



Original

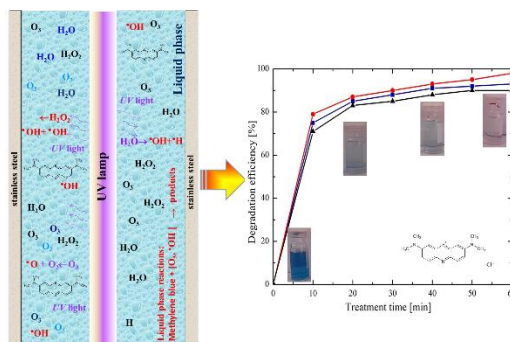
Methylene blue degradation assessment by advanced oxidation methods

B. Jaramillo-Sierra^{a*}, A. Mercado-Cabrera^b, A. N. Hernández-Arias^a,
R. Peña-Eguiluz^b, R. López-Callejas^b,
B. G. Rodríguez-Méndez^b, R. Valencia-Alvarado^b

^aTecnológico de Estudios Superiores de Tlanguistenco,
Carretera Tenango-La Marquesa km 22, 52650 Santiago Tlanguistenco, México

^bInstituto Nacional de Investigaciones Nucleares,
Plasma Physics Laboratory, Carretera México-Toluca S/N, 52750 Ocoyoacac, México

Abstract: Experimental investigation about methylene blue degradation in aqueous solution applying several Advanced Oxidation Processes such as O_3 , O_3/H_2O_2 , O_3/UV and $O_3/UV/H_2O_2$ was accomplished. Methylene blue treatment consisted in evaluating the degradation of an initial concentration of 22 ppm in 500 ml of aqueous solution. The contaminant degradation efficiencies were analyzed considering parameters such as: treatment time, three different pH values for the solution and O_3 and H_2O_2 as oxidizing reagents. The discoloration of the samples was examined throughout the experimental each 10 minutes. Using $O_3/UV/H_2O_2$ (10 ppm) with an initial 7 pH and a treatment time of 60 minutes the highest degradation efficiency of 98% was achieved.



Keywords: Methylene blue, Advanced Oxidation Processes, Degradation efficiency

1. INTRODUCTION

Dyes are organic compounds used mainly in the textile, pharmaceutical, cosmetic and food industries (Shao, Zheng Chen & Liu, 2017). They are characterized by having complex molecular structures with several

functional groups, presenting low biodegradability (Hassaan, El Nembr, & Madkour, 2017), and high stability to light and heat. Their presence in bodies of water can foster carcinogenic and teratogenic effects in species living there (Cotto-Maldonado, Duconge Morant, & Márquez, 2017; Hassaan et al., 2017; Shao et al., 2017) and avoid entry of solar radiation affecting the aquatic flora and fauna.

Methylene blue also called by IUPAC as 3,7-bis (Dimethylamino) phenothiazin-5-ium chloride is a dye

* Corresponding author.

E-mail address: bethsabet.jaramillo@est.edu.mx (B. Jaramillo-Sierra).

Peer Review under the responsibility of Universidad Nacional Autónoma de México.

which molecular structure is $C_{16}H_{18}N_3ClS$ (Figure 1). This dye is an aromatic heterocyclic cationic (Dawood & Sen, 2014). Used as medication, antiseptic and tissue colorant in some surgical processes (Cotto-Maldonado et al., 2017), and for dyeing cotton, wool, nylon, and other textile fibers (Turhan, Durukan, Ozturkcan, & Turgut, 2012). Its presence in effluents even at low concentrations becomes an important source of water pollution, contributing mainly to its eutrophication, affecting living beings. Physical, chemical and biological conventional methods are used for its degradation (Jian-Xiao, Ying, Guo-hong, Ling-yun, & Su-fen, 2011), however their application is not recommended, vis-à-vis the complexity of methylene blue chemical structure which demands large treatment times and energy, increasing degradation cost and sludge generation after treatment (Dawood & Sen, 2014; Hassaan et al., 2017; Lahunhlimi & Krishnaswamy, 2016; Shao et al., 2017). For these reasons, it is essential to develop and evaluate new methods able to provide high pollutant removal efficiencies and to be environmentally friendly.

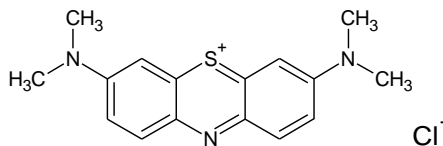


Fig. 1. Methylene blue molecular structure.

