-Cardenas et al. [2020] reviewed the state of the art of scientific publications on wastewater and advanced
oxidation, they verified the evolution of this line of research and observed countries conducted most comprehensive studies in the topics related to elimination of pollutants of biological origin, such as bacteria, and of industrial nature, such as pesticides or pharmaceutical products. One of the promising AOP techniques is the use of nonthermal plasma (NTP) or as commonly called “cold” or “nonequilibrium” plasma. Plasma constitutes mainly of electrons, ions, radicals, and UV radiation [Bruggeman et al. 2017]. Reactive species produced in water during plasma discharge can be in the form of radicals as atomic oxygen (O•) and hydroxyl radical (OH•), or in the form of neutral excited molecules such as hydrogen peroxide (H₂O₂) and ozone (O₃). The UV radiation produced by plasma with strong oxidizing effects can also affect organic water pollutants [Gorbanev et al. 2016, Zhang et al. 2018]. Plasma discharges have been recently used in various applications to ameliorate products and manufacture performances. In biomedical field, plasma applications extend from sterilization, wound healing to cancer fighting [Larroussi 2020]. In agriculture, plasma is used to treat seeds, improve crop growth, and assure food safety [Varilla et al. 2020]. In environmental applications, plasma is used in air purification control [Giarrella et al. 2020]. One of the most successful uses of plasma is in wastewater treatment [Olszewski et al. 2014]. For plasma discharges above the air-water interface, oxidizing agents are produced by plasma in the air close to the solution surface and penetrate the solution producing the desired effects [Wahyudiono et al. 2013, Hoffer et al. 2015]. Treatment of wastewater can be performed by plasma produced above the air-water interface or inside water bulk [El Shaer et al. 2020]. Plasma can be produced using many types of cold atmospheric plasma (CAP) discharges. Many authors have studied the applications of different types of CAP to wastewater treatment. For dye decolourisation in aqueous solution, one of the most popular plasma arrangements is the use of dielectric barrier discharge (DBD). Tichonovas et al. [2013] examined the degradation of a wide variety of industrial textile dyes in a semi-continuously operated pilot DBD plasma reactor and they found that the degradation by-products consisted mostly of carboxylic acids, nitrates, amides and amines and that the toxicity of the wastewater decreased to near-zero values. [Massima Mouele et al. 2015] give an overview of different DBD configurations concerning their applications and the in-situ mechanism of free reactive species generation for water and wastewater treatment, therefore they recommend the application of double cylindrical dielectric barrier configuration which represents an ideal and viable route for achieving greater water and wastewater purification efficiency. Wu et al. [2019] examined the degradation of methylene blue (MB) using an upgraded DBD plasma reactor based on the air plasma generated in the glass bead packed bed in the reactor, which propagated into the MB solution through a microporous diffuser plate and they pointed, by conducting comparison experiments, that the plasma treatment was preferable to the ozone treatment. Njiki et al., [2016] used gliding arc (GA) discharge, to treat crystal violet (CV), a triphenylmethane nonbiodegradable organic dye and they found that there is a positive synergism of bacterial and plasma treatments, which is useful in reducing the energy involved in complete mineralization of wastewater containing nonbiodegradable dyes. Gharagozalian et al. [2017] investigated the effects of AC powered GA plasma system on the treatment of water and their results indicated that GA plasma is a powerful and green tool to decontaminate water by producing plasma species, such as hydrogen peroxide, OH radicals, ultraviolet radiations, nitrogen, and oxygen. Attri et al. [2016] employed two needle-type atmospheric pressure nonthermal plasma jets, operating at Ar feed gas, for the treatment of methylene blue, methyl orange and congo red dyes and they concluded that the plasma treatment allows the degradation of the three different dyes, and not just one specific dye, and it has advantages over other techniques. Microwave plasma jet (MWPJ) submerged into water was used by [Hamdan et al. 2018] in order to study its feasibility in wastewater treatment and found that a significant improvement in the efficiency is achieved by adding 1–3% of N₂ to the Ar gas, which should be attributed to a combined effects of NH radicals, having high redox potential, and the backward reactions of H₂O₂ to form the OH radicals with NO and NO₂. [Preis et al. 2013] employed pulsed Corona discharge (PCD) with the objective of establishing the ratio of ozone and OH radicals contributions directly formed from water to oxidation of rapidly reacting phenol and slowly reacting oxalate and they concluded that the PCD method appeared to be highly effective in the oxidation of phenol,
surpassing the closest competitor, conventional ozonation, in energy efficiency.

