

Elimination of Remazole Blue-B by Advanced Oxidation Methods

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Abstract: *Different methods have been used to reduce or eliminate organic pollutants from wastewater and groundwater, Advanced oxidation methods means the cold combustion of organic impurities in the aqueous media by means of chemical oxidation methods, or what is called mineralization of organic pollutants. Remazol blue B. was taken as the model pollutant, (Ozone/ Hydrogen peroxide/ Ultraviolet light), were used to eliminate the pollutant from wastewater, which means the fast oxidation to produce CO_2 , H_2O , NO_3^- , SO_4^{2-} etc. The effect of pH, the initial concentration of hydrogen peroxide, the rate of ozonation, dose of UV and the influence of temperature were studied to find the optimum conditions for oxidation of this organic pollutant. Experimentally, a special system was constructed to follow the oxidation reaction of ozone with impurities. Experimental results indicated that the oxidation of Remazol blue B was faster at higher pH than at lower pH. Using suitable analytical methods such as visible spectrometry techniques, Chemical Oxygen Demand (COD), detailed kinetics and reaction mechanisms have been estimated. Recommendations, including advantages, disadvantages, optimum conditions, applicability and the economical side of similar purification / recycling projects designed to be used for treating or recycling industrial waste water, are introduced.*

Keywords: Advanced oxidation technology (AOT)- mineralization of organic pollutants- hardly oxidized impurities- remazol blue B- (COD)- ozone- ultraviolet radiation- H_2O_2 .

Introduction

Type and degree of water treatment are strongly dependent upon the source and intended use of the water^[1]. For hardly oxidized organic water pollutants mostly from industrial sources, water treatment at the same industrial location is recommended where the treated water could be reused (recycled) in addition to the environmental aspects and /or municipal regulations.

Advanced oxidation technology (AOT) which means clean oxidation of the organic pollutants, where mostly CO_2 and H_2O are the products of this cold combustion oxidation techniques. The main oxidizer in AOT is the peroxide free radical (OH^*) with a relatively high oxidation potential^[2],

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which is preferable over other halogen oxidants because of their byproducts^[3], it can be produced by different methods from the homolytic dissociation of H_2O_2 in the presence of a catalyst like Fe^{2+} ^[4], TiO_2 with ultraviolet radiation (254nm)^[5] or other methods including the presence of O_3 together with H_2O_2 ^[3]. ($\text{H}_2\text{O}_2/\text{UV}/\text{O}_3$ method) can be also used to eliminate hardly oxidized organic pollutant^[6].

Many studies have been conducted concerning hardly oxidized water pollutants such as phenol derivatives^[7], aromatic pesticides^[8, 9], fuel additives like MTBE and dyes^[10] and some other pharmaceutical drugs^[11], where good results have been achieved.

In this work ($\text{H}_2\text{O}_2/\text{UV}$, UV/O_3 , $\text{H}_2\text{O}_2/\text{O}_3$ and $\text{H}_2\text{O}_2/\text{UV}/\text{O}_3$ methods) were investigated for the elimination of remazol blue B ($\text{C}_{22}\text{H}_{16}\text{N}_2\text{O}_{11}\text{S}_3\cdot\text{Na}_2$)^[12] which is classified as industrial, hardly oxidized, tumorigenic pollutant^[13]. Kinetics of the oxidation process was studied, effect of operation parameters such as ozonation rate, UV dosage, H_2O_2 initial concentration, pH and temperature were investigated, partial reaction orders and the overall reaction order have been achieved, optimum conditions were observed, an interpretation of the results is introduced and the economical side is proposed.

Experimental

2.1-Materials:

Remazol blue "B", { (2-Anthracene sulfonic acid, 1-amino-9, 10-dihydro-4-(m-(2-hydroxyethyl) sulfonyl) anilino- 9,10-dioxo-, hydrogen sulfate (ester), disodium salt} commercial grade was purchased from (Brilliant Blue DyStar LP, India). H_2O_2 35% w/w, analytical grade has been purchased from (Akross, Belgium). Sulfuric acid 96 % was analytical grade of (Merck-Germany). Potassium dichromate $\text{K}_2\text{Cr}_2\text{O}_7$ was (B.D.H - England) product, it was also analytical grade. Potassium hydrogen phthalate KHP, analytical grade was (B.D.H-UK) product. MnO_2 powder was obtained from (B.D.H-U.K). Na_2HPO_4 was analytical grade, purchased from (Akross -Belgium). Water used was distilled to have 60 ppm (TDS).

