



Investigation of Ozone Microbubbles for the Degradation of Methylene Orange Contaminated Wastewater

Ola A. Nashmi^a, Ahmed A. Mohammed^a and Nada N. Abdulrazzaq^b

^aEnvironmental Engineering Department, College of Engineering, University of Baghdad

^bChemical Engineering Department, College of Engineering, University of Baghdad

Abstract

In the present study, semi – batch experiments were conducted to investigate the efficiency of ozone microbubbles (OMBs) in the treatment of aqueous dye solutions methylene orange under different reaction conditions such as effect of initial solution pH , ozone generation rate and initial MO-concentration. The results showed that the removal of MO by OMBs were very high at the acidic and alkaline media and upon increasing the generation rate of ozone from 0.498 to 0.83 mg/s, the removal efficiency dramatically increased from 75to 100% within 15 min. The rate of oxidation reaction followed a pseudo first- order kinetic model. The results demonstrated that OMBs is efficient in terms of the decline of methylene orange concentration and its total mineralization.

Keywords: Methylene orange, Ozone microbubble, Ozone generation rate, Removal efficiency

Received on 13/10/2019, Accepted on 23/02/2020, published on 30/06/2020

<https://doi.org/10.31699/IJCPE.2020.2.4>

1- Introduction

Organics contamination has long been a serious environmental issue and has drawn much attention .organic contaminants, such as, petrochemicals, dyes, and agrochemicals are major pollutant in wastewater, and can be extremely harmful to the environment and the human body [1].

Dyes are toxic contaminants in water and wastewater which causes remarkable threat to the environment if their concentration exceeds the acceptable limits [2].

They can remain in the environment for a long period of time if they are not addressed with an adequate treatment [3, 4].

In fact, the direct dye discharge that containing effluents into water is unfavorable, and that's not related to their color only, but also because various of these released dyes and their breakdown products be toxic, mutagenic or carcinogenic to life forms mainly owing to carcinogens, for instance benzidine , naphthalene and other aromatic compounds [5, 6].

Several technologies had been designed to remove such pollutants, as well as these technologies include chemical oxidation, physical adsorption, and biological processes [7]. Nevertheless, physical adsorption removal efficiency is extremely restricted for wastewater that contains complicated components [8].

Biological treatment techniques are ineffective for fairly persistent contaminants and typically required more time in comparison with chemical processes [9].

In addition, in the biological methods the microbial activities are extensively affected by the environmental conditions that around it, consequently, it was inappropriate for several cases like the therapy of wastewater with high salinity [10].

Chemical oxidation is the commonly used method for the treatment of organics contaminated wastewater [11, 12]. It is better than biological procedures and can be utilized for treating some consistent contaminants [9].

In chemical oxidation method, the oxidants that are used can competently break down organic contaminants and change it into less significant compounds or even convert them into water and carbon dioxide [13].

The best oxidant was chosen as a especially good agent for wastewater treatment is ozone for the reason that its strong oxidation ability [14].

It is commonly used to treat the pharmaceuticals present in water [15], and it may be used as a primary treatment to alter persistent contaminants into further more biodegradable compounds [16]. The rate of ozone mass transfer can be greatly enhanced by microbubble dispersal [17].

Micro bubble technology (MBs) were used extensively to get better based –advanced ozone oxidation processes for the treatment of water and wastewater because of their important physicochemical properties, MBs have a lower rising velocity in comparison with normal bubbles, and the negative charge of their shell, prevent them from coalescence, as a result, they are remain in water for a longer period of time [18].

Moreover, MBs possess large specific surface area and high internal pressure, and that is can be able to improve the rate of mass transfer from bubbles into the aqueous phase significantly, so as a result, more dissolved gas concentration in the liquid phase [19, 20].

MBs can be combined with ozone effectively for their appliance in wastewater treatment. MBs can extend the reactivity and furthermore increases the dissolved ozone concentration [21], thereby increasing the treatment efficiency of ozone. These properties are of great significance and effective in the term of enhancing the transfer of ozone into water and production of hydroxyl radicals, the hydroxyl radical ($\cdot\text{OH}$) is a strong oxidant with a standard redox potential of 2.8 V [22]. Consequently, the application of ozonation micro bubbles possibly an efficient alternative option for complete mineralization of MO from water.

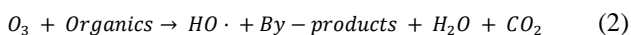
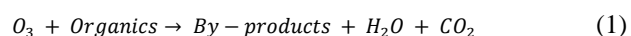
This study investigated the possibility and efficiency of utilization of the ozone micro bubbles in the simulated waste water treatment. Methylene orange (an important /panionic dye), was selected as the target contaminant to facilitate the influence of initial pH, initial MO concentration, ozonation rate and determination of mass transfer coefficient. The results proved that the use of ozonation micro bubbles was a promising technology for total removal of MO from water with the bubble diameter size determined by (ImageJ free software) on average was (32) micrometer.

2- Mechanism of Ozonation

Oxidation of dye particles in general, includes the oxidant assault on the sulfonic group or assault on the binary bond between N molecules (azo dyes). Despite the fact that the break of dye atoms is adequate to wipe out undesirable shading, different mixes are delivered during oxidation, which is once in a while hard to change over [23].

Ozonation might be a promising process for color degradation that is providing advantages such as its be able to degrade in cooperation color and organic pollutant in the one step, with no chemical sludge remaining after the process, and have less danger for the reason that residual ozone can be decomposed easily to oxygen in water [24] and no stock of any chemical (like hydrogen peroxide) is critical.

Depending on the media pH, ozone reactions were divided in to two reactions that are direct or indirect reaction. At acidic solution pH, the rate of ozone decomposition was very slow and negligible; therefore, as indicated by the responses given below [25], atomic ozone responds straightforwardly with organics or inorganics and oxidizes them:



When the dye molecules were oxidized by ozone, first of all it assaults the dye chromophore group as well as break down its construction [26, 27].

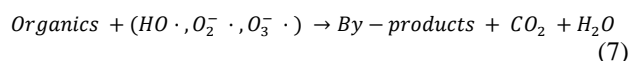
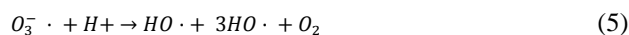
In accordance with the literature, molecular ozone reacts with organics such as phenols, aromatic compounds and amines easily; however, alternatively, the reaction of aldehydes, carboxylic acids and alcohols occurs more slowly with ozone [28].