In the last decade, the Advanced Oxidation Processes (AOPs) have been used as technologies for removal of pollutants in water at room temperature and at atmospheric pressure (Hassaan et al., 2017; Turhan et al., 2012). These technologies are characterized by the production of active species mainly hydroxyl radicals (OH) (Li, Qiang, Pulgarin, & Kiwi, 2016) and for that some procedures are implemented such as: addition of oxidizing reagents and catalytic compounds. Specifically ultraviolet (UV) radiation, ozone (O_3), hydrogen peroxide (H_2O_2), Fenton reactions (Fe^{2+}/H_2O_2), photocatalysts (TiO_2 , ZnO , MnO , CuO , CuS) (Julkapli, Bagheri, & Bee Abd Hamid, 2014), and their combinations can be used. The degradation is possible by molecular reactions of the active species and the pollutant through direct and indirect pathways (Hassaan et al., 2017), where the mineralization of the contaminant can be achieved. The method choice mainly depends on pollutant characteristics, concentration and effluent volume (Liotta, Gruttadauria, Di Carlo, Perrini, & Librando, 2009).

AOPs have been applied for degradation of various water pollutants (Hossain et al., 2016; Ortiz et al., 2016; Rad et al., 2015). Diverse authors have used these methods for oxidation of methylene blue; some of them are summarized in Table 1.

Table 1. Summary of methylene blue degradation studies.

Method used	Process conditions	Decolorization/ Degradation efficiency (%)	Reference
O_3	$C_{MB} = 3.12 \times 10^{-5} M$ $CO_3 = 6.2 \times 10^{-4} M$ Gas flow rate = 1 L/min T = 25 °C, pH 8	95.3% (liquid circulation) 28.2% (without liquid circulation)	(Al Jibouri, Wu, & Upreti, 2015)
O_3	$C_{MB} = 100 mg/L$ $CO_3 =$ input rate of 0.45 g/h V = 100 mL $C_{MB} = 200 mg/L$	82.2%	(Zhang, Lee, Cui, & Jeong, 2009)
O_3	$CO_3 = 5 g/h$ (A mixture of oxygen and ozone was introduced into the ozonation reactor) V = 450 mL pH = 11	90%	(Sumegova, Derco, & Melicher, 2013)
O_3 carbon-assisted	$C_{MB} = 30 mg/L$ $CO_3 =$ input rate of 5 g/h V = 250 mL pH = 11 $C_{MB} = 3, 5$ and 10 mg/L	100%	(Zhang, Wang, Zhang, Zhang, & Fan, 2013)
H_2O_2/UV	$CH_2O_2 = 0.25, 0.5, 1, 2.5, 5, 10, 20, 40, 80, 160$ and 240 mmol Lamp = 8 W $C_{MB} = 30 mg/L$ $CH_2O_2 = 3 mL$ (30% in H_2O)	The best results for the removal was performed with 1 Mmol of H_2O_2	(Masoumbeigi & Rezaee, 2015)
H_2O_2/UV	V = 30 mL pH = 4-5	80%	(Jian-xiao et al., 2011)
H_2O_2/UV	$C_{MB} = 7.5 mg/L$ $CH_2O_2 = 13.24 mmol$ (30% in H_2O) = 50 min Lamp = 10 W	85 %	(Xu, Tang, Liu, Jiang, & Tang, 2012)

However, due to the undesirable presence of more and more different pollutants in water bodies around the world, it is important to increase and diversify studies for the treatment and removal of contaminants in water. The method to be applied for each case will be in function of the technical capabilities and the presence of necessary regional resources to try to reestablish the environmental equilibrium. In addition to the consideration of the use of the fewer chemical components quantity and keeping in mind the goal to obtain high removal efficiencies for great volumes of water.

In this paper a comparative study of the degradation of methylene blue by combining various AOPs: O_3 , O_3/H_2O_2 , O_3/UV , $O_3/UV/H_2O_2$ and treatment time effect is presented. To evaluate qualitatively methylene blue degradation, color change of samples was considered as an indicator of degradation efficiency.

2. MATERIALS AND METHODS

2.1 MATERIALS

Methylene blue and hydrogen peroxide (30% W/W) from Fermont analytical grade were used. The ozone was provided by a generator as it is shown in next section.

