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Removal of methylene blue dye from aqueous solutions using ozone/persulfate oxidation process

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□ ABSTRACT □

In this research, the performance of ozone/persulfate oxidation process (O_3/PS) for the removal of the methylene blue (MB) from aqueous solution was studied. The experiments were conducted in a laboratory reactor. In this study, the effects of reaction time (0-120 min), pH (3-11), O_3 mass flow rate (0-1.21 gr hr^{-1}), and PS dose (1-7 mmol L^{-1}) on the removal of MB was evaluated in order to determine the optimum operating conditions.

The Maximum removal efficiency of MB at optimize operational conditions (reaction time: 30 min, pH 9, O_3 mass flow rate 0.81 gr hr^{-1} and PS dose 4 mmol L^{-1}) was 97% .

Keywords: Ozone, Persulfate, Removal efficiency, Methylene blue.

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استخدام عملية الأكسدة الأوزون / بيروسلفات لإزالة الميثيلين الأزرق من المحاليل المائية

علاء محمد صبح*

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□ ملخّص □

يكثر استخدام الميثيلين الأزرق في صباغة القطن والخشب والحرير، يسبب وجوده في مياه الصرف الملونة مشكلة بيئية خطيرة لذلك يجب إزالتها. في هذا البحث تم استخدام عملية الاأكسدة الأوزون / بيروسلفات لإزالة الميثيلين الأزرق من المحلول المائي. وقد أجريت التجارب على المقياس المختبري. في هذه الدراسة تم دراسة تاثير البارامترات التالية على عملية الاأكسدة الأوزون / بيروسلفات لإزالة الميثيلين الأزرق: زمن التفاعل (0–120 دقيقة) وتأثيرات درجة الحموضة (3–11) ومعدل تدفق كتلة الاوزون (0–1.21 غرام/ساعه) وتركيز بروسلفات (1–7 مليمول/ لتر) وذلك من أجل تحديد ظروف التشغيل المثلى. كانت كفاءة إزالة الميثيلين الأزرق في الظروف التشغيلية المثلى (زمن التفاعل: 30 دقيقة ودرجة الحموضة 9 ومعدل تدفق كتلة الاوزون 0.81 غرام/ساعه وتركيز بيروسلفات 4 مليمول/ لتر) هي 97 ٪.

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1-Introduction

The colored wastewater produced by industrial activities, such as textile industry and color production has toxic effects on aquatic ecosystems (Hung et al., 2016). The presence of aromatic rings in the structure of azo increases the toxicity of these compounds and reduces their biodegradability (Xiao et al., 2015). Dyes are among the most dangerous chemical compounds that can interfere with the process of photosynthesis in water resources. MB with molecular formula ($C_{16}H_{18}N_3SCl$) and molar mass: 319.85 g/mol is one of the azo-cationic dyes (Royer et al., 2009). Its chemical structure is shown in **Fig. 1**. MB is used in various industries such as textiles, paper paints and hair dye, it can cause some harmful effects where acute exposure to MB will cause increased heart rate, vomiting, shock, cyanosis, jaundice, quadriplegia and tissue necrosis in humans (Ding et al., 2016; Xiao et al., 2015). Therefore, due to environmental problems and human health, treatment of wastewater which contains these compounds has become a vital issue (Ding et al., 2016).

Fig. 1. Chemical structure of methylene blue.

Because of the complex structure of the dyes, the traditional treatment methods was considered insufficient to completely remove it (Zhang et al., 2009).

Ozone (O_3) has been widely used in water treatment technology because of its powerful oxidation (Beltrán, 2004). However, it has been reported, in most cases, that ozonation cannot completely degrade organic compounds and sometimes produce toxic intermediates. However, drawbacks of ozonation process include low solubility of ozone, low mass transfer efficiency and incomplete organic degradation. Thus, how to integrate ozonation with other oxidation processes (e.g., hydroxyl peroxide, ultraviolet, ultrasonication, persulfate) has become important for developing future systems. In such cases, the efficiency of oxidation can be improved by employing ozone together with hydrogen Peroxide (H_2O_2), Persulfate (PS), UV irradiation to generate free radicals with high oxidation potential (Gliniak et al., 2019).