Observably, it is able to conclude that the direct and indirect ozone reactions are selective and depends on the target compound. When pH exceeds 7, Ozone decomposition starts to occur by the reaction of hydroxyl ions (OH^-) with O_3 . Ozone decomposition provides the formation of hydroxyl radicals and enhances the hydroxyl radical reactions with organics [29].

Chu et al. [24] and Oyama et al. [30] had been mentioned that at acidic pH, molecular ozone reacts with organics and at pH values more than 7, the high rate of ozone decomposition causes the indirect reactions between hydroxyl radicals and organics to take place. Staehelin et al. [31] proposed the possible decomposition reaction of ozone as follows:



Initially, starting with the self-decomposition reaction of ozone, indirect oxidation reactions improved with $HO\cdot$ proceed to occur generally in alkaline medium. After ozone decomposition, the following reactions in aqueous phase occur:



Therefore, in the ozonation method, both direct and indirect oxidations by ozone and hydroxyl radicals were of great importance for the dye and COD removals

3- Experimental Work

3.1. Equipment

The chemicals have been used in the present work were Methylene orange (MO), sodium hydroxide (0.1M), hydrochloric acid (0.1M).

The aqueous solutions were prepared by using distilled water. Stock solution was prepared, which were diluted as per the requirements. The structure and properties of MO is shown in **Fig. 1**.

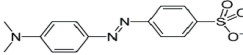
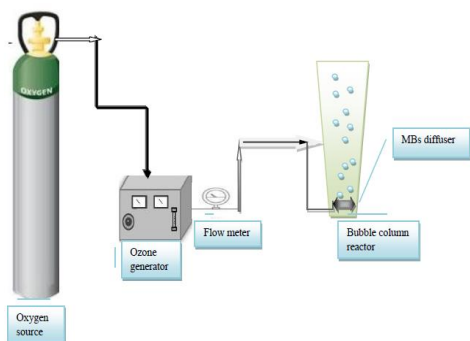
Properties	Methylene orange
Molecular Structure	
Type of Dye	Anionic
Chemical Formula	$C_{14}H_{14}N_3NaO_3S$
Molecular Weight (g/mol)	327.33
Molecular diameter (\AA)	26,14 \AA .
Maximum Absorption Wavelength (nm)	640

Fig. 1. Methylene orange structure and properties [41]

The schematic diagram for the semi-batch reactor of ozone micro bubble unit is shown in Fig.2. The setup comprises a column reactor, an oxygen source, an ozone generator (Shanghai ENALY M&E; model: OZX05K), and a gas distribution system (i.e. diffuser) to generate micro bubbles. As illustrated in the figure, Oxygen with high-purity (> 98% by volume), was supplied to the ozone generator which was used to convert oxygen gas to ozone gas via the corona-discharge technique. The generation rates of ozone that applied in this work were dominated in the range of 0.498–0.83 mg/s depending on the recommendation of the manufacturer.

The gas combination (i.e. oxygen and ozone) that released from the ozone generator was then entered to a flow meter in order to evaluate its flow rate before entering the microbubbles diffuser (Point For TM diffuser) (Riverforest Corporation, USA, AS MK –III) in the semi-batch column reactor where the micro bubbles be generated. In the micro bubble generator, the dissolution of gas in water was reached by applying an oxygen flow rate of 1 l/min, so micro bubbles are continuously produced by the discharge of pressure. The experiments were made in an air-conditioned room where the temperature was maintained at 298 ± 1 K. The initial concentration of MO in the aqueous solutions was 5ppm and the initial pH was 5.6, the pH of the solution be maintained by the use of 0.1M HCl and 0.1M NaOH solutions.

The samples from the reactor were collected initially every 1min and then after 7 min they were taken every 5min to measure their concentrations. Nearly all of the experiments were carried out with an Ozonation rate of 0.83 mg/s.



(a)



(b)

Fig. 2. Schematic diagram and actual photo of the experimental set-up (a) Schematic diagram of the experimental set-up, (b) Actual photo of the experimental set-up

3.2. Analytical Method

All aqueous solutions pH was measured by the use of a pH meter (ISOLAB.). Quantitative analysis of the MO dye concentration was made by an ultraviolet UV–visible spectrophotometer (Model: Cary-100 conc., Varian, USA). The wavelength of MO dye was detected at 552 nm.

4- Results and Discussion

4.1. Effect of MO Initial Concentration

Dyes concentration in wastewater changed in a wide range. Thus, it is essential to study the influence of MO initial concentration on its removal efficiency by ozone micro bubbles.

The experiments were carried out using different concentration of MO (5, 10, 15, 20, and 25ppm) at room temperature. Solution pH and the ozone generation rate were kept constant during these experiments at 5.6 and 0.83mg/s respectively and the results are presented in Fig. 3.

It can be seen from the results that the concentration profiles followed the same trend for all concentrations of MO applied in the current study. Upon increasing the initial concentration of MO from 5ppm to 25ppm, the removal efficiency decreased from about 100% to 85% within 15 min of ozonation time, indicating that more MO is oxidized by ozone at lower initial concentration.

This can be understood by considering that the reaction follows pseudo- first order kinetics. Therefore, the reaction rate decreased when MO concentration increased and that was accepted with the earlier work of Ayana et al. [32].

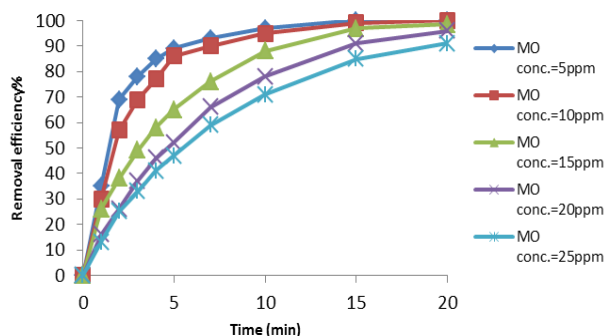


Fig. 3. Effect of the initial concentration MO on the removal efficiency (pH=5.6, ozone generation rate =0.83mg/sec)

4.2. Effect of the Initial pH of Feed Solution

It is important to investigate the effect of the solution pH on the oxidation of methylene orange (MO) since pH of the aqueous medium controls both the mechanism and the rate of the ozonation process. The ions that present in the ozonation system (i.e. H^+ or OH^-) possibly will enhance the free radicals production. Hence, the pH of the aqueous medium plays a vital role in the decomposition of ozone into OH [33]. Numerous literatures [34, 35, 36, and 37] have been proposed the mechanism of ozone decomposition in acidic and alkaline solutions and the recapitulated in the work of Khuntia et al. [38].