2.2-Instruments.

1. Ozone generator model (Gulps, Ontario Canada, N 7X4). have been used to give maximum production rate of ozone ($3.4 \times 10^{-5} \text{ g s}^{-1}$).
2. Ultra Violet linear system (6.0 watt), (YOUNG WOO WATER LINE CO., LTD- CANADA) have been used as shown in Fig. (1).
3. To control working temperature, thermostating jacket has been used as in Fig.(1) using recycled water at fixed temperatures ($\pm 0.5^\circ\text{C}$) in the range of ($10\text{--}50^\circ\text{C}$).
4. CECEIL/CE 1020 Spectrophotometer (CECEIL instrument, Cambridge – have been used for spectroscopic measurements.

5. A Hanna pH meter was used to adjust the pH of different solutions.

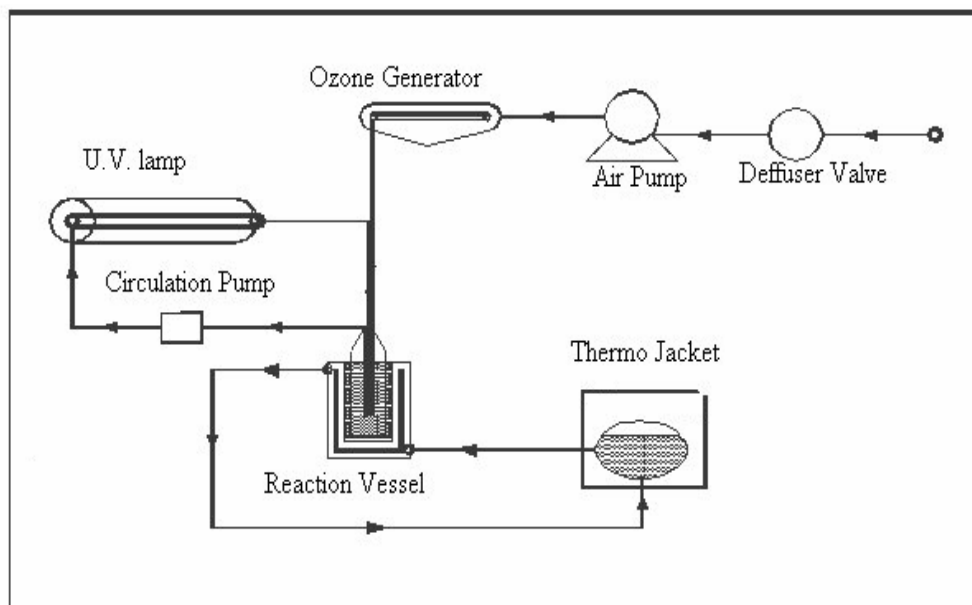


Figure (1): Experimental Installation.

2.3. Methodology:

2.3.a. Kinetic study of the decomposition of organic pollutants:

All kinetic experiments were performed using the experimental installation shown in Fig.(1).

The reactor is tubular with cylindrical tube with 2L capacity upper, the design of this reactor provides the possibilities of current circulating of (air and generated ozone) have been diffused in suitable amount of distilled water (1.0 L) for 20 min, to reach a saturation level of O_3 in water. Then the liquid (aqueous solution of the studied compounds and suitable amounts of H_2O_2) is added.

In each experimental run, reaction vessel was filled with a appropriate volume of the reaction solution, samples of 2.5 ml have been taken at different intervals of reaction time, dealt with MnO_2 to decompose any remaining H_2O_2 present in order to prevent the interference of H_2O_2 with COD measurements^[14]. Standard method of WHO have been conducted for the determination of COD.

Iodometric determination of ozone was always conducted to inshore the concentration of ozone at different times and conditions^[15].

2.3.b. Spectroscopic determination of remazol:

Remazol concentration has been followed spectro-photometrically at 585 nm wavelengths. A calibration plot was constructed using standard solution of remazol of (10 to 100 ppm). Direct readings of the samples have

been taken and were compared with the calibration curve to determine the concentration at different time intervals of each kinetic run.

