# Removing of Pesticides From water using Advanced Oxidation Processes including: $O_3$, $H_2O_2$ and UV in combination

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## Abstract:-

The performance of advanced oxidation processes involving the combination of $O_3$, UV and $H_2O_2$ was investigated in this study using semi batch lab scale experiments for the mineralization of the pesticides, atrazine (ATZ), alachlor (ALC) and diazinon (DIZ). Different parameters, $H_2O_2$ concentration, pesticide concentration and pH were tested to find the optimum conditions for the mineralization of ATZ. Mineralization of single, binary and ternary mixture of the pesticides was tested using the optimum conditions obtained for ATZ. The results show that ATZ and DIZ were mineralized completely, while ALC achieved 93% of mineralization by the combination of $O_3$, UV and $H_2O_2$(420mg/L) treatment for 5mg/L concentration of each pesticide. The mineralization of binary mixture of ALC+DIZ, ALC+ATZ and DIZ+ATZ achieved 100, 88 and 83% respectively. A ternary mixture of ALC, DIZ and ATZ achieved 78% of mineralization. A kinetic model was used to predict the experimental data, good fitting was observed between the model and the experimental data.

## 1. Introduction

Surface water in Iraq is contaminated with pesticides (Organochlorine) and their residues despite bans of the production and usage over a long time [4]. The World Health Organization mention that more than 3 million of individuals are poisoned by pesticides per annum over all the world, most of them in third world countries and 2000 of the poisoned victims are died, [6].

Pesticide may reach surface water from either point source of pollution like landfills, where disposals from agriculture and industry are buried, or it may come from nonpoint sources like general farming exercises, particularly in heavily agriculture area and unintentional spills [3]. Jawad [7] states that some Iraqi fishermen use various kinds of pesticides for fishing and as a result they affect aqua life and contaminate the river. Atrazine (ATZ), Diazinon (DIZ) and Alachlor (ALC) are among wide used pesticides. The problem that associated with these pesticides is that the traditional treatment methods cannot appreciably remove these contaminants. While advanced treatment technologies such adsorption and reverse osmosis can produce high quality water, but they only transfer and concentrate the pollutants from one phase to another, which needs further treatment. Advanced oxidation process (AOP), which is defined as "the process of generating hydroxyl radical in water in sufficient amount to oxidize the pollutant" this process seems to be a very promising option especially in the presence of suitable infrastructure [1].

AOPs may be combinations of $UV/O_3$ or $H_2O_2/O_3$. The addition of $H_2O_2$ to $O_3/UV$ process enhances the decomposition of $O_3$ resulting in increased rate of $OH^\bullet$ generation. This is an efficient method that allows fast and complete degradation and mineralization of pollutants, [2]. It is considered as one of the most effective treatment processes for high-polluted effluents. The reaction pathways leading to the generation of $OH^\bullet$ radicals in the $O_3/UV/H_2O_2$ treatment can be summaries by a global reaction as following:

$$2O_3 + H_2O_2 + h\nu \rightarrow 2OH^\bullet + 3O_2 \qquad (1)$$

The reaction is strongly dependent on the pH, type and the parameters of the UV radiation source, concentration of ozone and hydrogen peroxide, and the concentration and nature of the target compound (compounds) as well as the presence of radical scavengers. Thus the operation parameters should be carefully optimized for successful application of $O_3/UV/H_2O_2$ [5].

The main objective of this work is to study the effectiveness of $O_3$+UV+$H_2O_2$ treatment for the mineralization of different pesticides, ATZ, ALC and DIZ in single, binary and ternary mixture dissolved in wastewater.

## 2. Experimental work

### 2.1 Chemical used

Three types of pesticides were used in the present research, atrazine, alachlor and diazinon. All the pesticides were in commercial form and bought from Hebei Chinally International Trade Co. LTD (China). The purity of atrazine, alachlor and diazinon were 99%, 94% and 90% respectively .The chemical structure of each pesticide is depicted in Fig. 1. Table 1. shows the physical and chemical properties of these pesticides.