For MO an ionic dye its removal efficiency was showed slight dependence on pH similar results were as well reported in the literature, for instance, the Ozonation of CN^- ions was studied by Rice [39] and it was pointed out that pH had slight effect on cyanide Ozonation to cyanate. In accordance with the mechanism predicted by Staehelin and Hoigne [31], OH^- ions act in response with dissolved ozone to generate $\cdot O_2^-$ free radicals, and H^+ ions promote $\cdot O_2^-$ free radicals to convert into $HO_3\cdot$ free radicals, which are in turn decomposed to $\cdot OH$ free radicals [48]. Both H^+ and OH^- ions are needed for the production of OH free radicals.

Additionally, the MO dissociation constant (pK_a) was 3.4[40], and as a result MO will be in an ionic state when the pH state is higher or lower than this rate. An ionic structure of MO is more hydrophilic in solution and be able to degrade via dissolved ozone and $\cdot OH$ free radicals [41]. The dealing by ozone MBs involves direct oxidation via ozone molecules and oxidation by $\cdot OH$ radicals which were produced throughout ozone decomposition. Mechanism of oxidation involves hydroxyl replacement on the benzene rings and cavity of the aromatic rings [42].

Through the oxidation process, MO degradation proceeds throughout the cleavage of the azo group that attached the two aromatic rings [43], and by-products such as, p-xylene, toluene, 2,3,5-trimethyl hexane, and 4-aminoazobenzene are consequently produced [41, 44]. The by-products can be more oxidized to smaller molecules such as carbon dioxide, water, and sulfates.

As MO can also be oxidized by ozone directly, Ozonation MBs illustrated efficient treatment in a variety of pH ranges, the pH range was taken as (5.6, 8.2, 9.3, 10.3, 11.2) to examine the effect of the media on the removal rate, the highest removal efficiency was observed at pH of 5.6. Similar to these results were also reported by Sevimli et al. [45], in which the solution pH showed an insignificant influence on ozone utilization. Thus, in the current study, pH 5.6 was found to be the best possible condition for the treatment of methyl orange as shown in Fig. 4. The solution pH profile with different initial pH was investigated and the results are plotted in Fig.5. From this figure it can be seen that the extent of pH of the solution decreased with time for all initial pH solutions considered in this study, which is to be expected owing to the formation of organic acid intermediates during the oxidation of MO which is responsible for the lowering of the medium pH [40]

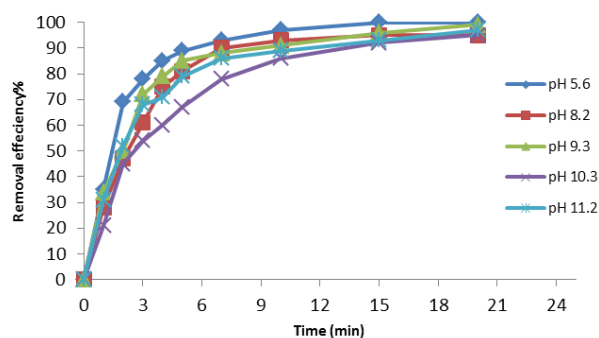


Fig. 4. The effect of pH with time on the removal efficiency of MO (25°C, MO concentration =5mg/l, ozone generation rate= 0.83 mg/sec)

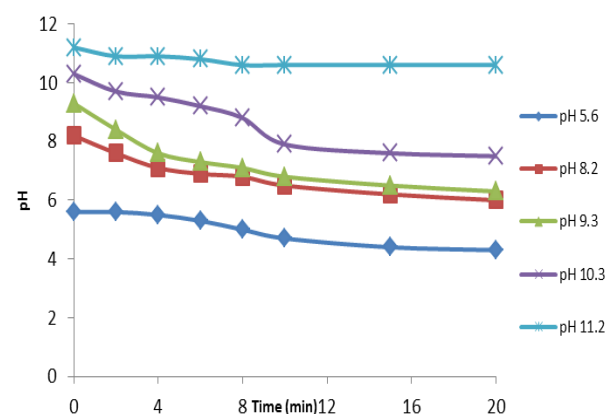


Fig. 5. Change of pH with time of MO (25°C, MO concentration =5mg/l, O3 rate= 0.83mg/sec)

4.3. Effect of Ozone Generation Rate

In the liquid phase, the ozonation rate has a major effect on the MO dye oxidation rate. In the current work, the ozonation experiments were made with a range of ozone generation rates starting from 0.498 to 0.83 mg/s to examine the influence of ozonation rate in the micro bubbles on the removal rate of MO dye.

Results of the experimental work are shown in **Fig. 6** which shows that the rate of removal efficiency of MO increased with increasing the generation rate of ozone. The effect of the ozonation rate on the decolorization rate of MO is significant [41]. From **Fig. 6**, it was obviously show when the generation rate of ozone increased from 0.498mg/sec to 0.83 mg/sec, the removal efficiency for MO increases from 69% to 100% through 20 min as seen in **Fig. 6**. Because this ionic (MO) dye removal can be occurred by direct reaction when the ozonation rate was high and by indirect reaction when the free OH⁻ radical was dominated. In addition, increasing the ozone generation rate causes an increase in the partial pressure of ozone in the gas mixture out come from the ozonator and this results in an augmentation in the ozonation rate in the aqueous phase, as predict by the Henry's law, so even at low ozonation rate the removal efficiency was 74% when the reaction still for 25 min.