2.3.c. pH Control:

Sodium hydrogen phosphate (Na_2HPO_4) 0.07M and 0.01M NaOH has been used to adjust the pH at the value of (9). Sodium dehydrogen phosphate (KH_2PO_4) and 0.01M HCl has been used to adjust the pH at the value of (5).

2.4. Data Treatment:

1. Absorbance readings were taken at different time intervals for the oxidation of remazol blue B. The relation between absorbance and concentration for standard solutions of remazol was plotted as a calibration plot, remazol concentrations of the reaction samples were estimated from their absorbance and the calibration curve.

2-Standard COD solutions were prepared from the stock KHP solution from 50 to 900 (ppm). A calibration plot between COD (ppm) and absorbance was obtained.

3. For each run, COD value was plotted against time, $\ln (\text{COD}_0/\text{COD})$ was then plotted against time, in the case of observing a straight line the reaction was considered a first order one and the slope of the line is taken as the reaction specific rate constant (k).

4. Different reaction parameters such as (temperature change, ozonation rate, UV dosage, reaction pH and initial concentrations of H_2O_2) were investigated and the resultant rate constants were plotted against readings (or values) of each parameter to clarify the relation graphically.

Results

The elimination of remazol by oxidation using advanced oxidation processes has been studied, the reaction kinetics have been followed, different conditions such as ozonation rate, UV dosage, initial concentration of H_2O_2 and change of temperature at a fixed initial concentration of remazol have been investigated.

The following results have been obtained through this investigation and an interpretation will follow.

3.1. Kinetics of the oxidation of Remazole blue B by AOM:

It follows from the results shown in fig (1) that the oxidation reaction has a first /or (pseudo first) order kinetics with respect to Remazole concentration since $\ln C_0/C$ has a straight line relationship with time.

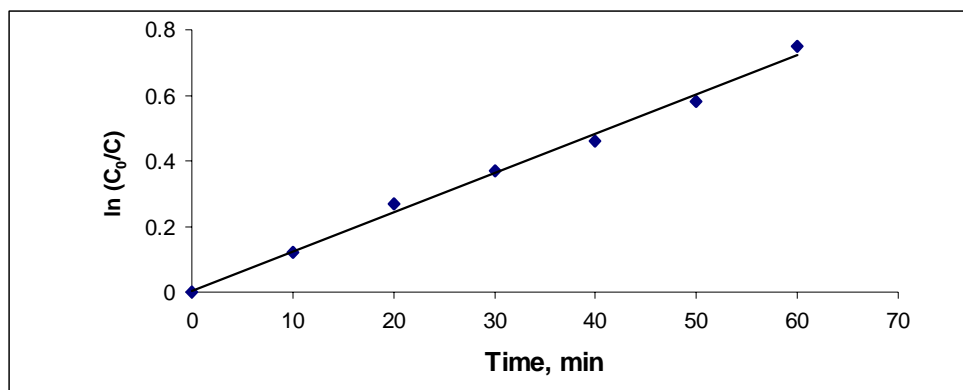
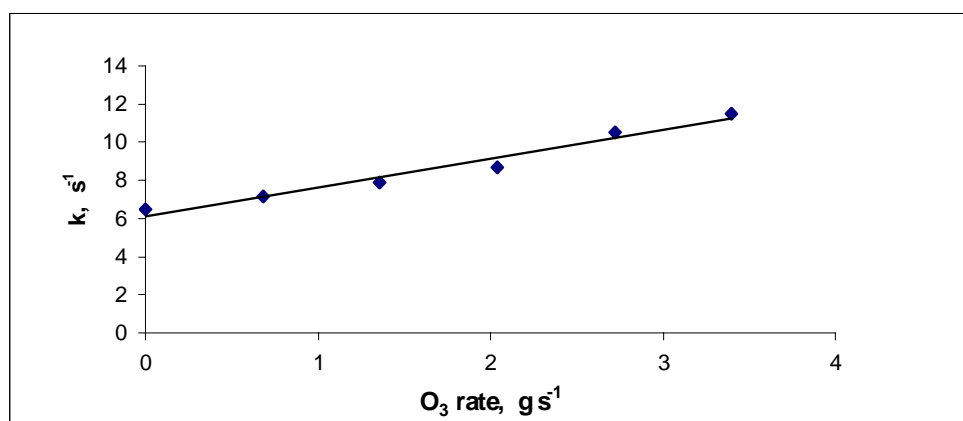