2.2 EXPERIMENTAL SETUP

Figure 2 shows the applied experimental setup featured by: (1) a treatment reactor of stainless steel cylindrical configuration with a length of 35 cm and diameter of 7 cm, placed in the center a 12 W Philips

quartz tube, (2) an OEM-XEGZO-30N ozone generator, (3) an UV-visible spectrometer model VELAB, (4) an Acton SP2500 spectrometer with iCCD PI-MAX3, (5) a Teledyne Instruments 460L ozone meter and, (6) a Hanna-Instruments Gro Line HI9814 multi-parameter.

The degradation study of methylene blue was accomplished preparing an aqueous solution containing a 22 ppm initial concentration in 500 mL of distilled water. The aqueous solution was placed inside of the stainless steel cylindrical reactor. This solution was circulated continuously with a submersible pump located in a reservoir next to reactor lower part, this reservoir is filled with the solution coming from the reactor. The submersible pump send the aqueous solution to the upper inlet of reactor, flowing inside and collected again into the reservoir (see figure 2). O_3 micro-bubbles as an oxidizing reagent were introduced to the reservoir to increase the degradation efficiency. When it was necessary, H_2O_2 was added to the solution in the reservoir with one of three initial concentrations considered: 5 ppm, 10 ppm, or 20 ppm. The pH value was established by the addition of hydrochloric acid and sodium hydroxide both at 1 M and quantified with the multi-parameter device. The treatment time was set at 60 minutes, whereas the samples were collected and analyzed every 10 minutes using an UV-visible spectrometer. Previously, it was established a calibration curve at known concentrations of methylene blue, where the wavelength analyzed was 665 nm corresponding to the maximum absorbance of the dye (Goby, Penner, Lajoie, & Kelly, 2017). Coloration change of the solution was observed throughout the treatment as a qualitative parameter.

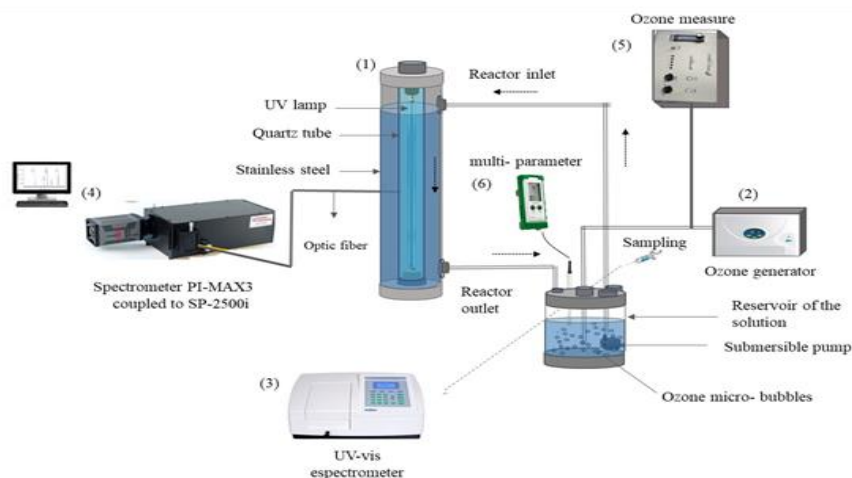


Fig. 2. Experimental setup.

3. RESULTS AND DISCUSSION

3.1 CHARACTERIZATION OF THE OZONE GENERATOR AND UV LAMP

Figure 3(a) shows the O_3 curve concentration at the output of the OEM-XEGZO-30N generator, which was feed with the atmospheric air as a precursor gas. From this figure, it can be observed that formed ozone concentration decreases progressively as the treatment time increases. From 30 minutes the resulting concentration was maintained quasi-constant at

approximately 350 ppm. Ozone micro-bubbles were incorporated into the methylene blue solution to achieve a better diffusion favoring the degradation process of the contaminant. The aqueous solution and the diffused ozone are transported from the reservoir to the reactor by the submersible pump operation. Figure 3(b) shows the emission spectrum of the used lamp, where it can be noticed the characteristic Hg emission at 254 nm which produces the photolysis of molecules such as O_3 , H_2O_2 and H_2O .