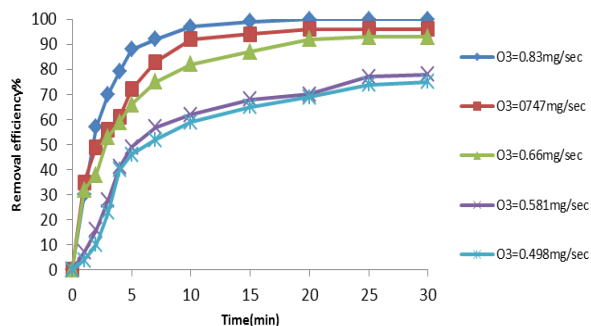


Fig. 6. Effect of ozonation Rate on MO Removal Efficiency (pH=5.6, MO conc. =10mg/l)

The change in the pH solution at different ozonation rates with time was also studied and the results are plotted in **Fig. 7**. From the results presented in this figure, it is evident that with increasing ozonation rate, the drop in the solution pH increased with time and this is due to the increase in the ozone transfer from the gas phase to the liquid phase [24] which leads, in turn, to increase the decolorization rate and decrease the pH solution through time as observed in **Fig. 7**. A similar result was reported by Constap el et al. [46], and the main reason for that is related to the formation of organic acids and aldehyde.

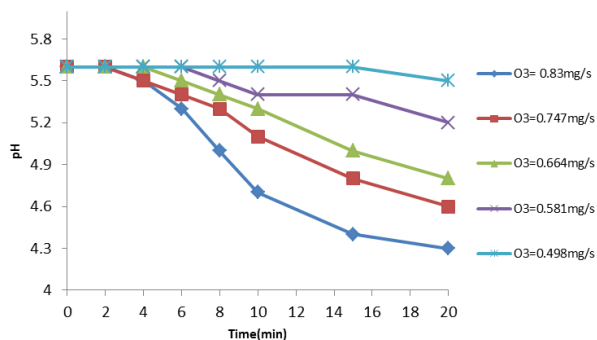


Fig. 7. Change of pH with ozonation rate at different time intervals (pH=5.6, MO conc.=5mg/l)

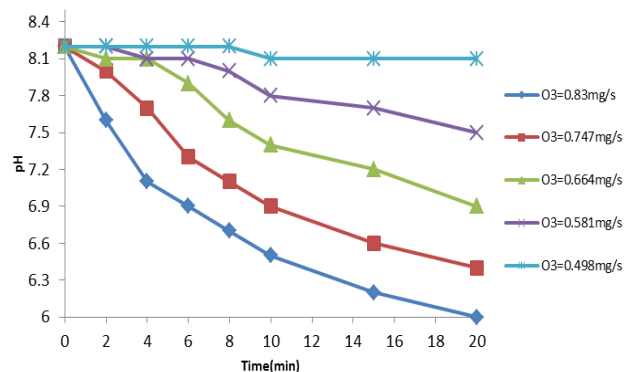


Fig. 8. Change of pH with ozonation rate at different time intervals (pH =8.2, MO conc.=5mg/l)

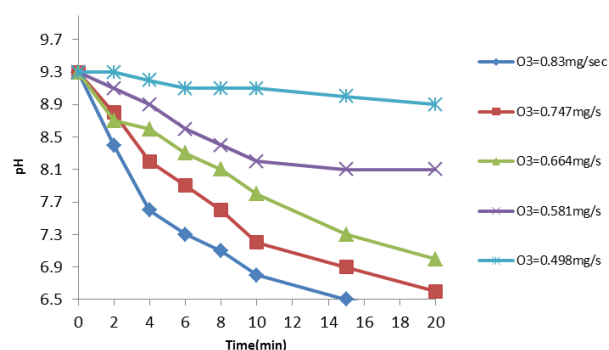


Fig. 9. Change of pH with Ozonation rate at different time intervals (pH= 9.3, MO conc.=5mg/l)

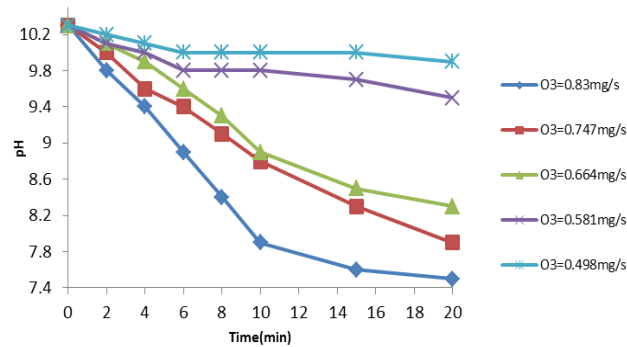


Fig. 10. Change of pH with Ozonation rate at different time intervals (pH =10.3, MO conc.=5mg/l)

From **Fig. 7-Fig. 10**, its clearly observed that when the ozonation rate decrease the drop off pH of the dyes solution also decreased until the lowest ozonation rate its nearly remain constant ,and that because when the ozone concentration is low that enhancing the indirect reaction when hydroxyl radical is produced in addition to strong acids that resulting from ozonation process so that the pH of the solution remain approximately constant or un change [41, 46]. The rapid de-colorization of MO was also visible within 10 min for all the applied MO concentration which range between 5–25 mg/l.

The spectral band changed (after ~5 min) due to the destruction of the structure of MO by ozone as shown in Fig. 11.



Fig. 11. MO samples before and after 20 min of Ozonation by microbubbles (MO concentration =25mg/l, O₃=0.83mg/s, pH=5.6 at room temperature)

4.4. Estimation of Ozone Self-Decomposition Rate Constant

Ozone mass transfer in the aqueous phase for non-reacting systems by micro bubbles had been reported previously in the literature by Khuntia et al; (2013)[47]. In current study, the ozone self-decomposition rate constant is determined through kinetic studies on our semi-batch reactor.

The dissolved ozone concentration in water has been calculated as a function of time and continue until it was reached saturation, which referred to the ozone concentration steady state, $[C_{AL}]_{ss}$.

After that, the generation of ozone was stopped and the reduction in the ozone concentration in the reactor was determined during the experiment time as shown in Fig.12.

The time taken to achieve steady state ozone concentration decreased when the pH of the medium increased. Ozone decomposition in water depends on the aqueous solution pH and it was followed a pseudo first-order kinetics and that reported as well in [47-49]. The self-decomposition reaction rate of ozone equation can be written as follows [50, 51]

$$-\frac{d[C_{AL}]}{dt} = k_d[C_{AL}] \quad (8)$$

Where: $[C_{AL}]$ is the ozone concentration in the aqueous solution and k_d is the rate constant of ozone self-decomposition. Equation (8) integrated with the boundary condition that at $t = 0$, $[C_{AL}] = [C_{AL}]_{ss}$ and this gives the following equation:

$$\ln \frac{[C_{AL}]_{ss}}{[C_{AL}]} = k_d t \quad (9)$$

Equation (9) predicts that k_d would be the slope of a straight line passing through the origin and this line is a plot of $\ln [C_{AL}]_{ss} / [C_{AL}]$ versus time t , Table 1 summarizes the experimental values of k_d at various pH.