Figure (1): The relation between $\ln(C_0/C)$ & time. $[H_2O_2]_0 = 1.6 \times 10^{-3} M$, Ozonation rate = $3.4 \times 10^{-5} g s^{-1}$, pH= 7.0, UV rate = $1.38 \times 10^{-5} Ei L^{-1}s^{-1}$, temperature = $(45 \pm 0.5) ^\circ C$.

3.2. Effect of ozonation rate on the kinetics of oxidation of remazol

Effect of ozonation rate on the rate constant k was studied at different ozonation rates, while fixing the other parameters. The results shown in Fig.(2) demonstrate that the increase of ozonation rate increases the reaction rate constant k , the relation is linear which means that the reaction is a first order reaction with respect to $[O_3]$ which itself is proportional to the ozonation rate.



Figure(2): The relation between the rate constant k & ozonation rate. $[H_2O_2]_0 = 1.6 \times 10^{-3} M$, $T = (45 \pm 0.5) ^\circ C$, pH= 7.0 UV rate = $1.38 \times 10^{-5} Ei s L^{-1}$.

3.3. The influence of dosage of UV on the kinetics of oxidation of remazol:

The effect of UV dosage have been studied by following the reaction rate at different reaction bulk volumes with fixing the other parameters, it was clear from the linear relation in fig (3) that the reaction rate constant was directly proportional to the U.V. light intensity per unit volume of reaction solution.

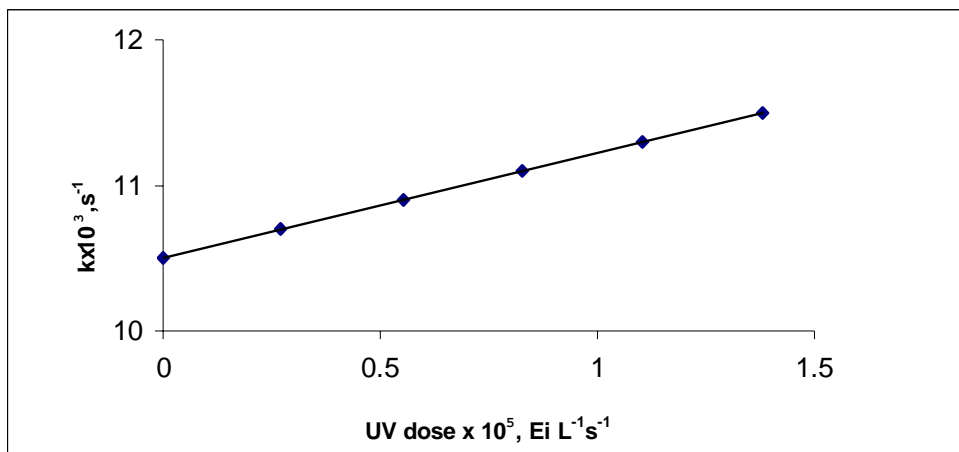


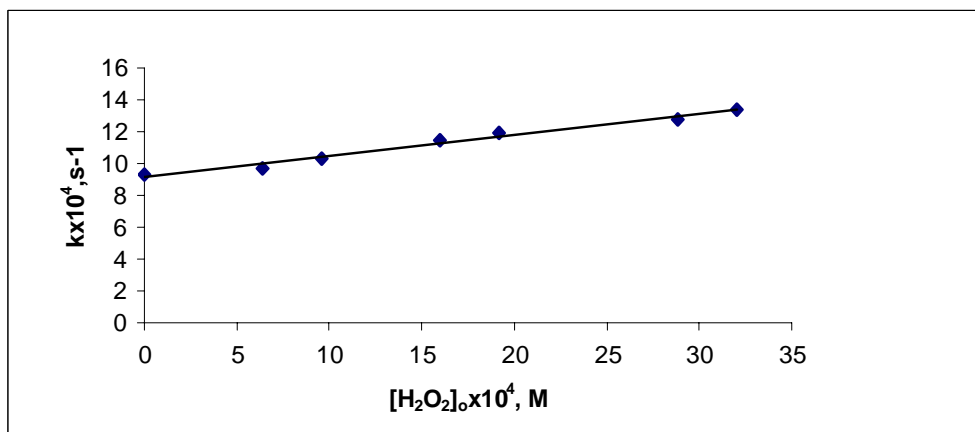
Fig. (3): The relation between rate constant k & UV dosage.

