

Degradation of bromophenol blue molecule during argon plasma jet irradiation

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Received: 27 May 2016 / Accepted: 16 April 2017
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Abstract The aim of this paper is to study degradation of a bromophenol blue molecule (C₁₉H₁₀Br₄O₅S) using direct irradiation of cold atmospheric argon plasma jet. The pH of the bromophenol blue solution has been measured as well as its absorbance spectra and conductivity before and after the irradiation of non-thermal plasma jet in various time durations. The results indicated that the lengths of conjugated systems in the molecular structure of bromophenol blue decreased, and that the bromophenol blue solution was decolorized as a result of the decomposition of bromophenol blue. This result shows that non-thermal plasma jet irradiation is capable of decomposing, and can also be used for water purification.

Keywords Bromophenol blue · Cold atmospheric plasma · Conductivity · Degradation · Spectrophotometry · pH

Introduction

During the past few years, many studies have been carried out to find the effect of low-temperature plasma with a variety of remote and local plasmas in atmospheric pressure on biological and industrial fields such as different surface treatment [1–9], sterilization, and purification

[10–12] processes using different electrical discharges including corona discharge, dielectric barrier discharge, micro-hollow cathode discharge, atmospheric pressure plasma jet, etc. One of the most important applications of plasma treatment is degradation of various molecules in water and other solutions. A number of papers have studied the generation of various plasma sources in water and also in contact with water [13–15]. Bruggeman et al. reviewed the atmospheric pressure non-thermal discharges in liquids and in contact with liquids [16]. Sugiarto et al. have investigated degradation of organic dyes by the pulsed discharge plasma in contaminated water in three discharge modes including streamer, spark, and spark–streamer mixed modes [17]. One of the most interesting topics, in recent years, has been studying degradation of different materials in aqueous solution such as degradation of methyl orange [18], methyl violet [19], phenol [20], methanol [21], diuron [22], 1-naphthylamine [23], pharmaceutical compound pentoxifylline [24], organophosphate pesticides [25], antibiotics [26], textile dyes [27], etc. In such studies, scientists are interested in investigating the effects of various parameters such as pH [28] and temperature [29] on the plasma-treatment process. The degradation process of some materials such as bromophenol blue during plasma irradiation has not been investigated; some studies concerned the degradation of bromophenol blue without using plasma irradiation [30–33]. On the other hand, the degradation process of some materials such as methyl blue has been well investigated. Some research concerned degradation and decolorization of methyl blue using different plasma sources such as dielectric barrier discharge [34, 35], radio frequency plasma [36], microwave discharge plasma [37], and corona discharge [38]. The aim of this paper is studying degradation of bromophenol blue molecules in water using

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capacitively coupled argon plasma jet irradiation. In the present study, atmospheric pressure plasma is irradiated to the solution of bromophenol blue to investigate the selected optical, chemical, and electrical properties of the solution after different treatment durations. The bromophenol blue solution was observed by spectrophotometry after 1, 5, and 10 min of irradiation, and they were compared with a solution without plasma treatment. Moreover, the pH and the conductivity behavior of the solution after different treatment durations of argon plasma were studied.

Materials and methods

Preparing bromophenol blue solution

Bromophenol blue (3,3',5,5'-tetrabromophenolsulfonphthalein) powder from Merck company has been used to prepare the solution. Its formula is $C_{19}H_{10}Br_4O_5S$ (CAS number: 115-39-9). Its molar mass equals 669.96 g/mol, and its bulk density equals 730 kg/m^3 . The bromophenol solution was prepared by dissolving its powder in distilled water with a concentration of 10 mg/L.

Developing plasma jet

In this paper, the capacitively coupled argon plasma jet has been developed. The working gas was pure argon. The gas discharges were generated by a power supply with a frequency of 23 kHz and an applied voltage of 5.4 kV. In this plasma jet, there was a quartz tube (length 70 mm; inner diameter 9 mm; and outer diameter 14 mm) and a copper tube (inner diameter 7 mm; outer diameter 8.8 mm; and length 5 mm) which was used as a discharge electrode. Another copper tube (length 5 mm; inner diameter 14.1 mm; and outer diameter 15.5 mm) was used as a grounding electrode. The gas flow rate was 5 L/min, and the purity of argon gas was 99.999%. When the AC high voltage is applied, dielectric barrier discharge is induced in the glass tube between two electrodes, and the inflowing gas is excited and then released into the atmosphere. The plasma jet was directly irradiated onto 10 mL of this solution. The distance between the end of the quartz tube of plasma jet and the surface of the bromophenol blue solution was approximately 15 mm. Figure 1 shows a visual picture of the experimental setup.