Persulfate ($S_2O_8^{2-}$) is the most active member of the peroxygen family, which has a high standard oxidation potential (E^o = 2.01 V) (Abu Amr et al., 2013; Soubh and Mokhtarani, 2016; Zhen et al., 2012). Therefore, it has been widely used for the oxidation of organic contaminants in recent years.The activation of PS has attracted the interest of many researchers especially in fields associated with the removal of pollutants (Abu Amr et al., 2013; Soubh and Mokhtarani, 2016; Zhen et al., 2012). Activating the PS leads to the generation of salt sulfate radical (SR, $SO_4^{\bullet-}$, E^o= 2.5-3.1 V). sulfate radical has proven to be very effective in degradation and total mineralization of most complex pollutants (Anipsitakis et al., 2006; Soubh, 2019). Transition metals, ozone, heat, or ultraviolet light irradiation were used to activate PS (Cao et al., 2008; Deng and Ezyske, 2011; Lin et al., 2011). O_3/PS system has been applied for the treatment of stabilized landfill leachate. The results showed that the combined of O_3 and PS was more effective than using each one alone (Abu Amr et al., 2013).

In this work, the performance of O_3/PS oxidation process in removing MB from aqueous solution was studied. Then the effects of parameters affecting the O_3/PS oxidation process as contact time, pH, O_3 dose and PS dose were examined for MB removal.

2- Materials and methods

2-1- Materials

Sodium persulfate ($Na_2S_2O_8$, 99%) was obtained from Loba – Chemie company, MB powder ($C_{16}H_{18}N_3SCl$, ≥97%), sulfuric acid (H_2SO_4, 98%), sodium hydroxide (NaOH, ≥97%) and hydrochloric acid (HCl, 37%) were obtained from Merck company.

2-2- Analytical methods

Dye concentration was measured by measuring the absorption of light at a maximum wavelength of 664 nm using a DR 5000 spectrophotometer made by Hach Company (Zhao et al., 2015). A Metrohm 691 pH meter was used to measure the pH of solutions.

2-3-Experimental procedure

Laboratory model which used to conduct this study was illustrated in **Fig 2.** The ozone contact reactor consisted of a Plexiglas column with 20 mm inner diameter and 800 mm height. Ozone generator (ARDA-COG 5S) with 5 g hr^{-1} nominal capacity was used to produce ozone gas from pure and dry oxygen. Ozone content was measured with a BMT-964 ozone analyzer. A rotameter was applied to measure the volume of injected gas to the column. Varian digital gas flow meter (Dfm-05) with flow range of 1 to 1000 mL min^{1} was also supplied to calibrate the rotameter. Ozone gas was continuously introduced into the column through a diffuser located at the bottom of the reactor. In order to prevent the emission of O_3 into the environment, the gas emitted from the reactor was passed through a 2% KI solution.