$[\text{H}_2\text{O}_2]_0 = 1.6 \times 10^{-3} \text{ M}$, Ozonation rate = $3.4 \times 10^{-5} \text{ g s}^{-1}$, $T = (45 \pm 0.5) ^\circ\text{C}$, $\text{pH} = 7.0$

3.4. Effect of the initial concentration of H_2O_2 on the oxidation rate:

Effect of the initial concentration of H_2O_2 on the rate constant k was studied under fixed ozonation rate, UV dose, and initial concentration of remazol (100 ppm).

It follows from the results shown in Fig. (4) that by increasing the initial concentration of H_2O_2 , the reaction rate constant k increases. The relation between rate constant values and H_2O_2 concentrations clarifies a straight line, which means that the reaction was a first order in H_2O_2 .



Figure(4): The relation between rate constant k , & $[\text{H}_2\text{O}_2]_0$. $T = (45 \pm 0.5) ^\circ\text{C}$, Ozonation rate = $3.4 \times 10^{-5} \text{ g s}^{-1}$, UV dose = $1.38 \times 10^{-5} \text{ Ei L}^{-1} \text{s}^{-1}$, $\text{pH} = 7.0$

3.5. Effect of temperature on the oxidation of remazol by A.O.M.

Effect of temperature on the oxidation of remazol has been studied in the range of $(10-45^\circ\text{C})$. This range is expected to cover the temperature

variation of treated polluted water through different processes. Arrhenius plot was obtained as shown in Fig. (5) which represents the effect of temperature on the rate constant k , the reaction rate constant was increasing by raising temperature. It is clear also from Fig. (5) that an inverse relationship was obtained between $\ln k$ and $1/T$ where a straight-line plot has been obtained; this means that the reaction shows Arrhenius type behavior.

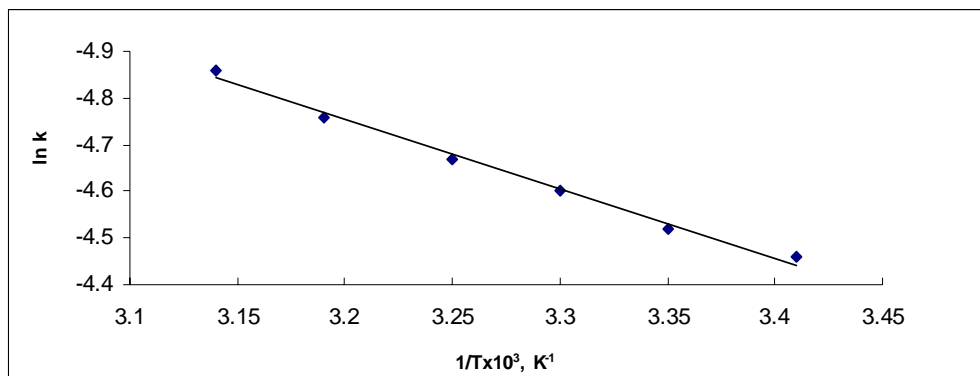
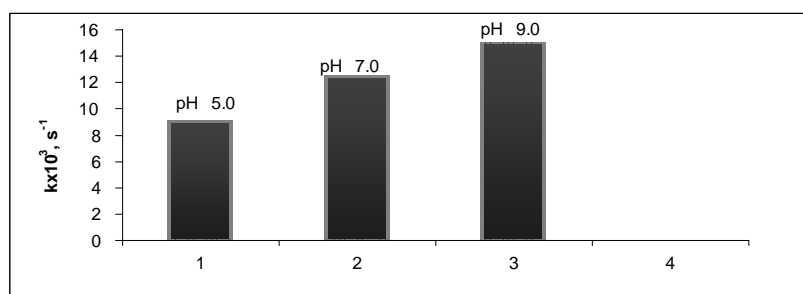