In most of the previously discussed discharge schemes, the parameters of aqueous solution such as pH conductivity, oxidation reduction potential (ORP) were mentioned as influencing the dye decolourization processes [Nguyen et al. 2019]. In this work, the important item of studying the effects of water parameters on the decolourization efficiencies of solution dyes, which was not emphasized in detail previously, was investigated using DBD plasma discharge produced above the dye solutions for two aqueous solutions containing methylene blue (MB) and malachite green (MG) as organic dye materials.

**MATERIALS AND METHODS**

**Sample preparation**

Two organic dyes widely used in textile industry were considered, namely methylene blue (MB) and malachite green (MG). MB is a heterocyclic aromatic chemical compound with the formula $C_{16}H_{18}N_3SCl$, belonging to the phenothiazine family. The MB dye solution was prepared by dissolving 0.02 gm of MB in the form of powder in 1000 mL filtered tap water to reach a concentration of 20 mg/L. MG of formula $C_{23}H_{25}ClN_2$ is a potential dye material, beside its use as an antimicrobial additive in aquaculture. The MG dye solution was made by dissolving 0.01 gm of MG in the form of powder in 1000 mL filtered tap water to reach a concentration of 10 mg/L. The treated volume for both solutions is 15 mL. The molecular structures of MB and MG are shown in Figures 1a and 1b, respectively.

**Experimental setup**

Plasma above water was initiated by a Pin-water surface dielectric barrier discharge (DBD) occurring in ambient air as discharge gas without gas injection, as shown in Figure 2. A 15 ml dye solution was placed in a glass container of 100 mm diameter and 40 mm height on a magnetic stirrer assuring good mixing of the solution during plasma treatment. The discharge occurred between two electrodes, a stainless-steel needle of 0.1 mm diameter placed 3 mm above the solution surface and a grounded counter electrode placed outside the glass container bottom which played the role of dielectric in the DBD arrangement setup.

The AC high voltage of around 2 kV and 5.7 kHz was generated by an ignition coil and a driver circuit. The voltage and current characteristics measured during the discharge are shown in Figures 3a and 3b, respectively.

**Figure 1.** The molecular structure of a – MB and b – MG

**Figure 2.** Pin-water surface DBD
INSTRUMENTATION

High voltage was measured using a high voltage probe 1000:1 (model p6015A, 75 MHZ Tektronix) and discharge current by means of a Rogowski coil (Pearson Electronics model4100), of sensitivity (1 volt/1ampere). The measured signals were displayed on a four-channel digital oscilloscope (Tektronix; model TDS2024C, 200 MHz). The UV–VIS absorption spectra of aqueous solutions before and after plasma treatment were measured by a UV-VIS-NIR spectrophotometer, Cary 6000i from Agilent Technologies in the wavelength range 200–800 nm. Optical emission spectroscopy on the UV-visible range was used to identify some atomic and molecular species produced during the discharge using a fiber optics spectrometer (AvaSpec-ULS2048 StarLine from AVANTES) with wavelength range of 200–1100 nm and resolution of 0.9 nm. Water parameters, i.e. the pH value and conductivity were measured using an HI98129 meter and oxidation reduction potential (ORP) by means of an HI98120 meter, both from Hanna Instruments. For the determination of H2O2 generated in dye solutions, due to plasma treatment, the test strips (QUANTOFIX® Peroxide 100) from Sigma Aldrich were used.

RESULTS AND DISCUSSION

Degradation of MB by plasma

Decolourization of dye solutions by plasma was assessed using the UV-VIS absorbance spectra of solutions treated by plasma for different time periods, as compared to the untreated ones. The UV-VIS spectra of the MB solution, both untreated and plasma treated for different treatment time periods of durations 20, 30 and 40 min, are shown in Figure 4a. The different spectra show two strong absorption bands in the visible spectral region with maxima at 664 nm and 612 nm as well as one strong absorption band in the UV spectral region with maximum at 291 nm. The absorption maxima decrease with the increasing treatment time indicating decolourization of the dye solution to become nearly colourless at treatment time of 40 min plasma exposure, as shown in Figure 4b.

Degradation of MG by plasma

The absorbance spectra for MG solution untreated and treated with plasma are shown in Figure 5a. The different spectra show two strong absorption bands in the visible spectral region with maxima at 617 and 425 nm and one strong absorption band in the UV spectral region with maximum at 316 nm. As for MB, the absorption maxima decrease with increasing treatment time indicating decolourization of the dye solution, which becomes nearly colourless at treatment time of 40 min plasma exposure, as shown in Figure 5b.