Table 1. The experimental values of k_d at different pH.

pH	5	7	9
$k_d (s^{-1}) \times 10$	2.5	3	3.9

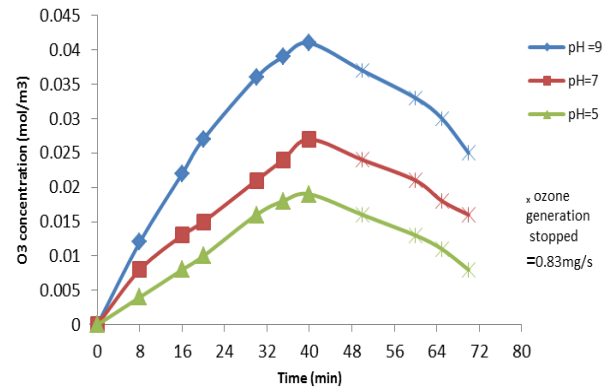


Fig. 12. Concentration profiles of ozone during its self-decomposition

One of the parameters that have a significant effect on ozone decay is pH. Therefore as to be aware of the influence of pH on ozone decay, a number of experiments were conducted at various pH values of 5, 7, and 9.

Fig. 13 illustrated the pH effect on the decay rate of ozone when the experiments were carried out in the absence of any dye. It was observed that at low pH the decay rate of is slow and it was increases when the pH increased. Moreover, that's means; the half-life time $t_{1/2}$ of ozone was pH dependent, for that reason, any increase in the pH leads to a decrease in the $t_{1/2}$.

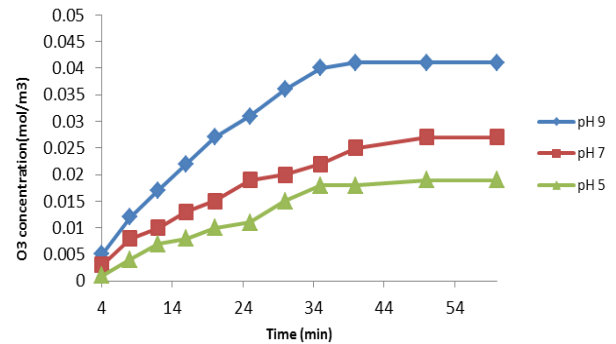


Fig. 13. Dissolved ozone concentration in water at different pH

4.5. Estimation of Volumetric Mass Transfer Coefficient $k_{La} (s^{-1})$

The absorption of ozone start to increase gradually with time until it reaches to the saturation value C_{AL}^* . The results reveal that after 30 min at any pH value, the saturated concentration of ozone was reached. The saturated concentration of the ozone was (0.04, 0.025 and 0.018) mol/m³ at pH of 9, 7 and 5 respectively as shown in Fig. 13.

The kinetic calculation will be performed at various pH values to investigate the influence of pH on the volumetric mass transfer coefficient for absorption processes.

For PH= 9: $K= 6.015 \times 10^2 s^{-1}$ and $k_{La}=5.6259 \times 10^2 s^{-1}$ and Figure.14 show the experimental and the theoretical data that obtained from the following equation [53]:

$$C_{AL} = \frac{k_{La}}{K} C_{AL}^* (1 - \exp(-Kt)) \quad (10)$$

Where: ($K = k_{La} + k_d$), k_d was determined from a separate experimental study as shown in Fig. 12 ; C_{AL}^* was determined from the Fig. 13.

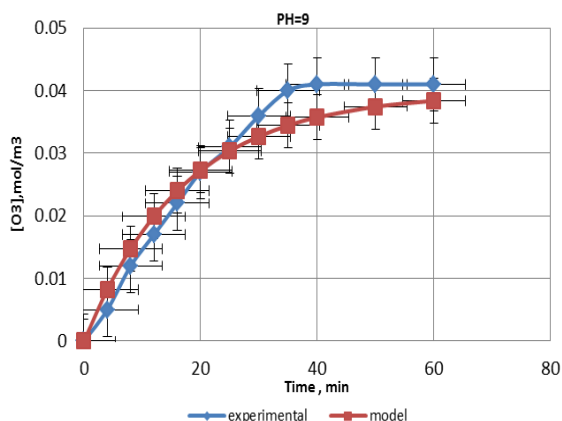


Fig. 14. The experimental and theoretical data at pH=9

For PH = 7, $K=5.336 \times 10^2 s^{-1}$ and the value of $k_{La}=5.0366 \times 10^2 s^{-1}$ and Fig. 15 shows the experimental and theoretical data.

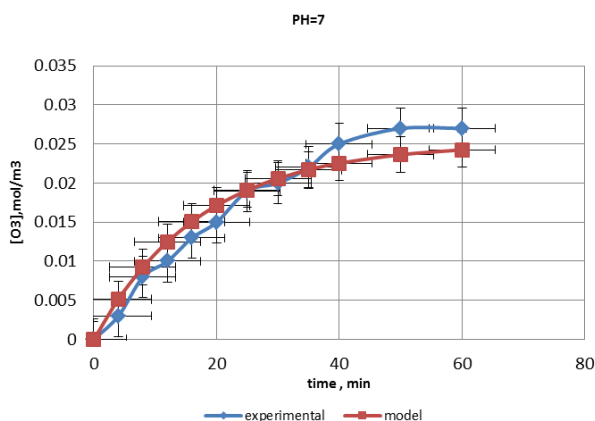


Fig. 15. The experimental and theoretical data at pH=7

For PH = 5 $K=5.47 \times 10^2 s^{-1}$ and $k_{La}=5.22 \times 10^2 s^{-1}$ and Fig. 16 shows the experimental and theoretical data.