Figure (5): Arrhenius plot for the oxidation of remazol by AOM. $[H_2O_2]_0 = 1.6 \times 10^{-3} M$, Ozonation rate = $3.4 \times 10^{-5} g s^{-1}$, UV rate = $1.38 \times 10^{-5} EiL^{-1} s^{-1}$, pH = 7.0

3.5. Effect of pH on the oxidation of remazol by A.O.M.

The effect of pH on the oxidation of remazol was examined, choosing three different values of pH namely pH 5.0, pH 7.0 and pH 9.0 at fixed oxidation conditions UV/ H_2O_2 /ozone at constant reaction temperature and constant initial concentration of remazol. The results are shown in Fig.(6). The results in Fig.(6) show that the oxidation of remazol by the method used is accelerated by rising pH or the process is more efficient for basic solutions.



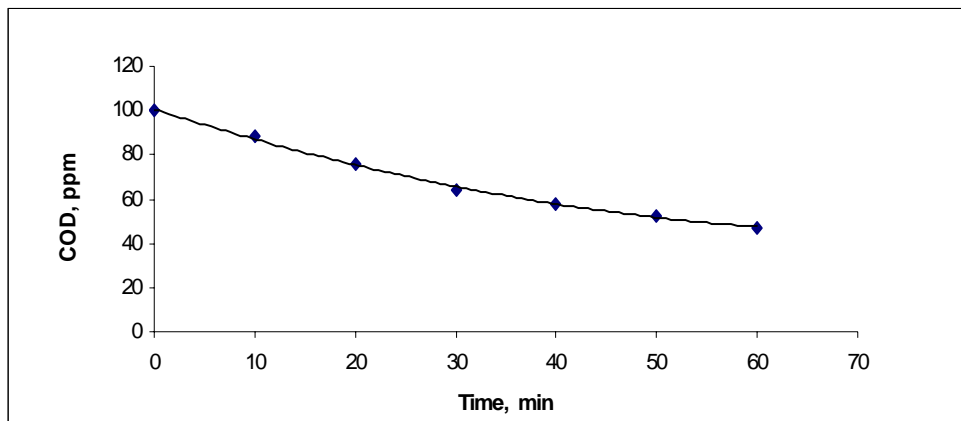
Figure(6): The change of oxidation rate constant k & pH.

$[H_2O_2]_0 = 1.6 \times 10^{-3} M$, Ozonation rate = $3.4 \times 10^{-5} g s^{-1}$, $T = (45 \pm 0.5) ^\circ C$, UV rate = $1.38 \times 10^{-5} Ei s^{-1}$, pH =, 5.0, 7.0, 9.0.

3.6. The change of Chemical oxygen demand (COD) through the course

of advanced oxidation method.

COD at different time intervals of the oxidation process was determined and plotted versus time of oxidation, the results shown in Fig. (7) demonstrate the total concentration of organic compounds which means (Remazole and/or oxidation derivatives) at each time.



Figure(7): The relation between COD and time.

UV rate = $1.38 \times 10^{-5} \text{ Ei s}^{-1}$, $T = (45 \pm 0.5) ^\circ\text{C}$, $[\text{H}_2\text{O}_2]_0 = 1.6 \times 10^{-3}$, ozonation rate = $3.4 \times 10^{-5} \text{ g s}^{-1}$, pH = 7.0.

The concentration of partial oxidation products through the course of A.O.P. which are called derivatives of remazol, was obtained by subtracting the remazol concentration in ppm from the total COD in ppm also (which is assumed to represent the total concentration of remazol and its derivatives), the relation in Fig.(8) shows that new compounds are formed by the beginning of the reaction, the total concentration of these compounds is increasing by time, arrive to a maximum and then starts to decrease as a result of further oxidation, that is due to their complete oxidation.