By comparing the two absorbance spectra in Figures 4 and 5, we can see that the absorbance maxima in the UV and visible ranges for MG are decreasing to a greater degree than the corresponding ones for MB, indicating more pronounced impact of plasma on MG than on MB for the corresponding plasma exposure time periods.
Hydroxyl radical formed in air and hydrogen peroxide produced in dye solutions by plasma

Hydrogen peroxide (H₂O₂) is considered as a very powerful non-selective oxidant for different pollutants. As hydrogen peroxide is a stable element, measurement of the hydrogen peroxide concentration produced in the solution by plasma discharge may indicate the effectiveness of plasma in the decolourization process. Figure 6 shows concentrations of H₂O₂ versus the plasma treatment time measured in filtered tap water and dye solutions of MB and MG during the plasma exposure. After 10 min of plasma exposure, the H₂O₂ concentration in pure tap water reached 60 mg/L, while in MB and MG solutions, it decreased to 30 mg/L and 17 mg/L, respectively.

The concentration of H₂O₂ generated in pure tap water due to the plasma exposure time was found to be higher than that measured in the solution of MB or MG. This effect can be related to the reaction of dye materials or their decomposition products which react directly with H₂O₂ or with the OH radicals produced by plasma. Plasma occurring in air close to water surface, generates many direct and indirect reactions in water, especially by the impact of electrons, producing hydroxyl radicals (OH) at the plasma-water interface [Liu et al. 2016, Groele et al. 2019] which contributes to the main process of H₂O₂ formation in the solution. However, the reaction scheme is rather complicated owing to secondary hydroxyl radicals produced by the action of plasma generated ozone and UV. The measurement of hydrogen peroxide in a solution can be considered as a good indicator of hydroxyl radical formation by CAP in dye solutions [Takeuchi et al. 2018]. The emission spectra of plasma produced in ambient air presented in Figure 7 show the nitrogen lines

Figure 4. a – UV-VIS spectra of untreated and plasma treated MB solution at different time intervals. b – from left to right, MB solution samples of untreated and plasma treated for 20, 30 and 40 minutes

Figure 5. a – UV-VIS spectra of untreated and plasma treated MG solution for different time intervals. b – from left to right, MG solution samples of untreated and plasma treated for 20, 30 and 40 minutes
Figure 6. Concentrations of H₂O₂ versus the plasma treatment time for filtered tap water and solutions of MB & MG subjected to NTP and the lines proper to OH radicals produced in the air above the discharge, which are expected to penetrate into the water solution [Maslani et al. 2014]. As OH radical is believed to be one of the strongest oxidative elements, it may contribute to dye decomposition and solution decolourization in its simple form or as complex combinations with other elements in dye solutions.

Parameters of dye solutions related to decolourization efficiency

The measurements of aqueous solution parameters, including pH, ORP and conductivity for MB and MG dye solutions during the plasma exposure time periods can be related to decolourization efficiency defined by Eq. (1):

\[
\text{Decolourization efficiency} = \frac{A_0 - A}{A_0} \times 100\%
\]  

where: \(A_0\) is the absorbance at wavelength showing maximum absorption at \(\lambda_{\text{max}}\) before plasma, and \(A\) is the absorbance at \(\lambda_{\text{max}}\) after plasma treatment.

The concentrations of dye solutions were determined from UV-VIS spectrum measurements by maximum absorbance at 664 nm for MB and 617 nm for MG. In Figure 8, the MB solution parameters such as pH, ORP, conductivity and decolourization efficiency are plotted versus plasma treatment time. With no plasma, the initial values of pH, ORP and conductivity of the MB solution solutions are 8.7, 110 mV and 1970 µS/cm, respectively. By applying plasma, pH showed a slow decrease after plasma was ignited, reaching 7.3 after 20 min of plasma exposure. Afterward, pH decreases sharply to 4.6 after 30 min treatment. The MB solution ORP showed an almost linear increase with treatment time, reaching 510 mV after 40 min plasma exposure. The solution conductivity increased continuously with treatment time, reaching 4100 µS/cm after 40 min plasma treatment time. The decolorization efficiency showed a gradual increase with plasma treatment, reaching 59% after 40 min of plasma exposure.

In Figure 9, the MG solution parameters such as pH, ORP, and conductivity as well as
decolourization efficiency are plotted versus plasma treatment time. The MG solution pH shows a sharp decrease after plasma application, reaching 3.6 after 20 min of plasma exposure, and then decreases gradually reaching 3.2 after 40 min plasma treatment. The MG solution ORP shows an almost linear increase with treatment time, reaching 515 mV after 40 min plasma exposure. On the other hand, the conductivity increases continuously with treatment time, reaching 4200 µS/cm after 40 min plasma treatment time. The decolourization efficiency of MG solution shows a rapid increase with plasma treatment, reaching 66.3% after 20 min of plasma exposure. Then, the decolourization efficiency increases gradually to 92% after 40 min of plasma exposure.