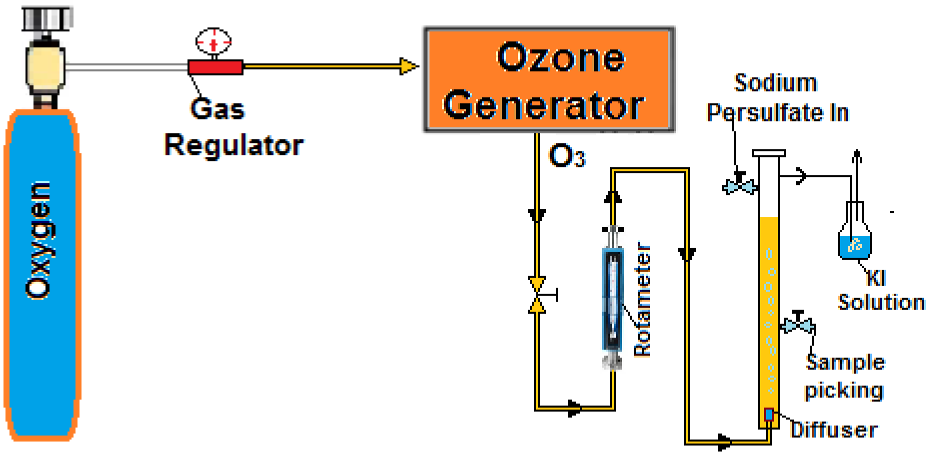

Fig. 2. Schematic laboratory setup

In each experiment, a specified amount of PS solution was added to aqueous solution contained 10 mg L^{-1} of MB in the reactor, at ambient temperature, and specified amount of ozone gas was blown to it. Samples were taken at different periods of time and filtered through a 0.45µm filter paper prior to analysis. The effect of some parameters such as reaction time, pH of solution, dsoe of PS, ozone mass flow rate on the simultaneous MB removal efficiency from aqueous solution was examined. It should be noted that in all of the experiments, the given amount of PS first was solved in 10mL of MB solution and then it was added to the reactor. The removal efficiency of MB was calculated according to the following equation (1), (Zhao et al., 2015):

$$Removel\ (\%) = \left[\left(C_i - C_f\right) / C_f\right] \times 100 \quad (1)$$

Where C_i and C_f indicate the initial and final MB concentration respectively.

In this study, the effects reaction time (0-120 min), pH (3-11), O_3 mass flow rate (0-1.21 gr hr^{-1}), and PS dose (1-6 mmol L^{-1}) on the removal of 10 mg L^{-1} MB from aqueous solution was studied.

3-Results and discussion

3-1-Effect of reaction time and Ozone consumption rate

Fig.3 presents the effect of O_3 and O_3/PS processes on removal of 10 mg L^{-1} MB from aqueous solution.

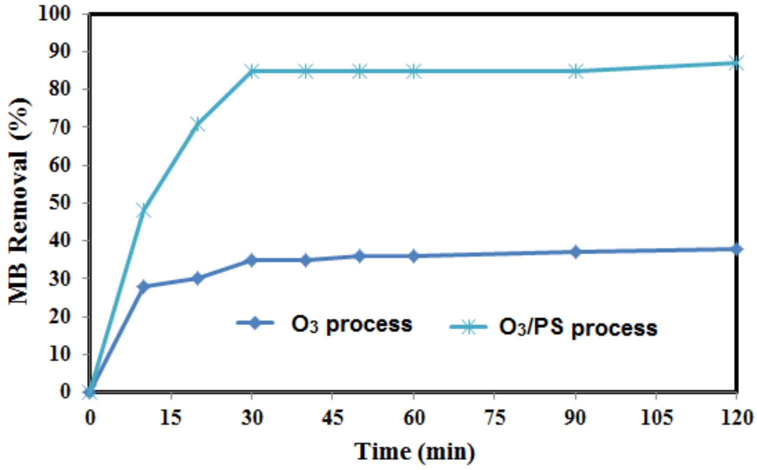

Fig.3. Effect of the reaction time on the MB removal efficiency: [PS dose= 3 mmol L^{-1}, ozone mass flow=0.65 g h^{-1}, pH= 8 and initial MB concentration= 10 mg L^{-1}]

As indicated in **Fig.3**, the improvement in removal effectiveness of MB continued until nearly 30 min where the removal efficiency of MB was 85% in the presence of PS and 35% in the absence of PS, respectively. After that no significant change was observed in removal efficiency. Thus, the reaction time of 30 min was selected as the optimum reaction time to perform the following experiments.