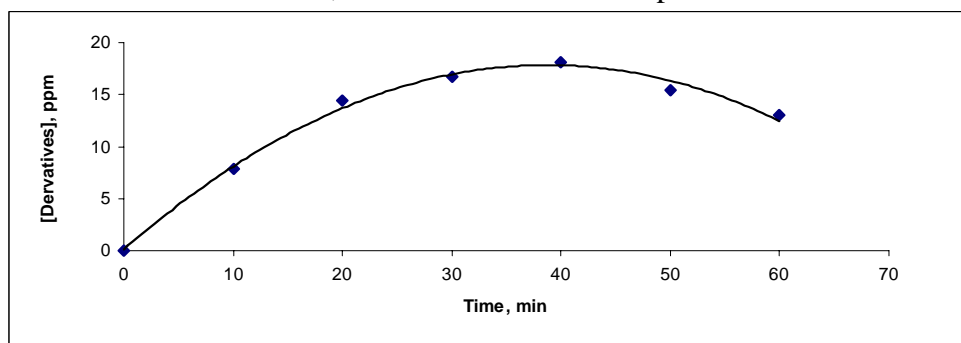


Figure (8): The relation between derivatives concentration of remazol & time. $[\text{H}_2\text{O}_2]_0 = 1.6 \times 10^{-3} \text{ M}$, ozonation rate = $3.4 \times 10^{-5} \text{ g s}^{-1}$, $T = (45 \pm 0.5) ^\circ\text{C}$, UV rate = $1.38 \times 10^{-5} \text{ Ei s}^{-1}$, pH=7.0

The experimental results obtained show that the best results were obtained at the highest temperature, the highest initial concentration of H_2O_2 , the highest dose of UV radiation and also the highest rate of ozonation at high pH.

Discussion

From the results demonstrated in (section 3), it can be concluded that advanced oxidation method is an efficient method for treating Remazole blue B which is a hardly oxidized water pollutant, it can also be concluded that the oxidation rate was directly proportional to each of [Remazole] H_2O_2 initial concentration, U.V. dosage, and ozonation rate (ozone concentration). No synergistic effect could be observed for the three factors when added to the other two (U.V. intensity, $[H_2O_2]$ and $[O_3]$) which means that parallel oxidation reactions are proceeding at the same time.

Reaction rate equation can be suggested according to the observed data to have the form:

$$Rate = -d[COD] / dt = k_1[H_2O_2] [COD] I + K_2[O_3][H_2O_2] [COD] + k_3 [COD] [O_3] I$$

At $[O_3] = 0$: the rate equation is: $-d[COD] / dt = k_1 [COD] [H_2O_2] I$

At $I = 0$: the rate equation is: $-d[COD] / dt = k_2 [COD] [O_3] [H_2O_2]$

At $[H_2O_2] = 0$: the rate equation is: $-d[COD] / dt = k_3 [COD] [O_3] I$

On the other hand remazol blue B exhibits higher oxidation rate at pH 9.0 and was decreased with decreasing pH which can be explained by some rule of OH^- in the reaction mechanism to produce ozonide radicals which is one of the main oxidizer species in the oxidation mechanism.^[16,17]

The Remazole derivatives concentration started to appear at the beginning of oxidation and reach maximum after 40 minutes and then show decreasing values with time due to complete oxidation to CO_2 and H_2O .

Evaluation of relative costs and effectiveness of treatment

Four physiochemical technologies were used in this study for the elimination of remazol from wastewater, the four methods vary in the overall costs and effectiveness of removing Remazole. Table (1) demonstrates the results.

The choice of technology in our study depends on the magnitude of the rate constant and costs of the used technology. It can be estimated from table (1) that the fastest system is ($O_3/UV/H_2O_2$) and the cheapest system is (O_3/UV). Calculations were performed on the bases of treatment of one cubic meter (m^3) of polluted water / for one hour.

Table (1): Relative cost and efficiency of removing remazol Blue B.
(Calculated for 1.0 hr. treatment/ 1.0 m³ of treated water)

Method	O ₃ / UV	O ₃ /H ₂ O	UV/ H ₂ O ₂	O ₃ /UV/H ₂ O ₂
k x10⁻³, s⁻¹	9.3	11.3	6.5	12.5
Cost, \$ m⁻³	1.8	2.2	1.6	2.8
Relative cost	100	102	126	117

Cost of electricity for production of ozone/h = 1.2 \$ h⁻¹

Cost of electricity for the irradiation of UV/h = 0.6 \$ h⁻¹

Cost of 1L of 50% H₂O₂ used = 01.0\$

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