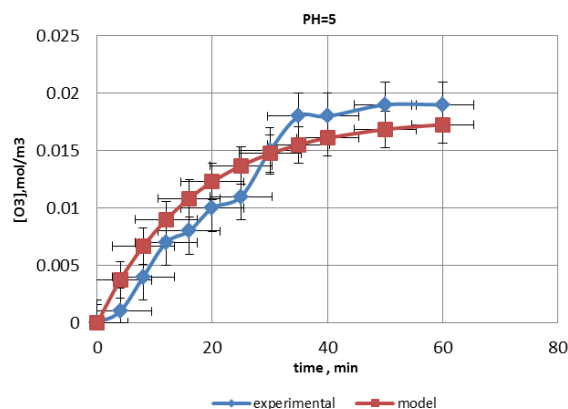


Fig. 16. The experimental theoretical data at pH=5

The result above shows the effect of pH value on the constant rate of absorption and decomposition of the ozone at different pH value.

When the pH value increases to 9 the constant rate of absorption also increases. pH was take place as a vital parameter in ozone reaction pathway.

Molecular ozone oxidation have a tendency to dominate in an acidic conditions whereas, free-radical oxidation is dominated at higher pH.

This owes to the generation of hydroxyl radicals (OH^\bullet) is improved in an alkaline condition. So, these radicals have an oxidation potential further more than ozone molecular [28], as shown from Table 2 the kinetic and mass transfer parameters at various pH (at ozonation rate of 0.83 mg/s).

Table 2. Values of the volumetric mass transfer at various pH and ozonation rate of 0.83mg/s

pH	5	7	9
$k_{La} \cdot (s^{-1}) \times 10^2$	5.22	5.0366	5.6259

The solubility and decomposition rate of ozone in water is affected by factors such as pH. The pH of the water is important because hydroxide ions effect ozone decomposition. The concentration of ozone in the solutions increases as alkalinity increases.

4.6. Removal of Chemical Oxygen Demand (COD) From MO Aqueous Solution

Results of the experiments were made and discussion of these results were obtained using methylene orange dye so as to evaluate ozonation process effect on the removal rate of COD as shown in Fig. 16.

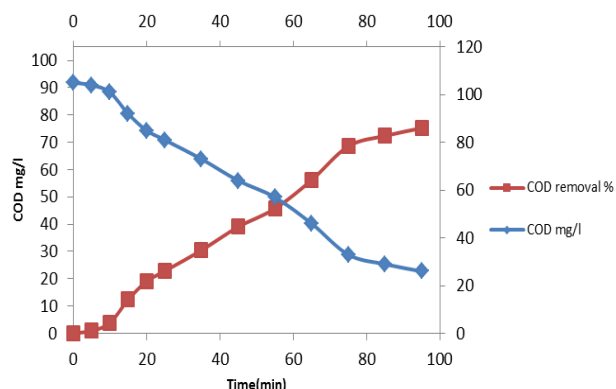


Fig. 17. Removal of COD in MO aqueous solution (MO=100 mg/l, pH =5.6, at room temperature)

In general, several organic chemicals such as dyes, biocides, ionic and non-ionic surfactants, carriers, sizing agents are contained in industrial wastewaters. As a result, it was difficult to establish the degradation rate for each organic compound present in wastewater individually.

Hence, some worldwide waste water parameters such as COD were used as an indication for the degradation kinetics of organic compounds by ozonation. For this purpose, experiments were carried out in order to assess the effect of ozonation process on the COD removal efficiency.

Fig. 17 shows the values of COD in solution after the Ozonation process. As can be seen from Figure .17 the removal rate of color was 5% within the first 10 min whereas, for the duration of the initial 30 min, the removal of color was relatively fast and its decolorization rate has increased with time. Between 30th and 60th minutes these removal rates continue to increase rapidly and after 60th minutes a slowdown has been noticed.

It is expected that the changes in the COD value for MO aqueous solution may be as a reason of the breakdown of azo bond (-N=N-) in MO and construction of nitric acid via ozonation process, because the degradation of MO dye by ozone MBs was occurred as a result of two following steps. Firstly, the decomposition of chromophore groups (-N=N-, -N-(CH₃)₂) step of MO by ozonation and the subsequent step is the breakdown of aromatic rings [32].

5- Conclusion

This study was paying attention on investigating the efficiency of using ozone micro bubbles for the oxidation of methylene orange dye (MO) from aqueous solutions. The data obtained from this work showed that this technique was very effective in removing MO from liquid medium. From the experimental work, it was found that acidic and alkaline condition enhances the separation efficiency of MO. Removal efficiencies of 100% was obtained under conditions of pH 5.6 And ozone generation rate of 0.83mg/s The direct and indirect reaction of ozonation process was dominant during the separation of MO process.

It was found also when generation rate of ozone increases, the concentration of dissolved ozone in the aqueous phase increased, which in turn improved MO oxidation rate. Complete mineralization was achieved at pH value of 5.6 and ozonation rate of 0.83 mg/s. Also, the oxidation of MO with ozone followed pseudo first-order kinetics which means that increasing the concentration of MO negatively affect its removal efficiency of the liquid solution.

Abbreviation

MO: Methylene orange
OMBs: ozone micro bubbles

References

- [1] [Ali, I.; Asim, M.; Khan, T.A. Low cost adsorbents for the removal of organic pollutants from wastewater. J. Environ. Manag. 2012, 113, 170–183.](#)
- [2] [Ramakrishna, K. R., & Viraraghavan, T. \(1997\). Dye removal using low cost adsorbents. Water Science and Technology, 36\(2-3\), 189–196.](#)
- [3] [Oliver J.Hao , Hyunook Kim & Pen-Chi Chiang \(2000\) Decolorization of Wastewater, Critical Reviews in Environmental Science and Technology, 30:4, 449-505.](#)
- [4] [M. A. Hanoon and M. J. Ahmed\(2019\). Adsorption of Methyl Orange from Wastewater by using Biochar. Iraqi Journal of Chemical and Petroleum Engineering, Vol.20 No.3 \(September 2019\).](#)
- [5] [Carmen, Z., & Daniel, S. \(2012\). Textile Organic Dyes – Characteristics, Polluting Effects and Separation/Elimination Procedures from Industrial Effluents – A Critical Overview. Organic Pollutants Ten Years After the Stockholm Convention - Environmental and Analytical Update.](#)
- [6] [A. Abbas Najim and A. A. Mohammed, “Biosorption of Methylene Blue from Aqueous Solution Using Mixed Algae”, *ijcpe*, vol. 19, no. 4, pp. 1-11, Dec. 2018.](#)
- [7] [Jones, K.C.; De Voogt, P. Persistent organic pollutants \(POPs\): State of the science. Environ. Pollut. 1999, 100, 209–221.](#)
- [8] [Liu, Z.; Kanjo, Y.; Mizutani, S. Removal mechanisms for endocrine disrupting compounds \(EDCs\) in wastewater treatment- physical means, biodegradation, and chemical advanced oxidation: A review. Sci. Total Environ. 2009, 407, 731–748.](#)
- [9] [Ikehata, K.; Gamal El-Din, M.; Snyder, S.A. Ozonation and advanced oxidation treatment of emerging organic pollutants in water and wastewater. Ozone-Sci. Eng. 2008, 30, 21–26.](#)
- [10] [Lefebvre, O.; Moletta, R. Treatment of organic pollution in industrial saline wastewater: A literature review. Water Res. 2006, 40, 3671–3682.](#)
- [11] [Sun, L.; Li, Y.; Li, A.M. Treatment of actual chemical wastewater by a heterogeneous fenton process using natural pyrite. Int. J. Environ. Res. Public Health 2015, 12, 13762–13778.](#)