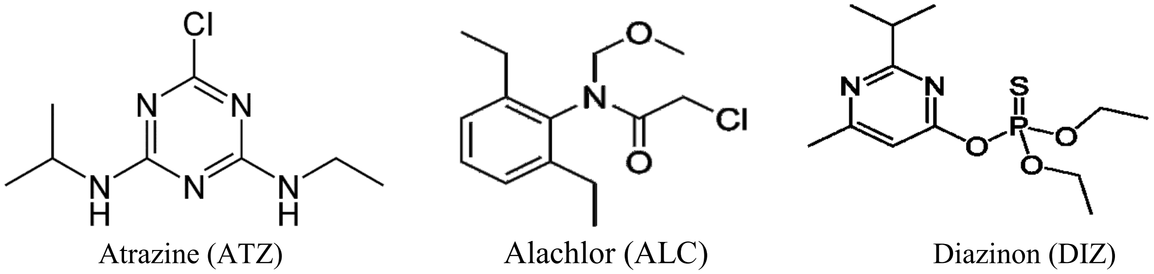

**Fig 1. Chemical structure of pesticides [3].**

**Table 1. List of pesticides properties [3]**

| Name | Atrazine (ATZ) |
|---|---|
| Formula is | $C_8H_{14}ClN_5$ |
| Molecular weight is | 215.68 g/mol |
| Solubility in water | 34 mg/L at 25C |
| Vapor Pressure | $3x10^{-7}$mm Hg at 20 $^oC$ |
| Kow | Log Kow = 2.75 |
| Name | Alachlor (ALC) |
| Formula | $C_{14}H_{20}ClNO_2$ |
| Molecular weight | 269.767 g/mol |
| Solubility in water | 140 mg/L at 23$^oC$ |
| Vapor Pressure | Negligible |
| Melting Point | 40-41 $^oC$ |
| Kow | Log Kow = 2.63 |
| Name | Diazinon (DIZ) |
| Formula | $C_{12}H_{21}N_2O_3PS$ |
| Molecular weight | 304.35 g/mol |
| Solubility in water | 40 mg/L |
| Vapor Pressure | $1.4x10^{-4}$mmHgat 20$^oC$ |
| Melting Point | Decomposes at > |

| | |
|---|---|
| | 120°C |
| Kow | Log Kow = 3.81 |

Table 2. Shows the other chemicals used in the experiments. All the samples were prepared by dissolving requisite quantity in distilled water. The pH of the solution was adjusted by using 0.1N NaOH.

**Table 2. List of chemicals used**

| Compound | Formula | Vender | Assay |
|---|---|---|---|
| Oxygen gas | $O_2$ | Local market | 99.99% |
| Hydrogen Peroxide | $H_2O_2$ | Hopkin and williams | >35 % |
| Sodium hydroxide | NaOH | BDH | 99% |
| Acetonitrile HPLC grade | $C_2H_3N$ | Sigma-Aldrich | 99.9% |

## 2.2 Equipments used

Semi batch experiments were carried out in the present work using laboratory scale system, Fig. 2. A glass cylindrical reactor with 5L volume, was used. Ozone gas was generated by Enally-Woodland model OZX-03K generator, USA. Ozone generated from oxygen with inlet flow rate of 3L/min, gives 3gm/hr ozone output. The generated ozone was introduced to the reactor by using teflon pipes and a ceramic diffuser. Peristaltic pump (BT300-2J) from Longer Company, China with flow rate of 1L/min was used to maintain the desired flow for circulation in the reactor. The Photo-reactor is a stainless steel cylindrical reactor, 2.4L in volume with the dimensions of (L=85cm and D=6.5cm). Irradiation was achieved by using low-pressure mercury vapor lamp, 4-pin single end, 40W, UV-C 254 nm (Philips Company). The lamp was sheathed in a glass sleeve for protection and fixed inside along the reactor. The pH of solution was monitored using pH meter from (WTW Co., German, INOLAB 720). The whole system was fixed inside a large fume hood from LabTech Company, to ventilate possible excess ozone and generated gasses.