The argon plasma jet was directly irradiated for 1–10 min onto 10 ml bromophenol blue solution in glass Petri dishes. The absorbance spectra of the bromophenol blue solution samples are obtained from spectrophotometer (Hach DR500), and the pH of the bromophenol blue solution samples is measured with pH meter (Metrohm 744), and the conductivity of samples is measured with conductometer (Metrohm 712). All measurements have

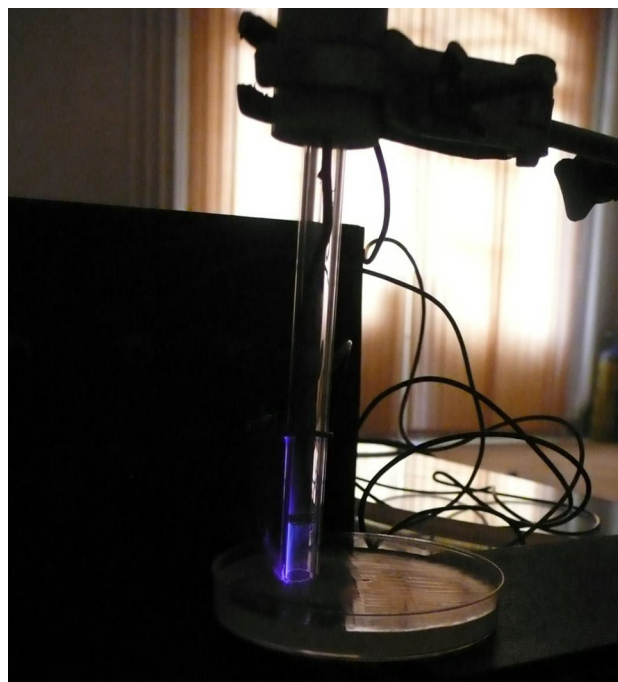


Fig. 1 A visual picture of the experimental setup

been made in four various time durations: first, before irradiation of plasma jet; second, 1 min after irradiation of the plasma jet; third, 5 min after irradiation of the plasma jet; and finally, 10 min after irradiation of the plasma jet.

Results and discussion

Figure 2 shows the absorbance spectra of the four samples with different time durations. As shown in the figure, the absorbance of samples has decreased with the increasing irradiation duration.