The two oxidation reactions compete for compounds to be oxidized. A key difference between the O_3 and O_3/PS processes is that the ozone process relies heavily on the direct oxidation of aqueous ozone molecule (E°=2.08 V), while O_3/PS process relies primarily on oxidation with salt sulfate radical (SR, $SO_4^{\bullet-}$, E^o= 2.5-3.1 V) (Cuerda-correa et al., 2020). In the O_3/PS process, the ozone residual is short lived because the added persulfate greatly accelerates the ozone decomposition. However, the increased oxidation achieved by the hydroxyl radical greatly outweighs the reduction in direct ozone oxidation because the sulfate radical is much more reactive. The net result is that oxidation is more efficient and much faster in the O_3/PS process compared to the molecular ozone process (Bakheet et al., 2013; Tizaoui et al., 2007). In O_3/PS process, when adding PS to solution, it reacts with $OH^{\bullet}$, according to **Eq. (4),** which formed from decomposing ozone under alkaline conditions, according to **Eqs. (2 and 3)** (Qiao et al., 2019)**.** This led to an improvement in the efficiency of removal.

$$O_3 + HO^- \rightarrow HO_2^- + O_2 \quad (2)$$

$$O_3 + HO_2^- \rightarrow HO^\bullet + O_2^{\bullet -} + O_2 \quad (3)$$

$$S_2O_8^{2-} + OH^\bullet \rightarrow HSO_4^{\bullet -} + SO_4^{\bullet -} + 1/2O_2 \quad (4)$$

Ozone consumption (OC) rate is defined as the ozone mass needed for the removal of a certain amount of MB **Fig.4**. The OC rate was calculated according to **Eq. 5.**

$$OC = \frac{QG}{V} \frac{\int_0^t (C_{in} - C_{out})\,dt}{MB_0 - MB_t} \quad (5)$$

Where, QG: is the inlet gas flow rate (L min^{-1}), V: is the sample volume (L), C_{in}: and C_{out}: are the ozone input and off gas concentration (mg L^{-1}), t: is the time (min) and MB_0 and MB_t: are the initial MB and MB of solution at the specified time, respectively (mg L^{-1}).

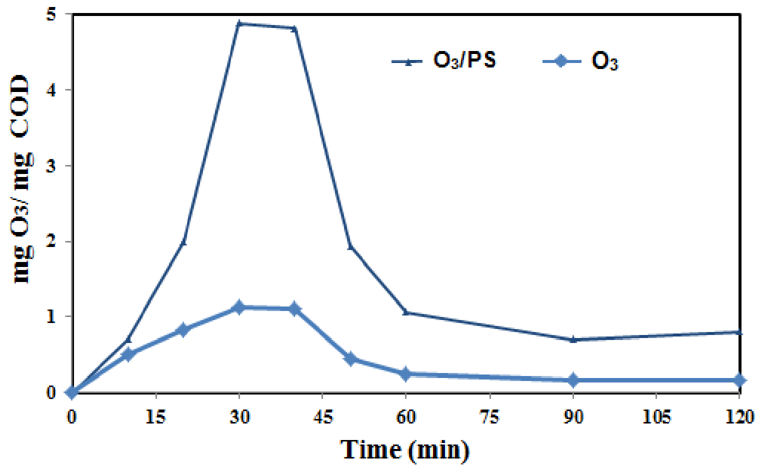

Fig.4.Ozone consumption : [PS dose= 3 mmol L-1, ozone mass flow=0.65 g h-1, pH= 8 and initial MB concentration= 10 mg L-1]

In the present study, the OC rates of O_3 and O_3/PS processes were 4.88 and 1.12 mg O_3 per mg MB, respectively, at 30 min as indicated in **Fig.4**. This reinforces the idea that in the O_3/ PS process O_3 is degraded more effectively.

3-2-Effect of pH

In order to investigate the effect of pH on the dye removal efficiency, different values of (3, 5, 7, 8, 9 and 11) were investigated **Fig. 5**.