From Figures 8 and 9, it can be noticed that the pH values of the two dye solutions decrease with increasing plasma treatment time, which is accompanied by an increase in ORPs and conductivities. The increase in decolourization efficiencies of the two dye solutions with plasma treatment can be correlated with the decrease of the pH values of the solutions and the increase of their ORPs and conductivities. The increase in the decolorization efficiencies should also be related to the increase in the hydrogen peroxide generated in the dye solutions along plasma treatment time periods. It can also be noticed that the increase in the decolourization rate of MG solution is more pronounced than that of MB. The decrease of the pH value during plasma treatment indicates acidic transformation of solutions. This
may come from nitrogen existing in air where the plasma discharge occurs, leading to the formation of nitrogen oxides that form nitrite $\text{NO}_2^-$ and nitrate ions $\text{NO}_3^-$ after dissociation into the dye solution. These, in turn, form nitric acid $\text{HNO}_3$ and peroxynitrous acid $\text{ONOOH}$ [Wu et al. 2019].

CONCLUSION

Decolourization of two organic dye solutions, namely methylene blue and malachite green was performed with nonthermal plasma generated above water surface using an AC pin-liquid surface DBD. Dye degradations were found to increase with the discharge time. After 40 minutes plasma discharge, 35% degradation of MB and 90% of MG were achieved. The concentration of hydrogen peroxide formed in the two dye solutions during plasma treatment was found to increase with the plasma treatment time. However, it is much lower than that produced by plasma in pure tap water under the same conditions. This may be due to the reaction with decomposition products. During plasma exposure, conductivities and ORPs of the two dye solutions increase gradually with plasma treatment time. However, the reduction of pH and increase of hydrogen peroxide in the two solutions during plasma treatment seem to influence the decolourization efficiencies of the two dyes the most. A decrease of pH of the dye solution, because of the plasma application above water surface, can be problematic through reuse of water for drinking or agriculture purposes. For an industrial scale treatment unit, the plasma discharge scheme employed should avoid turning the solution into acidic one. The dye degradation efficiency can be maintained as high as possible through the action of reactive species generated by plasma in the solution, especially hydrogen peroxide.

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REFERENCES

1. Anjaneyulu Y., Sreedhara Chary N., Samuel Suman Raj D. 2015. Decolourization of industrial effluents – available methods and emerging technologies – a review. Rev. Environ. Sci. Bio., 4, 245–273.
2. Atri P., Yusupov M., Park J.H., Lingamdinne L.P., Koduru J.R., Shiratani M., Choi E.H., Bogaerts A. 2016. Mechanism and comparison of needle-type non-thermal direct and indirect atmospheric pressure plasma jets on the degradation of dyes. Sci. Rep., 6(34419), 1–13.
3. Bruggeman, P.J., Iza, F., Brandenburg, R. 2017. Foundations of atmospheric pressure nonequilibrium plasmas. Plasma Sources Sci. Technol., 26(123002), 1–17.
4. Cesaro A., Naddeo V., Belgirorno V. 2013. Wastewater treatment by combination of advanced oxidation processes and conventional biological systems. J. Bioremed Biodeg., 4(208) 1–8.
5. El Shaer M., Eldaly M., Heikal G., Sharaf Y., Diab H., Mobasher M., Rousseau A. 2020. Antibiotics degradation and bacteria inactivation in water by cold atmospheric plasma discharges above and below water surface. Plasma Chem. Plasma Process., 40, 971–983.
6. Garrido-Cardenas J.A., Esteban-García B., Agüera A., Sánchez-Pérez J.A., Manzano-Agugliaro. 2020. Wastewater treatment by advanced oxidation process and their worldwide research trends. Int. J. Environ. Res. Public Health, 17(170), 1–19.
7. Gharagozalian M., Davoud Dorranian D., Ghorrann-eviss M. 2017. Water treatment by the AC gliding arc plasma. J. Theor. Appl. Phys., 11(3), 171–180.
8. Giardina, A., Schiorlin, M., Marotta, E., Paradisi, C. 2020. Atmospheric pressure non-thermal plasma for air purification: ions and ionic reactions induced by dc+ corona discharges in air contaminated with acetone and methanol. Plasma Chem. Plasma Process., 40, 1091–1107.
9. Gorbanev Y., O’Connell D., Chechik V. 2016. Non-thermal plasma in contact with water: the origin of species. Chem. Eur. J. 2016, 22, 3496–3505.
10. Groele J., Foster J. 2019. Hydrogen peroxide interference in chemical oxygen demand assessments of plasma treated waters. Plasma, 2, 294–302.
11. Hamdan A., Jing-Lin Liu J. L., Cha M. S. 2018. Microwave plasma jet in water: Characterization and feasibility to wastewater treatment. Plasma Chem. Plasma Process., 38, 1003–1020.
12. Hoffer P., Kolacek K., Stelmashuk V., Lukes P. 2015. Penetration of gas discharge through the gas-liquid interface into the bulk volume of conductive aqueous solution. IEEE T. Plasma Sc., 43(11), 3868-3875.
13. Kant R. 2012. Textile dyeing industry an environmental hazard. Nat. Sci., 4(1), 22–26.
14. Laroussi, M. 2020. Cold plasma in medicine and healthcare: The new frontier in low temperature plasma applications. Front. Phys., 8, art 74.