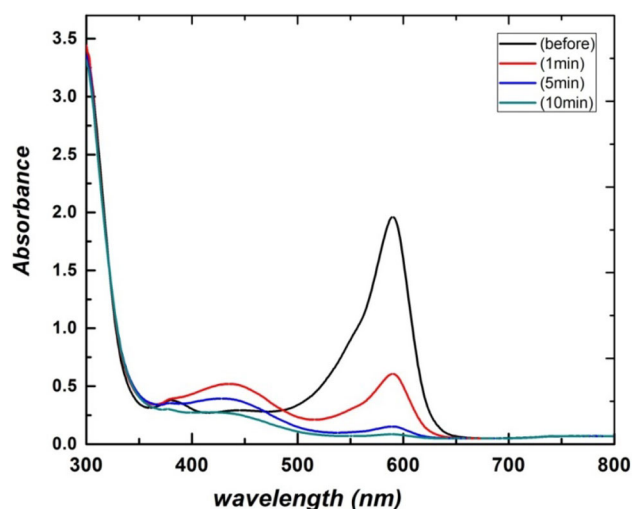


Fig. 2 The absorbance spectra of samples for different time durations

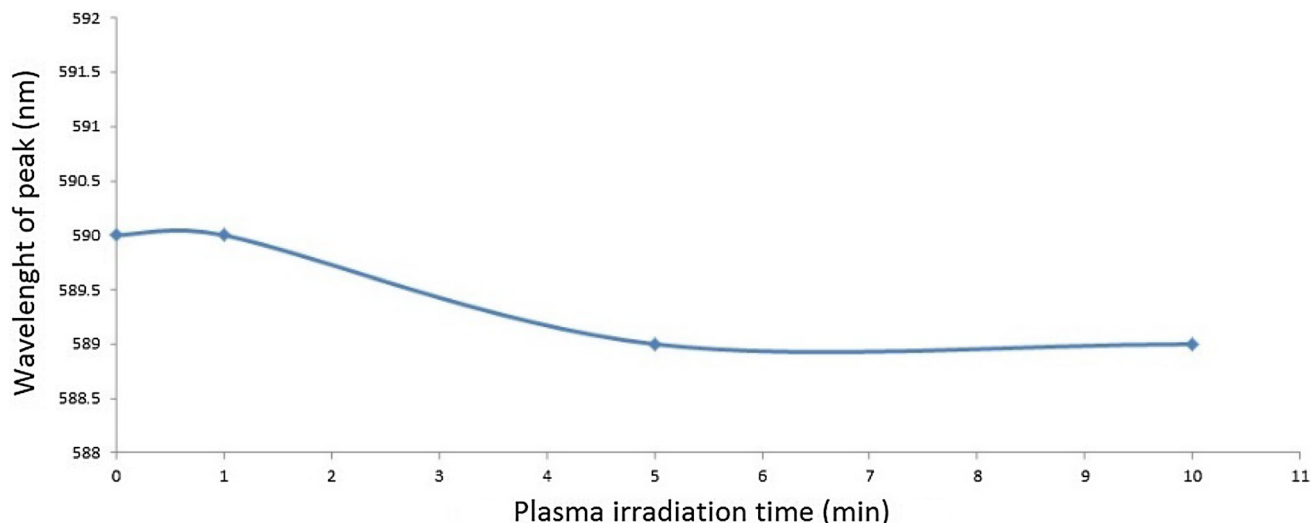


Fig. 3 The change in the wavelength of the peak with respect to plasma jet irradiation durations

This figure indicates the dependence of the absorbance spectrum of the bromophenol blue samples on the plasma jet irradiation duration. The peak wavelengths of all samples were observed around 590 nm.

Figure 3 shows a change in the peak wavelengths observed at approximately 590 nm with respect to plasma jet irradiation durations. The peaks shifted to the short wavelength region as the plasma jet irradiation time increased. It is known that the position of an absorbance peak is related to the lengths of conjugated systems in the molecular structure. A peak shifts to the long wavelength region when the lengths of conjugated systems increase, whereas it shifts to the short wavelength region when the lengths of that decrease [39]. The shift of peak wavelength to the short wavelengths indicates that the length of conjugated system in the bromophenol blue molecular structure has decreased due to plasma irradiation.

The variation of conductivity values during the reaction process has been shown in Fig. 4. The conductivity value of distilled water was measured about 10 ms/m and the conductivity value of the prepared bromophenol blue (BPB) solution before irradiation of plasma was measured about 3.2 ms/m. This distinction in conductivity values indicates that the addition of bromophenol blue powder to the distilled water resulted in a decrease in conductivity value of the solution; this is due to the fact that bromophenol blue powder increases the level of impurity. As it can be seen in the figure, the conductivity value has first decreased and then after 1 min increased. It can be hypothesized that during the first 1 min of plasma irradiation, plasma breaks the molecules of the solution into the neutral products and then after continuing the irradiation, the molecules in the solutions break up into the charged products. This behavior of BPB-related materials is proved