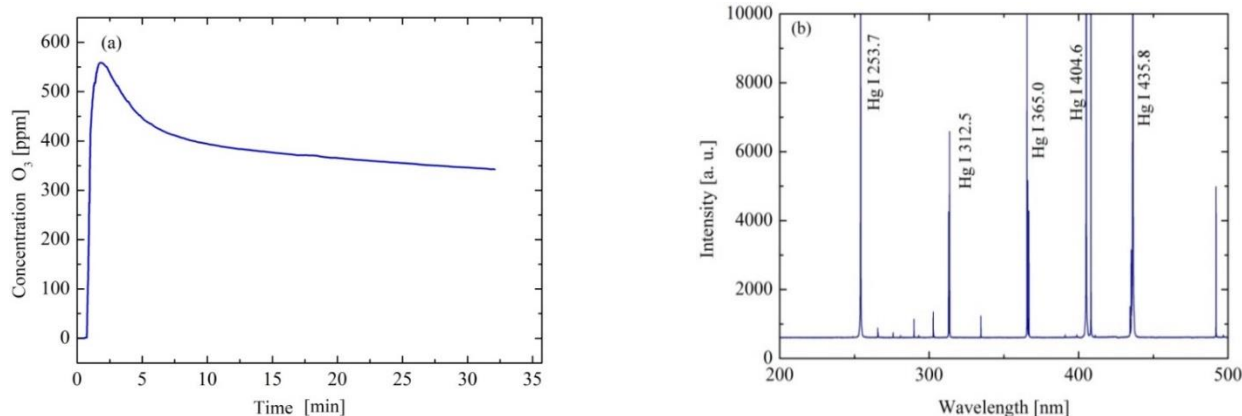
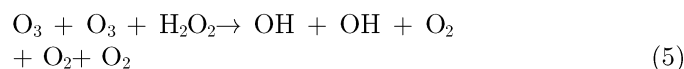
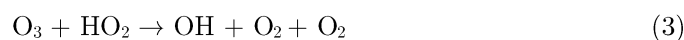
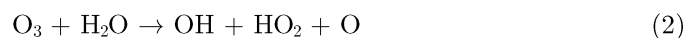


Fig. 3. (a) Ozone generation, (b) UV lamp emission spectrum.

3.2 DEGRADATION OF METHYLENE BLUE BY ADVANCED OXIDATION METHODS

3.2.1 O_3 Effects

Figure 4 shows the results obtained from methylene blue treatment with an initial concentration of 22 ppm. It was analyzed the ozone effect in a solution with one of three different initial pH values (4, 7 and 9). Efficiencies for the three different pH values were obtained up to 70%, with a pH of 9 and 60 minutes of treatment time. As higher the treatment time the higher efficiencies are obtained. The ozone degradation mechanism of methylene blue can be performed by two different oxidation pathways. The first one consists in the direct reaction of O_3 with the contaminant, see the reaction (1). Whereas the second one is due to the O_3 decomposition with intermediate species generating active species, mainly OH, which in turns reacts with the pollutant promoting its degradation, see reactions (2)-(6):



Greater effectiveness was observed from resulting curves of figure 4, when the pH was increased; some authors (Kusic, Koprivanac, & Bozic, 2006), have determined that the decomposition of O_3 is reached at alkaline pH. Hence, the generation of OH radicals is augmented; as a consequence a better degradation of methylene blue is promoted. Also, the OH radicals are non-selective (Zhang et al., 2009), and their reaction with the pollutant is more significant than the O_3 direct reaction process (Kusic et al., 2006).

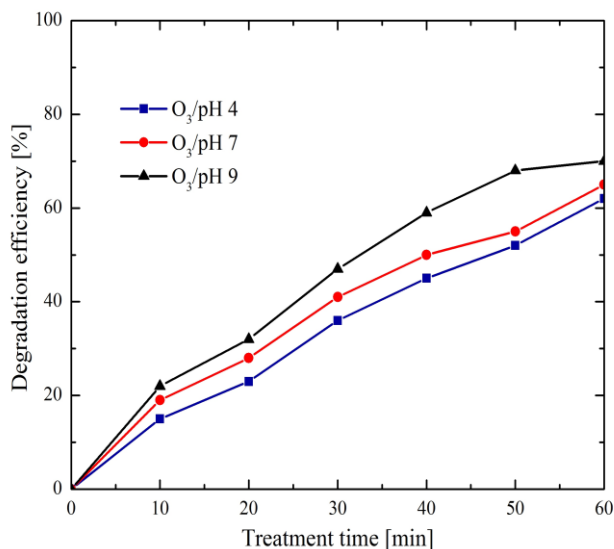
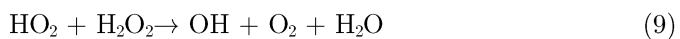
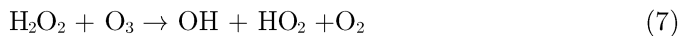


Fig. 4. Methylene blue degradation by O₃.

However, the removal efficiency in figure 4 can be considered relatively low, so other oxidizing agents in combination with ozone were evaluated as shown below.