15. Lellis B., Fávaro-Polonio C.Z., Pamphile J.A, Polo-nio J.C. 2019. Effects of textile dyes on health and the environment and bioremediation potential of living organisms. Biotech. Res. Innovation., 3, 275–290.

16. Liu J., He B, Chen Q., Li J., Xiong Q., Yue G., Zhang X., Yang S., Liu H., Liu Q.H. 2016. Direct synthesis of hydrogen peroxide from plasma-water interactions. Sci. Rep., 6(38454), 1–7.

17. Maslani A., Sember V. 2014. Emission spectroscopy of OH radical in water-argon arc plasma jet. J. Spectrosc. 2014 (952138), 1–6.

18. Massima Mouele E.S., Tijani J.O., Ojo O. Fatoba O.O., Petrik L.F. 2015. Degradation of organic pollutants and microorganisms from wastewater using different dielectric barrier discharge configurations – a critical review. Environ. Sci. Pollut. Res., 22, 18345–18362.

19. Nguyen D.V., Ho P.Q., Pham T.V., Nguyen T.V., Kim L. 2019. Treatment of surface water using cold plasma for domestic water supply. Environ. Eng. Res., 24(3), 412–417.

20. Njiki A., Kamgang-Youbi G., Laminsi S., Lontsi C.D., Payom G., Nola M., Ngameni E. 2016. Gliding arc discharge-assisted biodegradation of crystal violet in solution with Aeromonas hydrophila strain. Int. J. Environ. Sci. Technol., 13, 263–274.

21. Olszewski P., Li J.F., Liu D.X., Walsh J.L. 2014. Optimizing the electrical excitation of an atmospheric pressure plasma advanced oxidation process. J. Hazard. Mater., 279, 60–66.

22. Oturan M.A., Aaron J.J. 2014. Advanced oxidation processes in water/wastewater treatment: Principles and applications. A review. Crit. Rev. Env. Sci. Tec, 44, 2577–2641.

23. Preis S., Panorel I.C, Kornev I., Hatakka H., Kallas J. 2013. Pulsed corona discharge: the role of ozone and hydroxyl radical in aqueous pollutants oxidation. Water Sci. Technol., 68 (7), 1536–1542.

24. Takeuchi N., Ishibashi N. 2018. Generation mechanism of hydrogen peroxide in dc plasma with a liquid electrode. Plasma Sources Sci. Technol., 27(4), 1–9.

25. Tichonovas M., Krugly E., Racys V., Hippler R., Kauneliene V., Stasiulaitiene I., Martuzevicius D. 2013. Degradation of various textile dyes as wastewater pollutants under dielectric barrier discharge plasma treatment. Chem. Eng. J., 229, 9–19.

26. Varilla C., Marcone M., Amor G.A. 2020. Potential of cold plasma technology in ensuring the safety of foods and agricultural produce: A review. Foods, 9, 1–17.

27. Wahyudiono, Machmudah S., Goto M. 2013. Pulsed discharge plasma over a water surface induces decoloration of dyes. J. Phys. Conf. Ser., 441(012008), 1–7.

28. Wu L., Xie Q., Lv Y., Wu Z., Liang X., Lu M., Nie Y. 2019. Degradation of methylene blue via dielectric barrier discharge plasma treatment. Water, 11(1818), 1–13.

29. Yaseen D.A., Scholz M. 2019. Textile dye wastewater characteristics and constituents of synthetic effluents: a critical review. Int. J. Env. Sc. Technol., 16, 1193–1226.

30. Zhang Z., Shen J., Cheng C., Xu Z., Xia W. 2018. Generation of reactive species in atmospheric pressure dielectric barrier discharge with liquid water. Plasma Sci. Technol., 20(044009), 1–6.