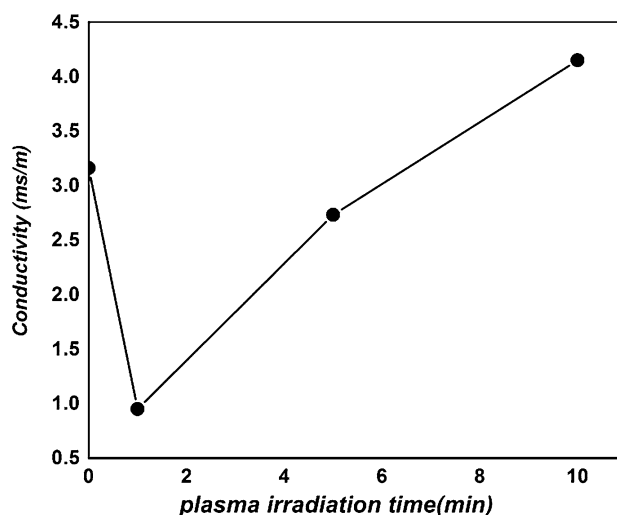
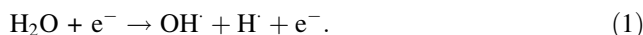


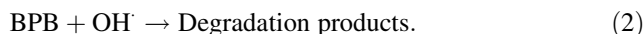
Fig. 4 The variation of conductivity values during the reaction process

by in situ resistance measurements of its ohmic response [40].

As shown in Eq. (1), high-energy electrons (e^-) in the plasma jet collide with H_2O molecules in the solution to generate hydroxyl (OH) radicals and hydrogen (H) [41]:



Sanroman et al. suggested that bromophenol blue (BPB) molecule interacts with hydroxyl radical (OH) as below [31]:



This argument is in agreement with our experiments, since hydroxyl (OH) radicals are used in Eq. (2) and hydrogen radicals (H) are left. There are some possible

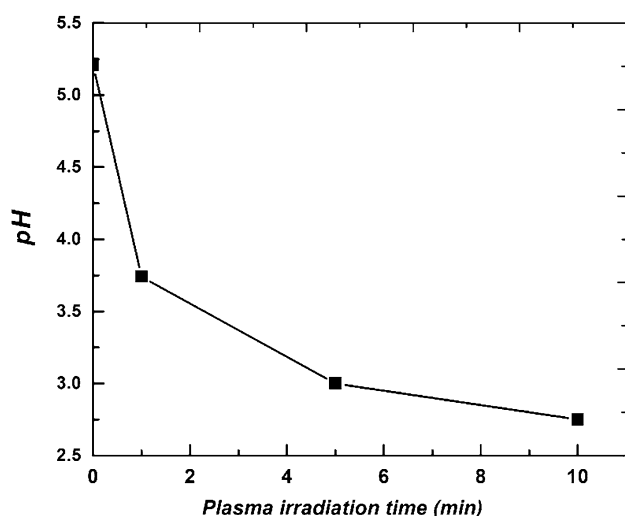


Fig. 5 The diagram of pH for the bromophenol blue solution plotted against plasma jet irradiation durations

degradation pathways. One can find the chemical mechanism and the possible degradation processes of bromophenol blue molecule in [31–33]. Figure 5 shows the diagram of pH for the bromophenol blue solutions plots against plasma jet irradiation durations. The decrease in pH value is due to the generation of hydrogen ions (H^+) in the solution. This result shows that the concentration of hydrogen ions in the solution increases as a result of plasma jet irradiation. This is in a good agreement with the results shown in Fig. 4, because, as shown in the figure, the conductivity value has increased with the increasing plasma irradiation duration and accordingly generating hydrogen ions (H^+) in the solution.

Figure 6 shows the color variation of different bromophenol blue solutions at different treatment durations. The solution was blue before irradiation, lightened after 5 min of irradiation, and became almost transparent after 10 min of irradiation.

The absorption and emission bands of material and as a consequence their colors depend on their molecular structure (energy levels). The colors of the solutions here are in a good agreement with their absorption spectra shown in Fig. 2. As is obvious from Fig. 2, before plasma treatment, the solution has a strong absorption in red region, medium absorption in green region and weak absorption in blue region; therefore, the main reflected/transmitted spectra must be in blue area, and it is in good agreement with the color of the solution before treatment. After 1 min of radiation, the solution has an equal absorption in whole regions, so it looks transparent. But after more irradiation of plasma, as it can be seen in the absorption spectra, due to the change in the molecular structure of the solution, it absorbs less light in red region in comparison with the solution with 1 min of plasma radiation, so it looks yellow