3.2.2 Effect of O₃/H₂O₂

Figure 5 shows the obtained results of methylene blue degradation by the combination of ozone and hydrogen peroxide. In this analyzed case one of three different initial concentrations of H₂O₂ (5 ppm, 10 ppm, or 20 ppm) was added to the solution at the beginning of the treatment; for all cases, an initial value of 7 pH was set. Degradation efficiencies up to 82% were obtained with the addition of 10 ppm of H₂O₂, which represents an improvement compared to the previous study case results. This can be attributed to the combination of oxidizing agents that increase the amount of OH radicals mainly by the mechanism of reaction (7). Also, the H₂O₂ contributes to the generation of OH radicals, through the reactions (8)-(9). Therefore the methylene blue degradation process is improved.



It also can be noticed when 20 ppm H₂O₂ were added the degradation efficiency decreased. Because a higher

OH radical production involves inhibitory reactions of reactive species avoiding their interaction with the pollutant. This inhibition processes can be attributed to:

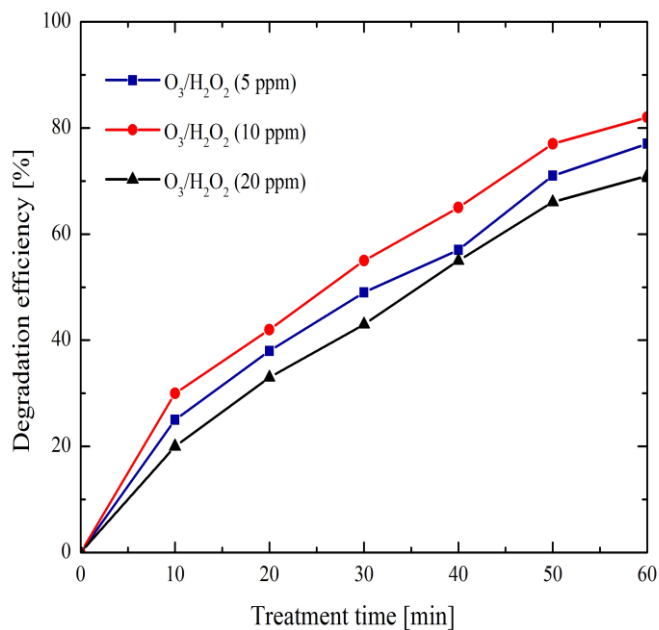


Fig. 5. Methylene blue degradation by O₃/H₂O₂.

3.2.3 O₃/UV effect

Figure 6 shows the results obtained from the degradation of methylene blue through of UV irradiation and O₃ addition. The solution was prepared for each one of three different initial pH values (4, 7 and 9). A degradation efficiency of 12% was obtained when only UV radiation was supplied; this low efficiency was considerably increased up to 79% with the presence of O₃ in solution with a pH 9. The UV radiation interaction with water and ozone allows the generation of several radicals following two different mechanisms. The first one, via the water photolysis at wavelengths between 200-280 nm defined by reaction (14); and the second one, by the molecular breakdown of chemical species including O₃ and H₂O₂, see reactions (15)-(21).

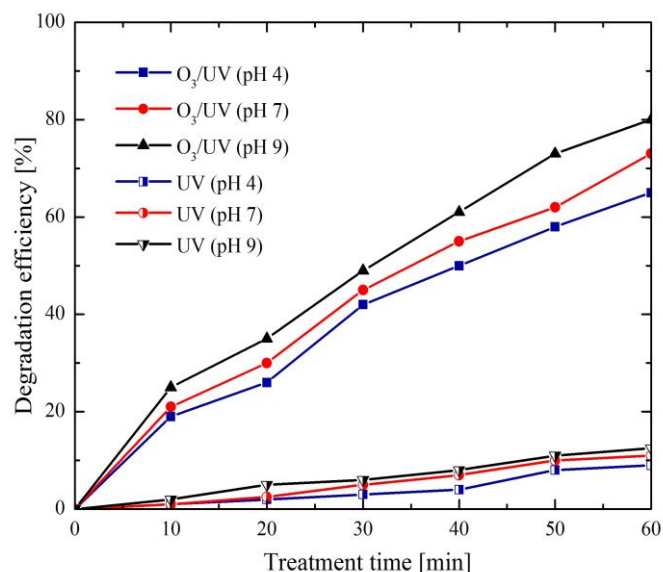
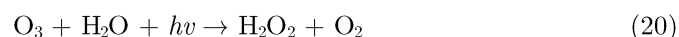


Fig. 6. Methylene blue degradation by $\text{H}_2\text{O}_2/\text{UV}$.