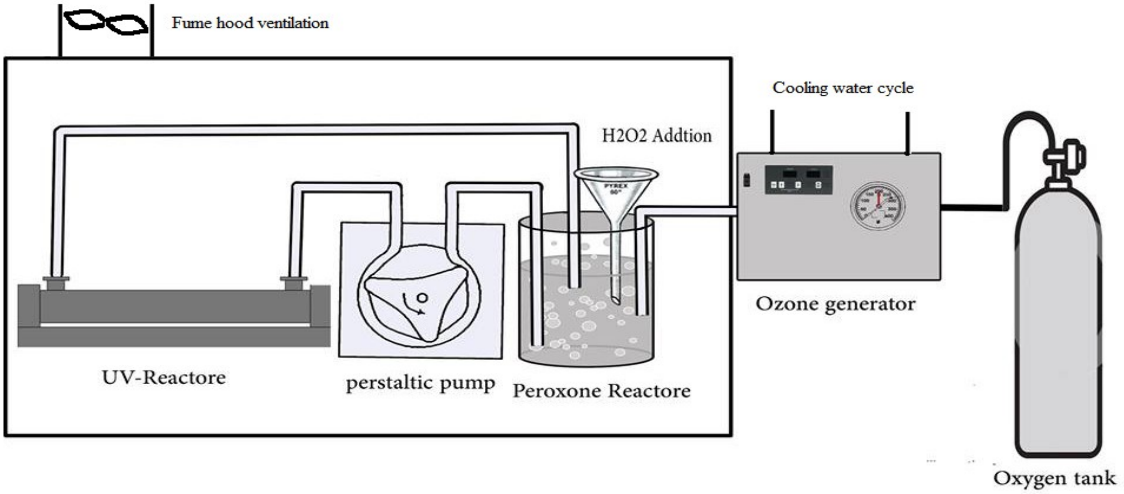

**Fig 2. Schematic diagram of AOP system set-up.**

## 2.3 Analysis

All the analyses were done in the laboratories of Environmental Engineering Department / University of Baghdad. High Performance Liquid Chromatography (HPLC), from Perkin Elmer series 200, (USA), was used to identify the pesticide concentration and the intermediate compounds which evolve through the oxidation reaction. The stationary phase is C18 column (with 250mm length and 4.6mm internal diameter, while its particle size was 5µm), Discovery, from Supelco. The mobile phase used was a mixture of acetonitrile and distilled water (45:55). Flow rate of 1mL/min was used to pump the mobile phase. Peaks were detected with a UV detector at 220nm. All samples were filtered using 0.2µm syringe filter. Fig.3 shows the standard curves obtained using HPLC for ATZ at concentration of 10 mg/L. The ATZ peak was identified after retention time 6.3min.

Chemical Oxygen Demand of samples was analyzed by COD Photometer system. Appropriate amount of sample (2ml) was introduced into digestion solution (MR-Range: 0-1500mg/L) containing ($K_2Cr_2O_7$, $H_2SO_4$ and $HgSO_4$). The mixture was then incubated for 120 min at 150$^{o}$C in the COD reactor (model RD-125, Lovibond Company, Germany). After the oxidation was completed, the COD value was measured by colorimetric method at 605 nm by DR/2010 spectrophotometer (model MD-100, Lovibond Company, Germany).

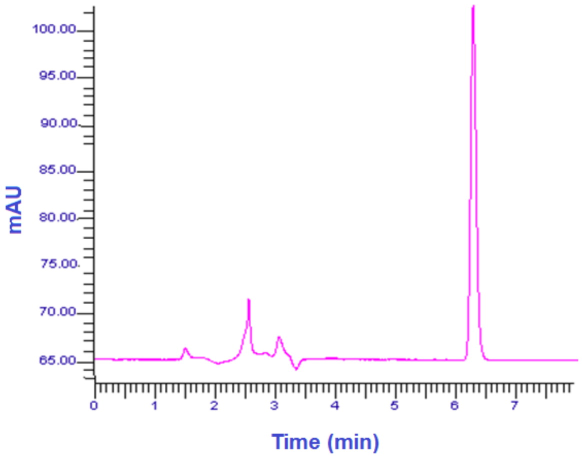

**Fig 3. Standard curves obtained using HPLC for the ATZ concentration of 10mg/L.**

## 2.4 Experimental procedure

The experimental procedure was performed at room temperature flowing the below steps:

1. The desired amount of pesticides were measured and diluted in distilled water. This solution was introduced into the glass reactor. Initial sample at t=0 was taken for analysis.
2. The pH value was adjusted to the desired values by adding NaOH.
3. Ozone generator was turned on and the generated ozone was introduced into the glass reactor by a teflon pipe and dispersed through the solution by using a ceramic diffuser.
4. The peristaltic pump was turned on and 2.4L of the solution was transferred to the UV reactor. Continues recirculation was maintained between the glass reactor and the UV reactor throughout the experiment.
5. UV lamp was turned on, and $H_2O_2$ was added to the pesticide solution in the glass reactor. Samples were taken out at different periods of the experiment for the analysis of pesticide concentration and pH.

## 3. Results and discussions

### 3.1 Atrazine

The synergistic effect of ozone, UV and hydrogen peroxide was studied. Experiment with ATZ concentration of 5 mg/L and 10 mg/L for 180 min process time was studied. ATZ of 5 mg/L was tested under inherent pH value of 7 and alkaline conditions at pH=12 were tested for 5 mg/L and 10 mg/L ATZ concentration. Different concentrations of $H_2O_2$ were tested, 120 and 420mg/L for 5mg/L ATZ and 420, 600 and 750mg/L for 10mg/L ATZ, in order to choose the best results. Fig. 4a shows the COD degradation (mineralization) of 5mg/L ATZ at different initial $H_2O_2$ concentrations and ph. Complete mineralization was achieved when 420 mg/L $H_2O_2$ was used at pH=12. The alkaline condition enhanced the reduction in COD, as it reached 70% at pH=12 for 140mg/L $H_2O_2$ while it reached 45% at pH7, as can be noticed from Fig. 4a. A fast conversion of the ATZ to the intermediate product was observed through the $O_3$+UV+$H_2O_2$ treatment, as shown in Fig.4b, after 15 min of treatment the ATZ was completely converted to the intermediate product.