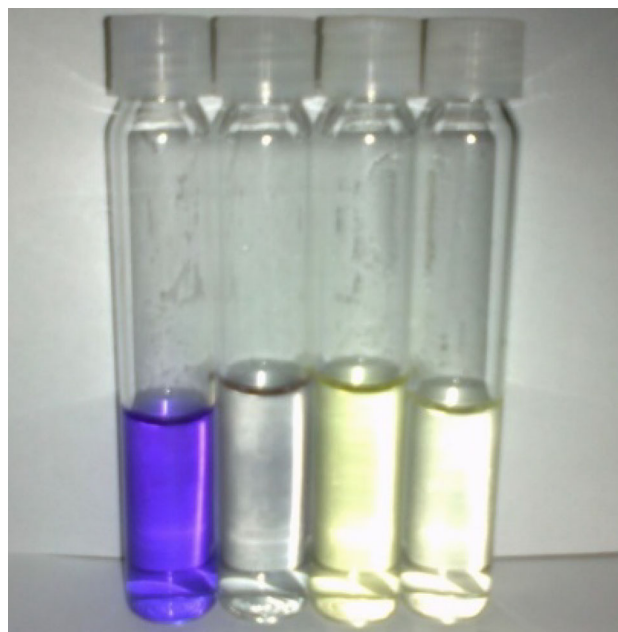


Fig. 6 The color variation of different bromophenol blue solutions at different treatment durations. *From left to right* without treatment, 1-min treatment, 5-min treatment, and 10 min treatment

(yellow color is the combination of blue absorption with red and green reflection/transmission).

Conclusion

The degradation process of bromophenol blue molecule by direct irradiation of non-thermal atmospheric argon plasma using a local plasma jet was experimentally studied. The absorbance spectra, the conductivity value, and the pH value of the bromophenol blue solutions have been measured before and after different plasma irradiation durations. The measured values were in good agreement and indicated that the lengths of conjugated systems in the molecular structure of bromophenol blue decreased, and that the bromophenol blue solution was decolorized as a result of plasma irradiation. Atmospheric cold plasmas have proved their potential to be effective in the treatment of aqueous solutions such as bromophenol blue.

Acknowledgements Hereby, the authors would like to express their deepest appreciation to Ms. Bahareh Abbasi and Dr. Ramin Rahmani for their guidance and persistent helps in editing the manuscript, and also Mr. Shahriar Mirpour for his scientific discussion.