As can be seen, a pH alkaline and the UV radiation contributed to increase the efficiency of degradation with regard to the case shown in figure 4, where O_3 was used only as a reactive agent. At pH alkaline O_3 undergoes a fast decomposition.

3.2.4 $\text{O}_3/\text{UV}/\text{H}_2\text{O}_2$ effect

In this last case, the aqueous solution containing methylene blue was prepared only with an initial pH 7 and three different H_2O_2 concentrations were evaluated: 5 ppm, 10 ppm, or 20 ppm. And for all combinations a UV radiation was supplied. Where the respectively obtained

degradation efficiencies were 94%, 98%, and 90%, which are depicted in Figure 7. Making a comparison of herein attained results, this last analyzed method provided the higher elimination efficiencies. Therefore, the combination of the two considered oxidizing agents and UV radiation made possible to obtain high efficiencies due to a synergistic effect. As it was observed in the implemented method of $\text{O}_3/\text{H}_2\text{O}_2$ (Figure 5) the higher degradation efficiency was achieved when 10 ppm of H_2O_2 was added to the solution, confirming the inhibition processes effect.

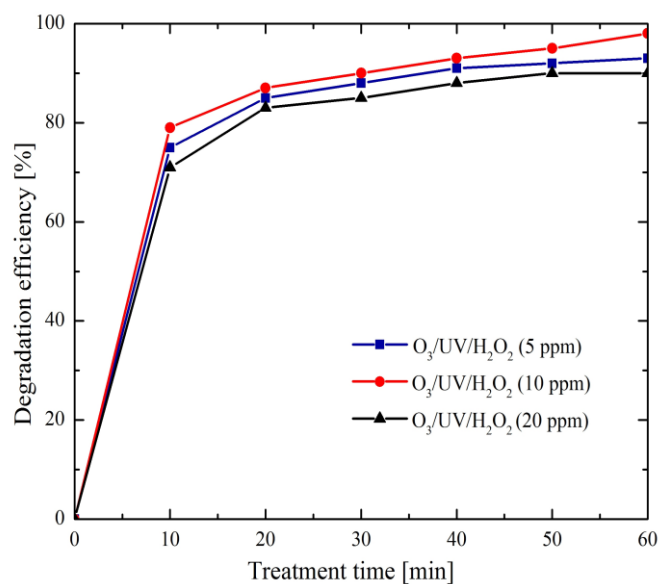


Fig. 7. Methylene blue degradation by $\text{O}_3/\text{UV}/\text{H}_2\text{O}_2$.

For this last case, the set of reactions (14)-(21) were reinforced and even more the reaction (21), when adding directly to the system the H_2O_2 oxidizing agent and of which it is known that its decomposition is accelerated by UV radiation.

3.3 IDENTIFICATION OF BYPRODUCTS OF OXIDATION: DECOLORATION OF METHYLENE BLUE IN SOLUTION

The decoloration of the methylene blue samples before treatment and each 10 minutes up to 60 minutes for a) O_3 at pH 9, b) $\text{O}_3/\text{H}_2\text{O}_2$ (10 ppm), c) O_3/UV at pH 9 and d) $\text{O}_3/\text{UV}/\text{H}_2\text{O}_2$ (10 ppm) are shown in Figure 8. It can be observed in all the cases a decoloration from the initial sample until the last one corresponding to the treatment end. When it was applied $\text{O}_3/\text{UV}/\text{H}_2\text{O}_2$ (10 ppm), a better