- [12] [Asghar, A.; Raman, A.A.A.; Daud, W.M.A.W. Advanced oxidation processes for in-sit production of hydrogen peroxide/hydroxyl radicals for textile wastewater treatment: A review. J. Clean. Prod. 2015, 87, 826–838.](#)
- [13] [Oturán, M.A.; Aaron, J.J. Advanced oxidation processes in water/wastewater treatment: Principles and applications. A review. Crit. Rev. Env. Sci. Technol. 2014, 44, 2577–2641.](#)
- [14] [Llyas, H.; Masih, L.; van der Hoek, J.P. Disinfection methods for swimming pool water: Byproduct formation and control. Water 2018, 10, 797.](#)
- [15] [Gomes, J.; Costa, R.; Quinta-Ferreira, R.M.; Martins, R.C. Application of ozonation for pharmaceuticals and personal care products removal from water. Sci. Total Environ. 2017, 586, 265–283.](#)
- [16] [Oller, I.; Malato, S.; Sánchez-Pérez, J.A. Combination of advanced oxidation processes and biological treatments for wastewater decontamination—A review. Sci. Total Environ. 2011, 409, 4141–4166.](#)
- [17] [Zhang, F., Xi, J., Huang, J.-J., Hu, H.-Y., 2013. Effect of inlet ozone concentration on the performance of a micro-bubble ozonation system for inactivation of Bacillus subtilis spores. Sep. Purif. Technol. 114, 126e133.](#)
- [18] [Seddon, J.R.T.; Lohse, D.; Ducker, W.A.; Craig, V.S.J. A deliberation on nanobubbles at surfaces and in bulk. ChemPhysChem 2012, 13, 2179–2187.](#)
- [19] [Li, H.; Hu, L.; Song, D.; Lin, F. Characteristics of micro-nano bubbles and potential application in groundwater bioremediation. Water Environ. Res. 2014, 86, 844–851.](#)
- [20] [Agarwal, A.; Ng, W.J.; Liu, Y. Principle and applications of microbubble and nanobubble technology for water treatment. Chemosphere 2011, 84, 1175–1180.](#)
- [21] [Hu, L.M.; Xia, Z.R. Application of ozone micro-nano-bubbles to groundwater remediation. J. Hazard. Mater. 2018, 342, 446–453.](#)
- [22] [Jabesa, A., & Ghosh, P. \(2016\). Removal of diethyl phthalate from water by ozone microbubbles in a pilot plant. Journal of Environmental Management, 180, 476–484.](#)
- [23] [F.Banat, S. Al.-Asheh, M. Al.-Rawashdeh, M. Nusair, "Photodegradation of methylene blue dye by UV/H₂O₂ and UV/acetone oxidation processes", Desalination, 181\(2005\)225.](#)
- [24] [Chu W. and Chi-Wai M. \(1999\). Quantitative prediction of direct and indirect dye ozonation kinetics. Water Res. 34 \(12\), 3153-3160.](#)
- [25] [Yurteri, C., and Gürol, M.D. \(1988\). Ozone Consumption in Natural Waters: Effects of Background Organic Matter, pH and Carbonate Species. Ozone Sci. Eng., 10, 272- 282.](#)
- [26] [Lopez-Lopez, A., Pic, J.S., Debellefontaine, H. \(2007\). Ozonation of azo dye in a semi-batch reactor: A determination of the molecular and radical contributions, Chemosphere, 66\(11\), 2120-2126.](#)
- [27] [Soares G.P., Saloma O., Orfao J.J.M., Portela D., Vieira A., Pereira M.R., \(2006\). Ozonation of Textile Effluents and Dye Solutions under Continuous Operation: Influence of Operating Parameters. J. Hazard. Mater. B137, 1664- 1673.](#)
- [28] [Hoigne, J., Bader, H., 1983. Rate constants of reactions of ozone with organic and inorganic compounds in waterI: non-dissociating organic compounds. Water Res. 17 \(2\), 173-183.](#)
- [29] [Park J.S., Choi H., Cho J. \(2004\). Kinetic decomposition of ozone and parachlorobenzoic acid \(p-CBA\) during catalytic ozonation. Water Res. 38\(9\), 2285-2292.](#)
- [30] [Oyama, S.T. \(2000\). Chemical and Catalytic Properties of Ozone. Catal. Today, 42\(3\), 279-322.](#)
- [31] [Staehelin, J. and Hoigne, J. \(1985\). Decomposition of Ozone in Water in the Presence of Organic Solutes Acting as Promoters and Inhibitors of Radical Chain Reactions. Environ. Sci. Technol., 19\(12\), 1206-1213.](#)
- [32] [Ayana SHIMIZU , Yasuhiko TAKUMA , Shigeru KATO , Akihiro YAMASAKI, Toshinori KOJIMA , Kohei URASAKI , Shigeo SATOKAWA. Degradation kinetics of azo dye by ozonation in water. J. Fac. Sci.Tech., Seikei Univ. Vol.50 No.2 \(2013\)pp.1-4.](#)
- [33] [Beltran, F.J., 2004. Ozone Reaction Kinetics for Water and Wastewater Systems. Lewis Publishers, Boca Raton.](#)
- [34] [Staehelin, J., Buehler, R.E., Hoigne, J., Ozone decomposition in water studied by pulse radiolysis. 2. Hydroxyl and hydrogen tetroxide \(HO₄\) as chain intermediates. J. Phys. Chem. 88 \(24\), 5999-6004, 1984.](#)
- [35] [Tomiyasu, H., Fukutomi, H., Gordon, G., Kinetics and mechanism of ozone decomposition in basic aqueous solution. Inorg. Chem. 24 \(19\), 2962-2966, 1985.](#)
- [36] [Gardoni, D., Vailati, A., Canziani, R., 2012. Decay of ozone in water: a review. Ozone Sci. Eng. 34 \(4\), 233-242.](#)
- [37] [Sehested, K., Corfitzen, H., Holcman, J., Fischer, C.H., Hart, E.J., 1991. The primary reaction in the decomposition of ozone in acidic aqueous solutions. Environ. Sci. Technol. 25 \(9\), 1589-1596.](#)
- [38] [Khuntia, S., Majumder, S.K., Ghosh, P., Quantitative prediction of generation of hydroxyl radicals from ozone microbubbles. Chem. Eng. Res. Des. 98, 231-239, 2015.](#)
- [39] [Rice R. G., "Applications of ozone for industrial wastewater treatment": A review. Ozone Sci. & Eng. 18, 477-515, 1996.](#)
- [40] [Grabowski, L. R., Veldhuizen, E. M. van, Pemen, A. J. M., & Rutgers, W. R. "Breakdown of methylene blue and methyl orange by pulsed corona discharge". Plasma Sources Science and Technology, 16\(2\), 226–232, 2007.](#)