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References

- Nijdam, S., van Veldhuizen, E., Bruggeman, P., Ebert, U.: An introduction to nonequilibrium plasmas at atmospheric pressure. In: Parvulescu, V.I., Magureanu, M., Lukes, P. (eds.) *Plasma Chemistry and Catalysis in Gases and Liquids*, pp. 1–44. Wiley-VCH Verlag & Co. KGaA, Weinheim, Germany (2012)
- Attri, P., Arora, B., Choi, E.H.: Utility of plasma: a new road from physics to chemistry. *RSC Adv.* **3**(31), 12540–12567 (2013)
- Nehra, V., Kumar, A., Dwivedi, H.: Atmospheric non-thermal plasma sources. *Int. J. Eng.* **2**(1), 53 (2008)
- Tendero, C., Tixier, C., Tristant, P., Desmaison, J., Leprince, P.: Atmospheric pressure plasmas: a review. *Spectrochim. Acta Part B* **61**(1), 2–30 (2006)
- Schutze, A., Jeong, J.Y., Babayan, S.E., Park, J., Selwyn, G.S., Hicks, R.F.: The atmospheric-pressure plasma jet: a review and comparison to other plasma sources. *Plasma Sci. IEEE Trans.* **26**(6), 1685–1694 (1998)
- Laroussi, M., Akan, T.: Arc-free atmospheric pressure cold plasma jets: a review. *Plasma Process. Polym.* **4**(9), 777–788 (2007)
- Konesky, G.: Dwell time considerations for large area Cold Plasma decontamination. In: *SPIE Defense, Security, and Sensing*, International Society for Optics and Photonics (2009)
- Manolache, S., Jiang, H., Rowell, R.M., Denes, F.S.: Hydrophobic wood surfaces generated by non-equilibrium, atmospheric pressure (NEAPP) plasma-enhanced coating. *Mol. Cryst. Liq. Cryst.* **483**(1), 348–351 (2008)
- Yun, T.K., Kim, J.H., Lee, D.K.: Enhancing the surface wettability of poly (ethylene terephthalate) film by atmospheric pressure plasma treatment with Ar and N₂ gas mixture. *Mol. Cryst. Liq. Cryst.* **586**(1), 188–195 (2013)
- de Brito Benetoli, L.O., Cadorin, B.M., Baldissarelli, V.Z., Geremias, R., de Souza, I.G., Debacher, N.A.: Pyrite-enhanced methylene blue degradation in non-thermal plasma water treatment reactor. *J. Hazard. Mater.* **237**, 55–62 (2012)
- Gao, J.: A novel technique for waste water treatment by contact glow-discharge electrolysis. *Pak. J. Biol. Sci.* **9**(2), 323–329 (2006)
- Malik, M.A., Ghaffar, A., Malik, S.A.: Water purification by electrical discharges. *Plasma Sources Sci. Technol.* **10**(1), 82 (2001)
- Foster, J., Sommers, B., Weatherford, B., Yee, B., Gupta, M.: Characterization of the evolution of underwater DBD plasma jet. *Plasma Sources Sci. Technol.* **20**(3), 034018 (2011)
- Sato, M.: Environmental and biotechnological applications of high-voltage pulsed discharges in water. *Plasma Sources Sci. Technol.* **17**(2), 024021 (2008)
- Locke, B., Sato, M., Sunka, P., Hoffmann, M., Chang, J.-S.: Electrohydraulic discharge and nonthermal plasma for water treatment. *Ind. Eng. Chem. Res.* **45**(3), 882–905 (2006)
- Bruggeman, P., Leys, C.: Non-thermal plasmas in and in contact with liquids. *J. Phys. D Appl. Phys.* **42**(5), 053001 (2009)
- Sugiarto, A.T., Ito, S., Ohshima, T., Sato, M., Skalny, J.D.: Oxidative decoloration of dyes by pulsed discharge plasma in water. *J. Electrostat.* **58**(1), 135–145 (2003)
- Huang, F., Chen, L., Wang, H., Feng, T., Yan, Z.: Degradation of methyl orange by atmospheric DBD plasma: Analysis of the degradation effects and degradation path. *J. Electrostat.* **70**(1), 43–47 (2012)
- Chen, G., Zhou, M., Chen, S., Chen, W.: The different effects of oxygen and air DBD plasma byproducts on the degradation of methyl violet 5BN. *J. Hazard. Mater.* **172**(2), 786–791 (2009)
- Sato, M., Tokutake, T., Ohshima, T., Sugiarto, A.T.: Aqueous phenol decomposition by pulsed discharge on water surface. In: *Industry Applications Conference, 2005. Fortieth IAS Annual Meeting. Conference Record of the 2005, IEEE* (2005)
- Ma, Y., Chen, J., Yang, B., Yu, Q.: Degradation of high concentration methanol in aqueous solution by dielectric barrier discharge. *Plasma Sci. IEEE Trans.* **41**(7), 1716–1724 (2013)