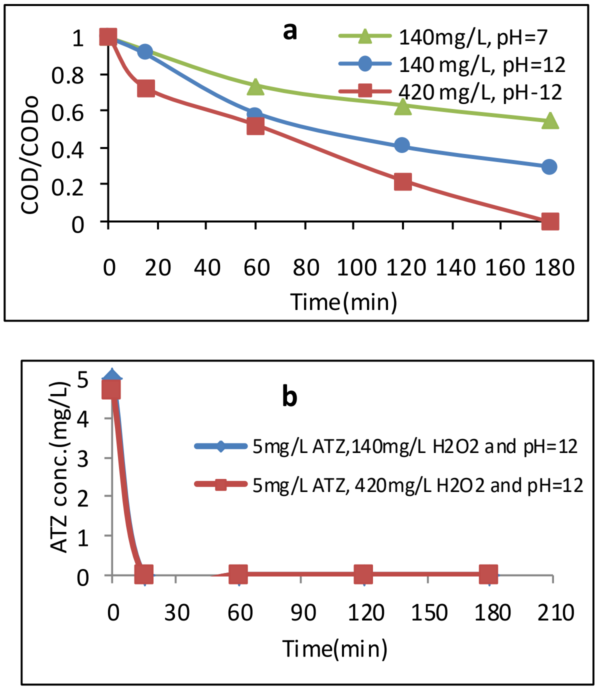

**Fig 4. Ozone+UV+$H_2O_2$ treatment at different initial $H_2O_2$ concentrations and pH, ATZconcentration =5mg/L, (a) COD degradation (b) ATZ degradation.**

Fig. 5 shows the COD degradation of 10mg/L ATZ at different initial $H_2O_2$ concentrations at pH value = 12. At initial $H_2O_2$ concentration of 750mg/L a complete mineralization was achieved.

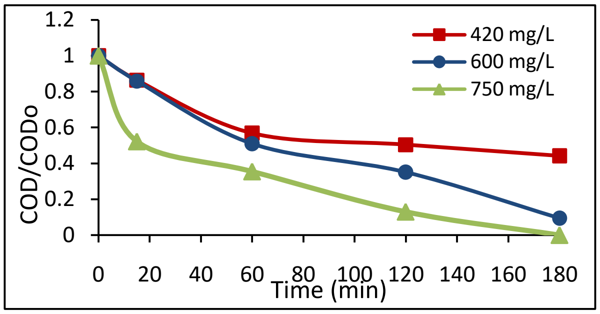

**Fig 5. COD degradation for $O_3$+UV+$H_2O_2$ treatment at different initial $H_2O_2$ concentrations, ATZ concentration =10mg/L and pH=12.**

Fig. 6 illustrates the variation of pH through the $O_3$+UV+$H_2O_2$ treatment. Acidic conditions inhibit the formation of radicals and decrease the treatment efficiency. It was clear that at initial pH =7, the pH reduces to the acidic value of 3 which decreases the reduction in the COD.

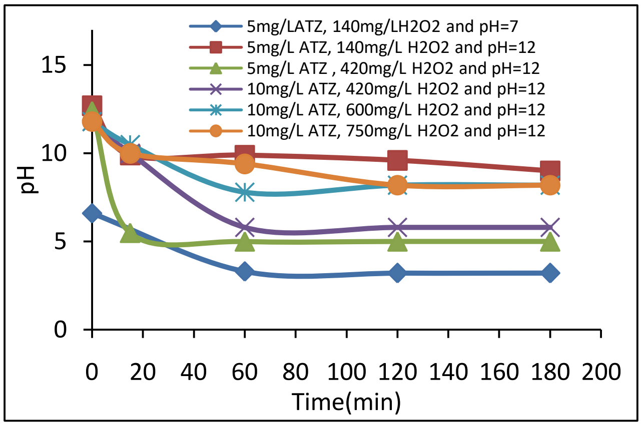

**Fig 6. pH variation for $O_3$+UV+$H_2O_2$ treatment.**

### 3.2 Treatment of binary and ternary mixture of ATZ, ALC and DIZ

Real wastewater usually contains a mixture of different pesticides. Therefore after confirming the feasibility of treating ATZ with the combination of $O_3$, UV and $H_2O_2$, the mixtures of pesticides (ATZ, ALC and DIZ) were treated in the same system and conditions. All the experiments were performed at initial pH=12 and $H_2O_2$ concentration of 420mg/L.