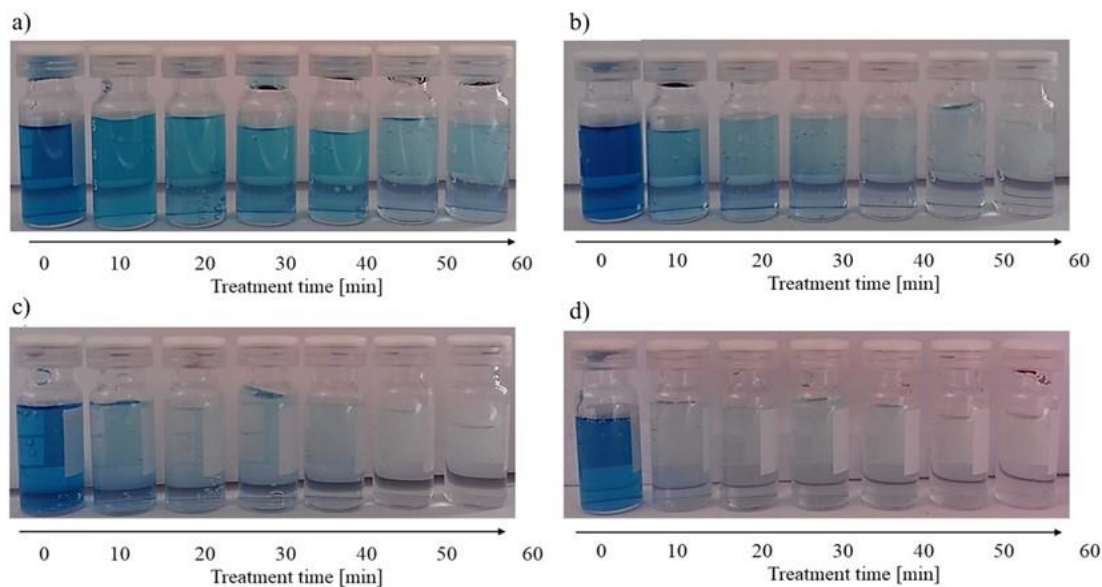


Fig. 8. Coloration change of samples obtained from the solution containing methylene blue before treatment and every ten minutes up to it send for a) O_3 at pH 9, b) O_3/H_2O_2 (10 ppm), c) O_3/UV at pH 9 and d) $O_3/UV/H_2O_2$ (10 ppm).

discoloration was obtained from the first ten minutes of treatment (case d). This can be attributed to the combined effect of the two oxidizing agents and the UV radiation, which generate an optimal quantity of OH radicals; these last oxidize the contaminant generating its decoloration.

4. CONCLUSIONS

The methylene blue degradation study was performed assessing some Advanced Oxidation Processes. In all the analyzed cases, it was observed as the higher treatment time; the higher degradation efficiencies were obtained. Furthermore, when H_2O_2 was added to the system, the increase in degradation efficiency allows to conclude that the degradation process occurs by an indirect mechanism, i.e. the electrophilic addition of the OH radical to the double bonds present in the compound molecule, this is still more reinforced when the pH is lightly alkaline and the UV radiation is supplied, since these last two conditions accelerate the chemical dissociation of O_3 and H_2O_2 and OH radical formation. It was also observed that when H_2O_2 is added to the solution, it existed an optimal concentration and that excess was in detrimental to the degradation process. The combination of $O_3/UV/H_2O_2$

generated a synergistic effect, and the highest elimination efficiencies were achieved (98%) without the addition of supplementary chemicals. Qualitatively a decrease in color was observed as the treatment time increased.

ACKNOWLEDGMENTS

COMECYT, Mexico partially funded this work.

CONFLICT INTEREST

The authors have no conflicts of interest to declare.

REFERENCES

- Al jibouri A. K. H., Wu J., & Upreti S. R. (2015). Continuous ozonation of methylene blue in water. *Journal of Water Process Engineering*, 8, 142–150. <https://doi.org/10.1016/j.jwpe.2015.10.002>
- Cotto-Maldonado M. C., Duconge J., Morant C., & Márquez., F. (2017). Fenton Process for the Degradation of Methylene Blue using Different Nanostructured Catalysts. *American Journal of Engineering and Applied Sciences*, 10,2, 373-381.
- Dawood, S., & SenT. K. (2014). Review on Dye Removal from Its Aqueous Solution into Alternative Cost Effective and Non-Conventional Adsorbents. *Journal of Chemical and Process Engineering*, 1, 1-7.