- Feng, J., Zheng, Z., Sun, Y., Luan, J., Wang, Z., Wang, L., Feng, J.: Degradation of diuron in aqueous solution by dielectric barrier discharge. *J. Hazard. Mater.* **154**(1), 1081–1089 (2008)
- Gao, J., Yu, J., Lu, Q., Yang, W., Li, Y., Pu, L.: Plasma degradation of 1-naphthylamine by glow-discharge electrolysis. *Pak. J. Biol. Sci.* **7**(10), 1715–1720 (2004)
- Magureanu, M., Piroi, D., Mandache, N.B., David, V., Medvedovici, A., Parvulescu, V.I.: Degradation of pharmaceutical compound pentoxifylline in water by non-thermal plasma treatment. *Water Res.* **44**(11), 3445–3453 (2010)
- Hu, Y., Bai, Y., Yu, H., Zhang, C., Chen, J.: Degradation of selected organophosphate pesticides in wastewater by dielectric barrier discharge plasma. *Bull. Environ. Contam. Toxicol.* **91**(3), 314–319 (2013)
- Magureanu, M., Piroi, D., Mandache, N., David, V., Medvedovici, A., Bradu, C., Parvulescu, V.: Degradation of antibiotics in water by non-thermal plasma treatment. *Water Res.* **45**(11), 3407–3416 (2011)
- Tichonovas, M., Krugly, E., Racys, V., Hippler, R., Kauneliene, V., Stasiulaitiene, I., Martuzevicius, D.: Degradation of various textile dyes as wastewater pollutants under dielectric barrier discharge plasma treatment. *Chem. Eng. J.* **229**, 9–19 (2013)
- Ikawa, S., Kitano, K., Hamaguchi, S.: Effects of pH on bacterial inactivation in aqueous solutions due to low-temperature atmospheric pressure plasma application. *Plasma Process. Polym.* **7**(1), 33–42 (2010)
- Benetoli, L.O.D.B., Cadorin, B.M., Postiglione, C.D.S., Souza, I.G.D., Debacher, N.A.: Effect of temperature on methylene blue decolorization in aqueous medium in electrical discharge plasma reactor. *J. Braz. Chem. Soc.* **22**(9), 1669–1678 (2011)
- Sanroman, M.A., Pazos, M., Ricart, M.T., Cameselle, C.: Electrochemical decolorisation of structurally different dyes. *Chemosphere* **57**(3), 233–239 (2004)
- Salem, I.A.: Kinetics of the oxidative color removal and degradation of bromophenol blue with hydrogen peroxide catalyzed by copper (II)-supported alumina and zirconia. *Appl. Catal. B* **28**(3), 153–162 (2000)
- Hong, J., Ta, N., Yang, S.G., Liu, Y.Z., Sun, C.: Microwave-assisted direct photolysis of bromophenol blue using electrodeless discharge lamps. *Desalination* **214**(1), 62–69 (2007)
- Dlamini, L.N., Krause, R.W., Kulkarni, G.U., Durbach, S.H.: Photodegradation of bromophenol blue with fluorinated TiO₂ composite. *Appl. Water Sci.* **1**(1–2), 19–24 (2011)
- Manoj Kumar Reddy, P., Rama Raju, B., Karuppiiah, J., Linga Reddy, E., Subrahmanyam, C.: Degradation and mineralization of methylene blue by dielectric barrier discharge non-thermal plasma reactor. *Chem. Eng. J.* **217**, 41–47 (2012)
- Huang, F., Chen, L., Wang, H., Yan, Z.: Analysis of the degradation mechanism of methylene blue by atmospheric pressure dielectric barrier discharge plasma. *Chem. Eng. J.* **162**(1), 250–256 (2010)
- Miyamoto, I., Maehara, T., Miyaoka, H., Onishi, S., Mukasa, S., Toyota, H., Kuramoto, M., Nomura, S., Kawashima, A.: Effect of the temperature of water on the degradation of methylene blue by the generation of radio frequency plasma in water. *J. Plasma Fusion Res. Ser.* **8**, 0627–0631 (2009)
- Wang, B., Sun, B., Zhu, X., Yan, Z., Liu, Y., Liu, H.: Degradation of methylene blue by microwave discharge plasma in liquid. *Contrib. Plasma Phys.* **53**(9), 697–702 (2013)
- Magureanu, M., Piroi, D., Gherendi, F., Mandache, N.B., Parvulescu, V.: Decomposition of methylene blue in water by corona discharges. *Plasma Chem. Plasma Process.* **28**(6), 677–688 (2008)



39. Kuwahata, H., Kimura, K., Ohya, R.-I.: Decolorization of methylene blue aqueous solution by atmospheric-pressure plasma jet. *J. Surface Sci. Nanotechnol.* **8**, 381–383 (2010)
40. Ferreira, J., Giroto, E.M.: pH effects on the ohmic properties of bromophenol blue-doped polypyrrole film. *J. Braz. Chem. Soc.* **21**(2), 312–318 (2010)
41. Kuwahata, H., Mikami, I.: Generation of H_2O_2 in distilled water irradiated with atmospheric-pressure plasma jet. *J. Surface Sci. Nanotechnol.* **11**, 113–115 (2013)