For single pesticide, 5 mg/L of each ALC, DIZ and ATZ was treated individually with $O_3$+UV+$H_2O_2$ (420 mg/L) for 180 min. The results are plotted in Fig. 7.

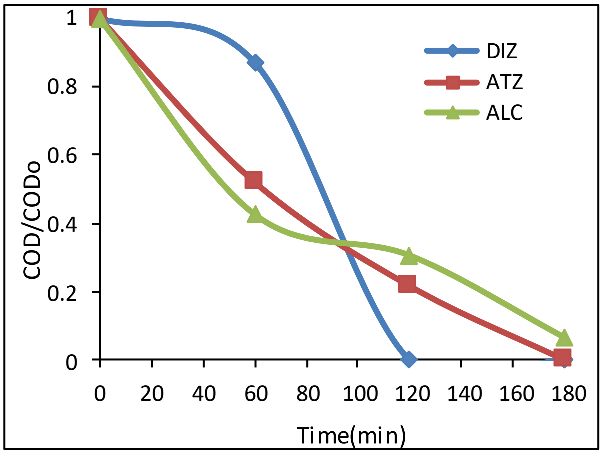

**Fig 7. COD degradation during $O_3$+UV+$H_2O_2$ treatment for different individual pesticides, at $H_2O_2$= 420mg/L, pesticide concentration=5mg/L and pH=12.**

Fig. 7 shows that DIZ was mineralized completely after 120min, followed by ATZ which mineralized completely after 180 min of treatment.

ALC mineralization of 93% was reach after 180min of treatment. For ALC further work is required to check the best $H_2O_2$ concentration needed for treatment, because ALC has a structure that can be degraded easier than ATZ as confirmed with Hernando et al.,(2005) [3]

Fig. 8 shows the variation of the pH with time through the treatment of the pesticides, ALC, DIZ and ATZ. From this figure it can be seen that there is no observed decrease in pH for DIZ, while for ALC and ATZ the pH decreases to a value of 8.3 and 5 respectively. This decrease in pH was a result of the mineralization and intermediate products present in the solution.

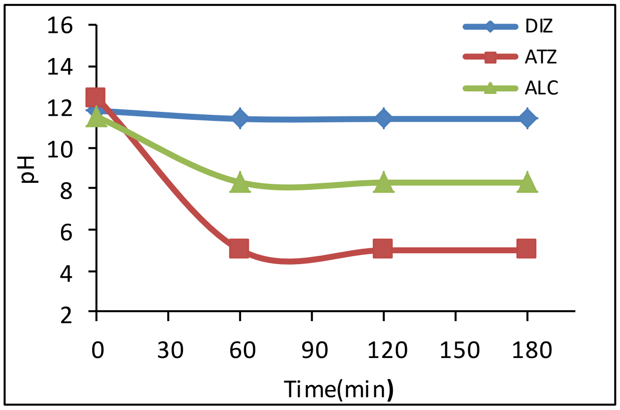

**Fig 8. pH variation during $O_3$+UV+$H_2O_2$ treatment for different pesticide.**

For a mixture of ALC+DIZ, ALC+ATZ, DIZ+ATZ, 2.5mg/L of each pesticide was treated with $O_3$+ UV+ $H_2O_2$ (420mg/L) for 180 min, while for ALC+ATZ+DIZ mixture, 1.6 mg/L of each individual pesticide in a mixture was used. The results are plotted in Fig. 9.

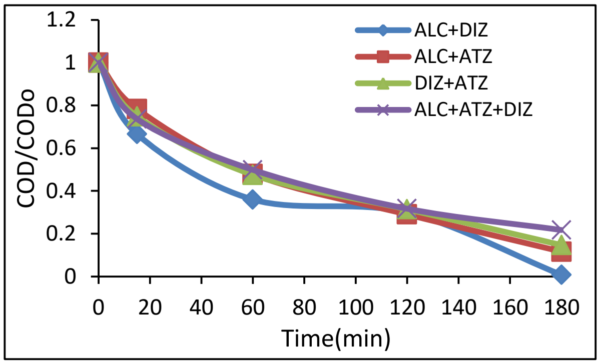

**Fig 9. COD degradation during $O_3$+UV+$H_2O_2$ treatment for pesticides mixture, at $H_2O_2$= 420mg/L, pesticide concentration=2.5 and 1.6mg/L for binary and ternary system respectively, pH=12.**