- Goby J. D., Penner M. H., Lajoie C. A., & Kelly C. J. (2017). Methylene blue as a lignin surrogate in manganese peroxidase reaction systems. *Analytical Biochemistry*, 537, 37-40. 10.1016/j.ab.2017.08.010
- Hassaan, M. A., El Nemr, A., & Madkour F. F. (2017). Testing the advanced oxidation processes on the degradation of Direct Blue 86 dye in wastewater. *Egyptian Journal of Aquatic Research*, 43, 11-19. <https://doi.org/10.1016/j.ejar.2016.09.006>
- Hossain A., Rayhan A. B. M. S., Raihan Md. J., Nargis A., Ismail Iqbal M. I., Habib A., & Mahmood A. J. (2016). Kinetics of Degradation of Eosin Y by One of the Advanced Oxidation Processes (AOPs)- Fenton's Process. *American J. of Analytical Chemistry*, 7, 863-879. 10.4236/ajac.2016.712074
- Jian-xiao L. V., Ying C., Guo-hong X., Ling-yun Z. & Su-fen W. (2011). Decoloration of methylene blue simulated wastewater using a UV-H₂O₂ combined system. *Journal of Water Reuse and Desalination*, 45-51.
- Julkapli N. M., Bagheri S., & Bee Abd Hamid S., (2014). Recent Advances in Heterogeneous Photocatalytic Decolorization of Synthetic Dyes, *The Scientific World Journal*, 692307. 10.1155/2014/692307
- Kusic H., Koprivanac N., & Bozic A. L. (2006). Minimization of organic pollutant content in aqueous solution by means of AOPs: UV-and ozone-based technologies. *Chemical Engineering Journal*, 123,3, 127-137. <https://doi.org/10.1016/j.cej.2006.07.011>
- Lalnunhlimi S., & Krishnaswamy V., (2016). Decolorization of azo dyes (Direct Blue 151 and Direct Red 31) by moderately alkaliphilic bacterial consortium. *Brazilian Journal of Microbiology*, 47, 39-46.
- Li M., Qiang Z., PulgarinC., & Kiwi J. (2016). Accelerated methylene blue (MB) degradation by Fenton reagent exposed to UV or VUV/UV light in an innovative micro photo-reactor. *Applied B: Environmental*, 187, 83-89. <https://doi.org/10.1016/j.apcatb.2016.01.014>
- Liotta L. F., Gruttadauria M., Di Carlo G., PerriniG., & Librando V. (2009). Heterogeneous catalytic degradation of phenolic substrates: catalysts activity. *Journal of Hazardous Materials*, 162, 588-606. <https://doi.org/10.1016/j.jhazmat.2008.05.115>
- Masoumbeigi H., & Rezaee A., (2015). Removal of Methylene Blue (MB) dye from synthetic wastewater using UV/H₂O₂ advanced oxidation process. *Journal of Health Policy and Sustainable Health*, 2, 1, 160-166.
- Ortiz E., Gómez Chávez V., Cortés-Romero C. M., Solís H., Ruiz-Ramos R., & Loera-Serna S. (2016). Degradation of Indigo Carmine Using Advanced Oxidation Processes: Synergy Effects and Toxicological Study. *Journal of Environmental Protection*, 7, 1693-1706. 10.4236/jep.2016.712137
- Rad L. R., Irani M., Divsar F., Pourahmad H., Sayyafan M. S., & Haririan I. (2015). Simultaneous degradation of phenol and paracetamol during photo-Fenton process: Design and optimization. *Journal of the Taiwan Institute of Chemical Engineers*, 47, 190-196. <https://doi.org/10.1016/j.jtice.2014.10.014>
- Shao, H., Li, Y., Zheng, L., Chen, T., & Liu, J. (2017). Removal of methylene blue by chemically modified defatted brown algae *Laminaria japonica*. *Journal of the Taiwan Institute of Chemical Engineers*, 80, 525-532. <https://doi.org/10.1016/j.jtice.2017.08.023>
- Sumegova L., Derco J., & Melicher M. (2013). Influence of reaction conditions on the ozonation process. *Acta Chimica Slovaca*, 6, 2, 168-172.
- Turhan, K., Durukan I., Ozturkcan, S. A., & Turgut, Z. (2012). Decolorization of textile basic dye in aqueous solution by ozone.--*Dyes and Pigments*, 92, 3, 897-901. <https://doi.org/10.1016/j.dyepig.2011.07.012>
- Xu H., Tang Q., Liu Y., Jiang Y., & Tang H. (2012). Degradation Kinetics and Mechanisms of Methylene Blue by Complex Ultraviolet and Hydrogen Peroxide Process. *Advanced Materials Research*, 356-360, 1066-1069.
- Zhang J., Lee K.-H., Cui L., & Jeong T.-S. (2009). Degradation of methylene blue in aqueous solution by ozone-based processes. *Journal of Industrial and Engineering Chemistry*, 15, 185-189. <https://doi.org/10.1016/j.jiec.2008.09.014>
- Zhang S., Wang D., Zhang S., Zhang X., & Fan P. (2013). Ozonation and carbon-assisted ozonation of methylene blue as model compound: Effect of solution pH. *Procedia Environmental Sciences*, 18, 493-502. <https://doi.org/10.1016/j.proenv.2013.04.066>