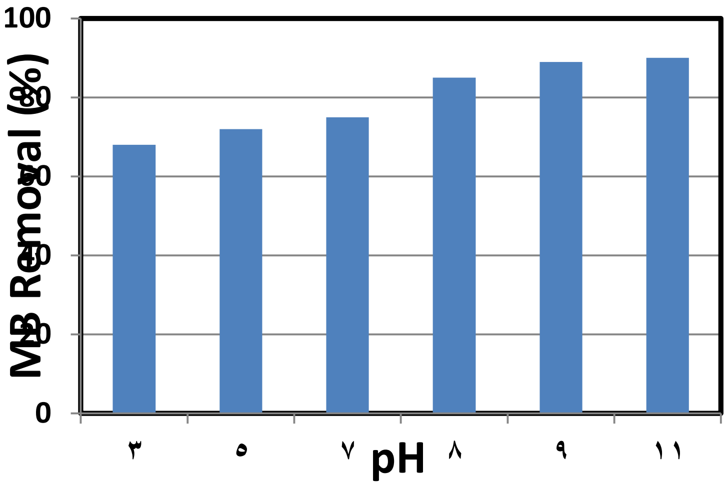

Fig (5): Effect of pH on the MB removal efficiency: [PS dose= 3 mmol L^{-1}, ozone mass flow=0.65 g h^{-1}, reaction time: 30 min and initial MB concentration= 10 mg L^{-1}]

In advanced oxidation processes (AOPs), changes in pH affect the type and quantity of radicals produced, i.e. active ingredient in treatment of the organic compounds (Liang et al., 2007; Soubh, 2019; Soubh et al., 2019). As shown in (**Fig. 5**), by increasing pH, the removal efficiencies were also increased. The increase in removal efficiency can be related to the ability of O_3 to initiate hydroxyl radical (E^o = 2.8 V) formation at high pH values (Abu Amr et al., 2013). Thereafter, according to eqn (3), under the effect of hydroxyl radicals, persulfate can be activated to initiate sulfate radical creation. Due to its high oxidation and reduction potentials, the sulfate radical plays an important role in the removal of MB.

The removal efficiencies of MB at pH 11 were very close to that at pH 9. therefore the removal efficiency of MB at pH 9 was chosen to perform the following experiments.

3-3-Effect of O_3 and PS doses

In order to investigate the effect of ozone mass flow rate on the dye removal efficiency, the effect of ozone mass flow rate on the removal of MB was illustrated in **Fig 6**.

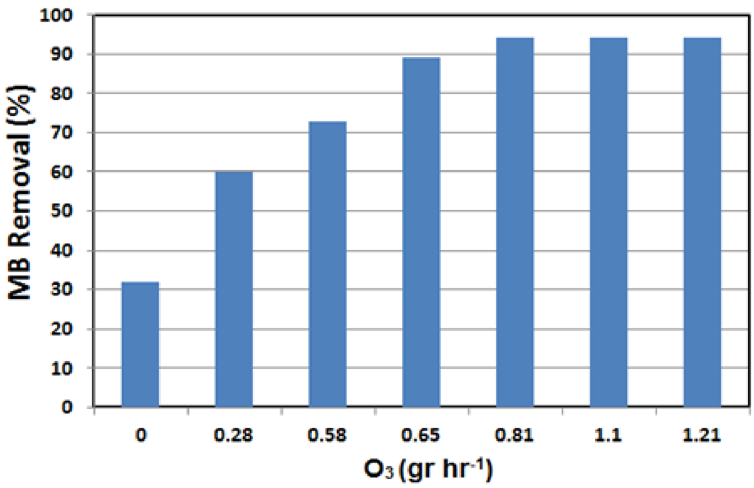

Fig (6): Effect of the ozone mass flow rate on the MB removal efficiency: [PS dose= 3 mmol L^{-1}, pH= 9, reaction time: 30 min and initial MB concentration= 10 mg L^{-1}]

As can be seen in **Fig. 6**, by increasing the O_3 mass flow rate from 0 to 0.81 gr hr^{-1}, the removal efficiencies of MB increased significantly from 32% to 94%. As result of a higher production of hydroxyl radicals. then there was stability in removal efficiency, this can be explained, the high doses of O_3 mass flow rates which above the required limit can be interfered with formed free radicals and can discourage them (Gliniak et al., 2019). Based on the results of this stage, the O_3 mass flow rate of 0.81 gr hr^{-1} was chosen to perform the following experiments.