A complete mineralization was achieved for ALC+DIZ mixture, while for ALC+ATZ and DIZ+ATZ the mineralization reached 88 and 83% respectively. For a ternary mixture ALC+ATZ+DIZ the mineralization achieved was 78%. Fig. 10 shows the variation in pH with time through the treatment of the mixtures of pesticides. A decrease of the initial pH to a value of 7.8-8.2 was observed through the treatment. This decrease in pH was a result of the mineralization and intermediate products present in the solution.

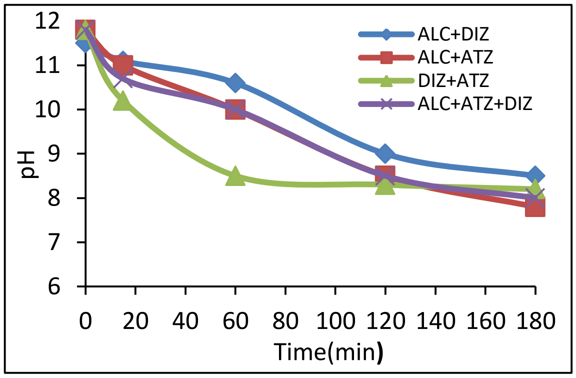

**Fig10. pH variation during O3+UV+H2O2 treatment for different pesticide mixtures.**

## 4. Kinetic modeling

A kinetic model has been adopted in the present study to predict the experimental results for single, binary and ternary systems. Pseudo first order kinetic was suggested by Hernando et al. [3]

$$\ln\left(\frac{C_t}{C_i}\right) = -\,kt \qquad (2)$$

Where, $C_i$ is the initial concentration of pollutant (mg/L), $C_t$ is pollutant concentration at time t (mg/L), t is treatment time (min), k is the reaction rate constant ($\text{min}^{-1}$).

The reaction rate constant represents the sum of constants for the contributing treatment. The pseudo-first-order reaction constant of each experiment was estimated from the slope of the plot of Ln ($COD/COD_o$) verses t, as shown in Fig.11.

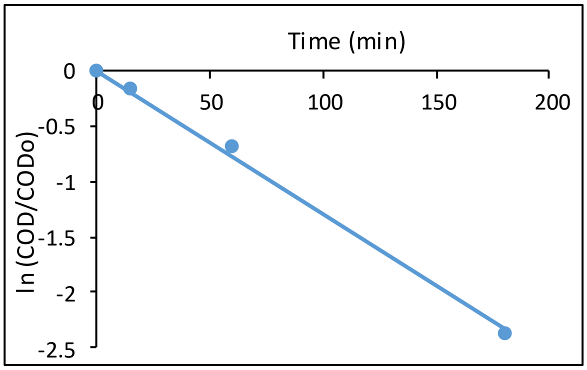

**Fig 11. Pseudo-first-order rate constant for ATZ concentration=10 mg/L treated with $O_3$+UV+ $H_2O_2$(420 mg/L) at pH=12.**

The pseudo-first-order rate constants for different treatments are presented in Tables 3 and 4. Good fitting was observed between the model and the experimental results, Figs. (12 a, b) (13. a, b, c).