- [41] [Chen, L.C. Effects of factors and interacted factors on the optimal decolorization process of methyl orange by ozone. *Water Res.* 2000, 34, 974–982.](#)
- [42] [Petrella, A.; Mascolo, G.; Murgolo, S.; Petruzzelli, V.; Ranieri, E.; Spasiano, D.; Petruzzelli, D. Photocatalytic oxidation of organic micro-pollutants: Pilot plant investigation and mechanistic aspects of the degradation reaction. *Chem. Eng. Commun.* 2016, 203, 1298–1307.](#)
- [43] [Devi, L.G.; Kumar, S.G.; Reddy, K.M.; Munikrishnappa, C. Photo degradation of methyl orange an azo dye by advanced Fenton process using zero valent metallic iron: Influence of various reaction parameters and its degradation mechanism. *J. Hazard. Mater.* 2009, 164, 459–467.](#)
- [44] [Ge, D.M.; Zeng, Z.Q.; Arowo, M.; Zou, H.K.; Chen, J.F.; Shao, L. Degradation of methyl orange by ozone in the presence of ferrous and persulfate ions in a rotating packed bed. *Chemosphere* 2016, 146, 413–418.](#)
- [45] [Sevimli, M.F.; Sarikaya, H.Z. Ozone treatment of textile effluents and dyes: Effect of applied ozone dose, pH and dye concentration. *J. Chem. Technol. Biotechnol.* 2002, 77, 842–850.](#)
- [46] [Constapel, M.; Schellenräger, M.; Marzinkowski, J.M.; Gäb, S. Degradation of reactive dyes in wastewater from the textile industry by ozone: Analysis of the products by accurate masses. *Water Res.* 2009, 43, 733–743.](#)
- [47] [Khuntia S, Majumder SK, Ghosh P. Removal of ammonia from water by ozone microbubbles. *Ind Eng Chem Res.* 2013;52:318–326.](#)
- [48] [Sotelo JL, Beltrán FJ, Benitez FJ, et al. Henry's law constant for the ozone–water system. *Water Res.* 1989;23:1239–1246.](#)
- [49] [Sotelo JL, Beltran FJ, Benitez FJ, et al. Ozone decomposition in water: kinetic study. *Ind Eng Chem Res.* 1987;26:39–43.](#)
- [50] [Gao M-T, Hirata M, Takanashi H, et al. Ozone mass transfer in a new gas–liquid contactor – Karman contactor. *Sep Purif Technol.* 2005;42:145–149.](#)
- [51] [Kukuzaki M, Fujimoto K, Kai S, et al. Ozone mass transfer in an ozone–water contacting process with Shirasu porous glass \(SPG\) membranes – a comparative study of hydrophilic and hydrophobic membranes. *Sep Purif Technol.* 2010;72:347–356.](#)
- [52] [YC Hsu, TY Chen, JH Chen and C. W. Lay, Ozone transfer into water in a gas-inducing reactor. *Ind Eng Chem Res.* 2002; 41:120–127.](#)
- [53] [Grima, N. M. M. *Kinetic and mass transfer studies of ozone degradation of organics in liquid/gas-ozone and liquid/solid-ozone systems.* Diss. University of Bradford, 2009.](#)

دراسة تأثير استخدام فقاعات الاوزون الصغيرة في معالجة المياه الملوثة بصبغة الميثيلين البرتقالي

علا عبد الكاظم نشمي¹, احمد عبد محمد¹ و ندى نعم عبد الرزاق²

¹جامعة بغداد/كلية الهندسة /قسم هندسة البيئة

²جامعة بغداد/كلية الهندسة /قسم الهندسة الكيميائية

الخلاصة

يبحث هذا العمل في إزالة صبغة الميثيلين البرتقالي من الماء باستخدام فقاعات الأوزون الصغيرة. تم إجراء تجارب في ظل ظروف تفاعل مختلفة لفحص آثار التركيز الأولي لصبغة الميثيلين البرتقالي ، ودرجة الحموضة في الوسط ومعدل توليد الأوزون. تمت إزالة الميثيلين البرتقالي بشكل فعال بواسطة فقاعات الأوزون. أظهرت النتائج أن إزالة بواسطة فقاعات الأوزون كانت عالية جدًا في الوسط الحمضي والقلوي وعند زيادة معدل توليد الأوزون من 0.498 إلى 0.83 ملغم / ثانية ، زادت كفاءة الإزالة بشكل كبير من 75 إلى 100٪ خلال 15 دقيقة. يتبع معدل تفاعل الأكسدة نموذجًا حركيًا من الدرجة الأولى. أظهرت النتائج أن فقاعات الأوزون تكون فعالة من حيث انخفاض تركيز الصبغة وإزالتها الكلية.

الكلمات الدالة: الميثيلين البرتقالي, فقاعات الاوزون الصغيرة, معدل تولد الاوزون, كفاءة الازالة