In sulfate radical advanced oxidation processes (SR-AOPs), persulfate dose is one of the effective factors in removing the target contaminant (Abu Amr et al., 2013). Therefore effect of PS dose (in the range of 1 to 6 mmol L^{-1}) on the removal efficiency of MB was studied, **Fig. 7.**

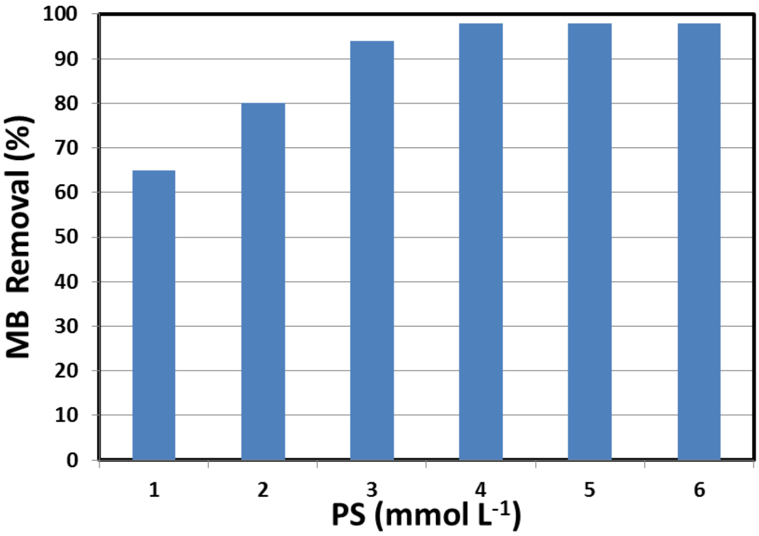

Fig (7): Effect of PS dose on the MB removal efficiency: [ozone mass flow=0.81 g h^{-1}, pH= 9, reaction time: 30 min and initial MB concentration= 10 mg L^{-1}]

As shown in **Fig. 7,** By increasing the PS dose from 1 to 4 mmol L^{-1}, the removal efficiency increased from 65 to 98%. By increasing the PS dose above 4 mmol L^{-1}, the removal efficiency remained almost constant. This is explained by the fact that high concentrations of PS dose can cause discouragement for formed radical sulfate, according to **Eq (6),** or they can discourage each other, according to **Eq (7)** (Deng et al., 2013; Soubh et al., 2018). Therefore, the PS dose= 4 mmol L-1 was selected to perform experiments in O3/PS process.

$$SO_4^{\bullet-} + S_2O_8^{2-} \rightarrow S_2O_8^{-} + SO_4^{2-} \quad (6)$$

$$SO_4^{\bullet-} + SO_4^{\bullet-} \rightarrow S_2O_8^{2-} \quad (7)$$

3-4-Kinetic Study

For reaction kinetic studies, a first order kinetic model **Eq (8)** was employed to evaluate the catalytic reaction kinetics, **Fig. 8** (Wang et al., 2015). Where, C_t is the concentration of MB at time (t) and C_0 is the initial MB concentration. K is the first-order reaction rate constant.