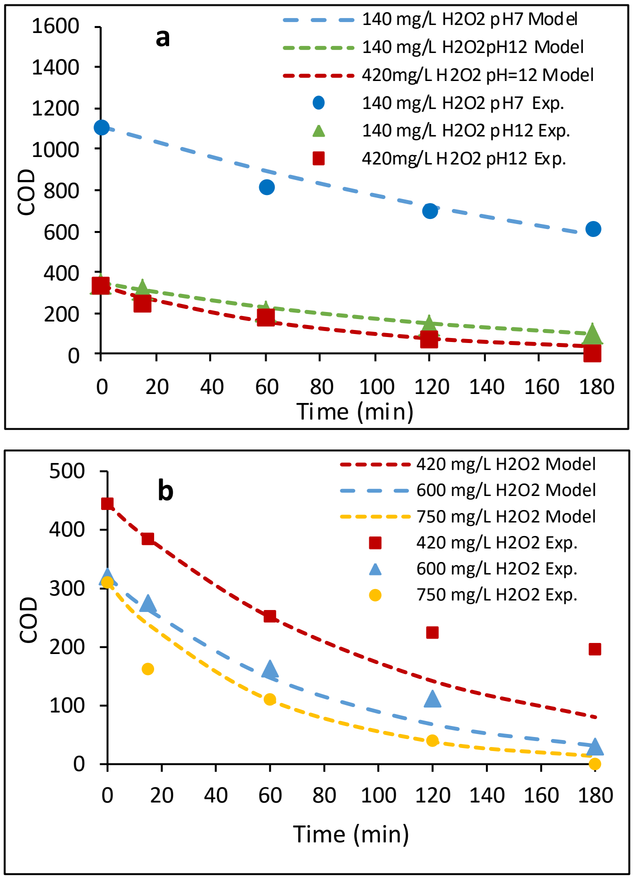

**Fig.12: Comparison between experimental results and kinetic model for $O_3$+UV+$H_2O_2$ treatment, (a) 5mg/L pH=12, (b) 10mg/L pH=7**

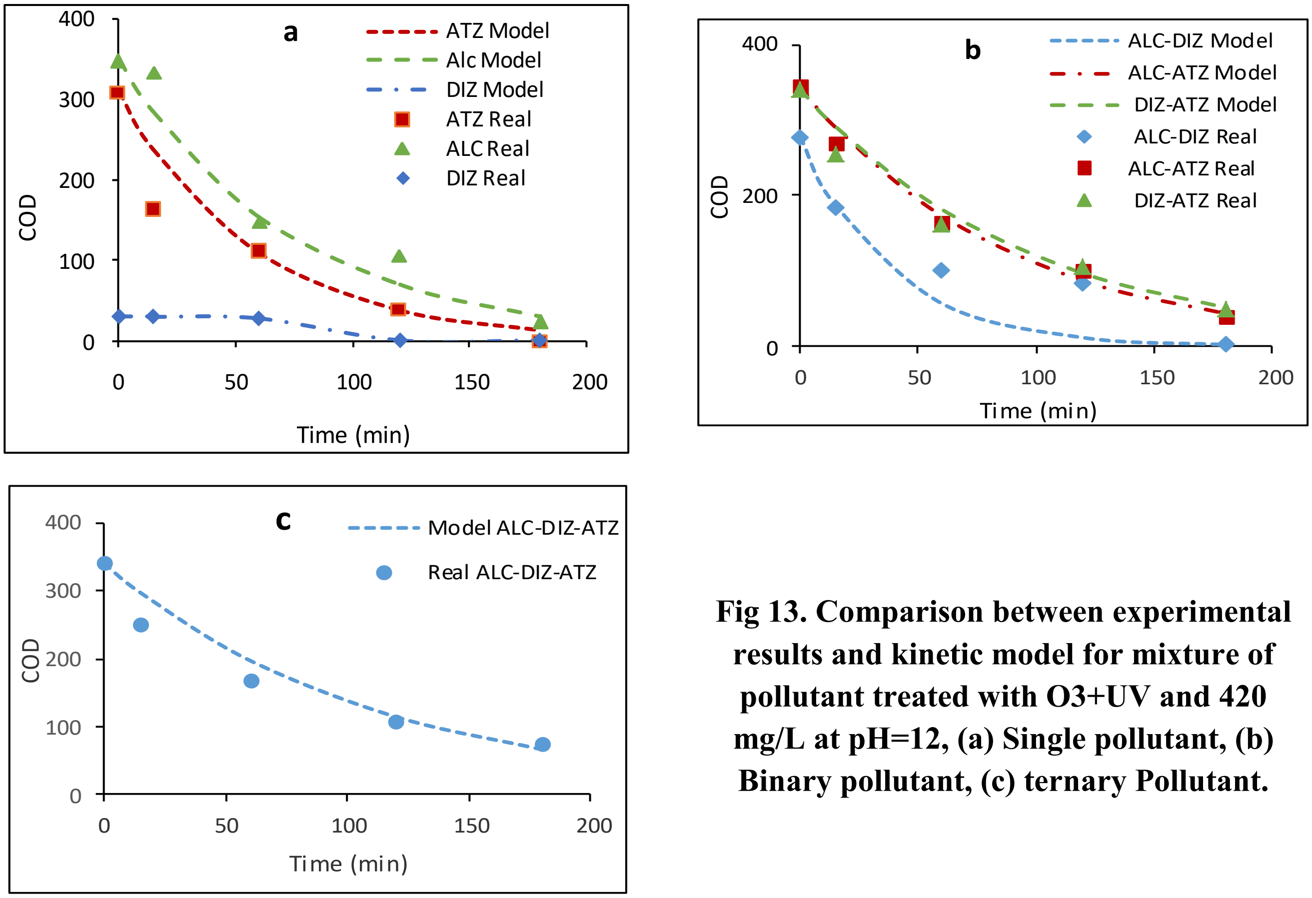

**Fig 13. Comparison between experimental results and kinetic model for mixture of pollutant treated with O3+UV and 420 mg/L at pH=12, (a) Single pollutant, (b) Binary pollutant, (c) ternary Pollutant.**