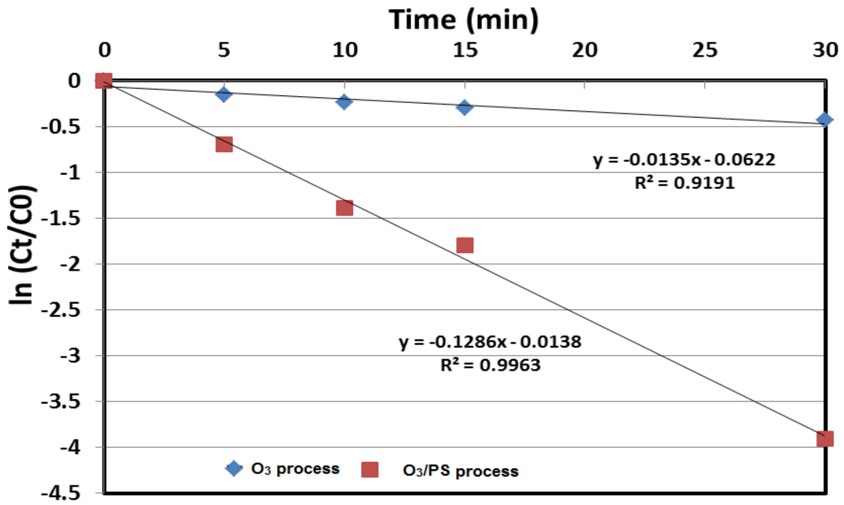

Fig (8): Kinetic study under optimal conditions: [PS dose= 4 mmol L-1, ozone mass flow=0.81 g h-1, pH= 9, reaction time: 30 min and initial MB concentration= 10 mg L-1]

$$\ln(C_t / C_0) = -kt \quad (8)$$

As shown in **Fig. 8**, the reaction rate constants in the O_3/PS and PS processes were 0.1286 and 0.0135 min^{-1}, respectively. Which shows using the O_3 with PS was 9.5 times more effective than O_3 alone for removing MB.

3-5-Variations in pH after PS addition

For pH changes studies during the reaction under optimal conditions, The pH changes in preceding conditions was studied, **Fig (9)**.

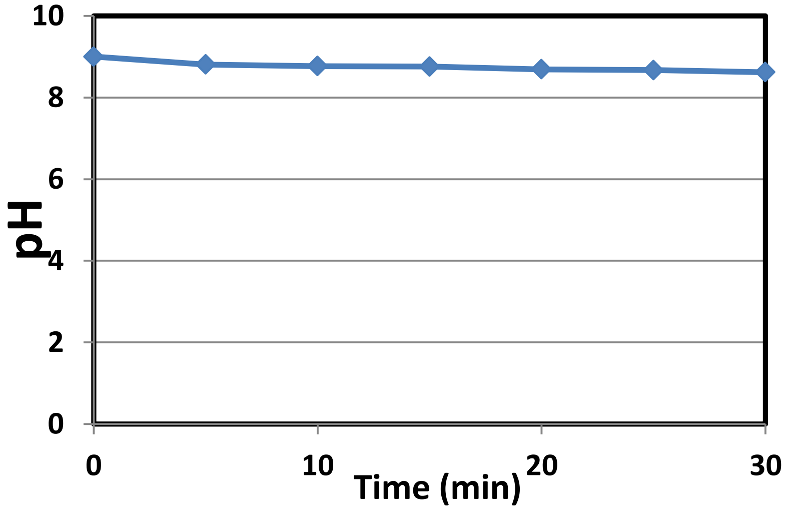

Fig (9): pH changes during the reaction under optimal conditions: [PS dose= 4 mmol L-1, ozone mass flow=0.81 g h-1, pH= 9, reaction time: 30 min and initial MB concentration= 10 mg L-1]

Addition of persulfate alone reduces the pH of the solution gradually from 9 to 8.62, which can be attributed to produce the of positive ions resulting from decomposition of PS, according to **Eqs (9** and **10)** (Kusic et al., 2011).

$$S_2O_8^{2-} + H_2O \rightarrow 2HSO_4^- + \frac{1}{2}O_2 \quad (9)$$

$$HSO_4^- \rightarrow SO_4^{2-} + H^+ \quad (10)$$

4-Conclusion

In this research, the performance of each O_3 and O_3/PS process for removal of MB from aqueous solution was evaluated. Results showed that O_3/PS process were more effective than from using O_3 process separately. The reaction rate constants in the O_3/PS and PS processes were 0.1286 and 0.0135 min-1, respectively. Which shows using the O_3 with PS was 9.5 times more effective than O_3 alone for removing MB. The addition of persulfate alone reduces pH of solution gradually from 9 to 8.62.

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