**Table 3: Pseudo-first-order rate constant for ATZ treatment with $O_3$+ UV+$H_2O_2$**

| Concentration (mg/L) | $H_2O_2$ concentration (mg/L) | initial pH value | K ($min^{-1}$) | $R^2$ | COD removal efficiency% |
|---|---|---|---|---|---|
| 5 | 140 | 7 | 0.003 | 0.94 | 45 |
| 5 | 140 | 12 | 0.007 | 0.98 | 70 |
| 5 | 420 | 12 | 0.015 | 0.97 | 100 |
| 10 | 420 | 12 | 0.01 | 0.99 | 56 |
| 10 | 600 | 12 | 0.013 | 0.99 | 91 |
| 10 | 750 | 12 | 0.017 | 0.93 | 100 |

Table 4: Pseudo-first-order rate constant for mixture of pollutant treatment with $O_3$+UV+ $H_2O_2$(420 mg/L) at pH=12

| Pollutant | K ($min^{-1}$) | $R^2$ | COD Removal Eff. |
|---|---|---|---|
| ATZ | 0.015 | 0.97 | 100 |
| ALC | 0.0135 | 0.94 | 93 |
| DIZ | 0.0021 | 0.89 | 100 |
| ALC-DIZ | 0.0264 | 0.98 | 100 |
| ATZ-DIZ | 0.0105 | 0.98 | 85 |
| ALC-ATZ | 0.0115 | 0.98 | 88 |
| ALC-ATZ-DIZ | 0.0091 | 0.95 | 78 |

## Conclusions

A complete COD reduction was obtained when treating ATZ with the system $O_3$+UV+$H_2O_2$. For 5mg/L ATZ a complete reduction in COD required 420 mg/L $H_2O_2$ while for 10 mg/L ATZ, 700 mg/L of $H_2O_2$was required for complete reduction in COD.

$O_3$+UV+420mg/L $H_2O_2$ treatment was efficient in complete removal of DIZ and 93% of ALC as individual pesticides. For binary systems AIC+DIZ, ALC+ATZ and DIZ+ATZ the mineralization at the same treatment achieved 100, 88 and 83% respectively, while for a ternary system ALC+ATZ+DIZ the mineralization achieved 78%.

Good fittings were obtained between the experimental and the predicted results using Pseudo-first order kinetic model for the single, binary and turnery systems.

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# أزالة المبيدات الزراعية من الماء بأستخدام تقنيات الأكسدة المتقدمة المتضمنة دمج الاوزون وبيروكسيد الهيدروجين والاشعة فوق البنفسجية

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## الخلاصة :-

تم التحقق من فاعلية استخدام طريقة الاكسدة المتقدمة المتضمنة الدمج بين الاوزون وبيروكسيد الهيدروجين والاشعة فوق البنفسجية في معالجة المياه الملوثة بمبيد الأترازين والديازنون والالكلور بأستخدام منظومة مختبرية تعمل بنظام شبه الدفعات (semi batch). تم دراسة تغيير العوامل المختلفة مثل تركيز بيروكسيد الهيدروجين وتركيز المبيد و الدالة الحامضية لغرض تحديد القيم المثالية لازالة الاترازين . كذلك تم دراسة معالجة انظمة ذات ملوث واحد وخليط من ملوثين مختلفين وخليط من ثلاث ملوثات باعتماد الظروف المثالية المستخدمة في ازالة الاترازين .تم الحصول على نسبة ازالة كاملة لمبيد الاترازين و الديازينون كذلك تمت ازالة مبيد الالكلور بنسبة 93٪ باستخدام الطريقة انفة الذكر وباستخدام 420 ملغم/لتر من بيروكسيد الهيدروجين ودالة حامضية =12. بالنسبة للانضمة ثنائية الملوث (الكلور-ديازينون) (الكلور-اترازين) (ديازينون -اترازين) فقد تمت الازالة بنسبة 100٪ و 88و 83٪ على التوالي بينما كانت الازالة 78٪ للنضام ثلاثي الملوث (اترازين- الالكلور-ديازينون). تم اعداد موديل رياضي مبني على حركية التفاعل pseudo first order kinetics واعطى تطابق جيد بين القيم المقاسة عمليا مع القيم المحسوبة بواسطة الموديل المذكور.