

Combined advanced oxidation and biological treatment processes for the removal of pesticides from aqueous solutions

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Abstract

Advanced oxidation processes were combined with biological treatment processes in this study to remove both pesticides and then the COD load from aqueous solutions. It was found that O_3 and O_3/UV oxidation systems were able to reach 90 and 100% removal of the pesticide Deltamethrin, respectively, in a period of 210 min. The use of O_3 combined with UV radiation enhances pesticides degradation and the residual pesticide reaches zero in the case of Deltamethrin. The combined O_3/UV system can reduce COD up to 20% if the pH of the solution is above 4. Both pesticide degradation and COD removal in the combined O_3/UV system follow the pseudo-first-order kinetics and the parameters of this model were evaluated. The application of the biological treatment to remove the bulk COD from different types of feed solution was investigated. More than 95% COD removal was achieved when treated wastewater by the O_3/UV system was fed to the bioreactor. The parameters of the proposed Grau model were estimated.

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1. Introduction

Pesticides are among the major organic compounds encountered as pollutants in wastewater effluents of pesticide industry and agricultural activities. Water pollution by pesticides is considered as a pervasive problem [1] because these compounds usually have direct adverse effect on the living organisms. These compounds are toxic and carcinogenic in nature even at low concentration [2]. For these reasons, many strict environmental regulations in many countries including Jordan are applied in order to remove pesticide loads from industrial wastewater effluents.

As a consequence, many treatment processes have been applied for the removal of pesticides from industrial wastewater. These processes include: photo-oxidation, chemical coagulation, sedimentation, filtration, disinfection and adsorption. In these processes, partial elimination of pesticides is achieved and the efficiency of pesticide removal or degradation is heav-

ily dependent on the chemical nature of the pesticides being treated [3], in addition to the mechanism of the treatment process itself. Consequently, this fact has forced to the development of new alternatives, like stronger oxidizing agents or what is called advanced oxidation processes (AOPs). These AOPs usually constituted by a combination of several oxidants characterized by the generation of very reactive free radicals in aqueous solutions, such as hydroxyl radicals, which have a significant destruction power [4]. These radicals attack most of the organic molecules with rate constants usually in the order of 10^6 – 10^9 $M^{-1} S^{-1}$. Additionally, these radicals are characterized by a little selectivity of attack, which is a useful attribute for an oxidant used in wastewater that may contain different compounds [5]. AOPs are characterized by the fact that no more toxic compound can be produced during the degradation process and the possibility to achieve a complete mineralization of the organic contaminant [6,7]. Furthermore, the radicals produced from these oxidants can substitute halogens attached to aromatic rings, thus generating biodegradable compounds, although the reaction takes place in a slow rate [8].

Based on the literature information, pesticide degradation has been accomplished by different photochemical processes including those using artificial light source [9] or solar energy

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[10]. It was shown that such degradation process requires long treatment periods and rarely achieves complete degradation of the pesticides [11]. Accordingly, the degradation power of photochemical oxidation process could be improved using an additional homogenous or heterogeneous oxidant [12]. Homogenous systems utilize H_2O_2 , O_3 [13], or combination of O_3/H_2O_2 , H_2O_2/UV and $O_3/UV/Fe^{+2}$ [14], Fe^{+3}/UV , Fe^{+2}/H_2O_2 [15,16], Fe^{+3}/H_2O_2 [17] as oxidants whereas heterogeneous systems use semiconductor slurries of TiO_2/UV or ZnO/UV for catalysis [11].

In all the previous investigations, it was reported that the AOPs were able to degrade different types of pesticides as well as different inhibitory organic compounds. However, two major drawbacks are associated with the use of AOPs: their operational cost is relatively high compared to that of biological treatment processes and the COD load caused by the produced biodegradable intermediates are still above the regulation standards of many countries like Jordan [18,19]. Consequently, AOPs could be combined with biological treatment process in order to overcome the previous drawbacks. The AOPs can be used as a pre-treatment step for converting pollutants such as pesticides or any inhibitory compounds to more readily biodegradable intermediates or to the point where the inhibition effect of these compounds is not significant. Then, this step will be followed by a biological treatment step for bulk COD removal by converting the resulting intermediates to biomass, biogas, CO_2 , HCl and water [20,21].

Literatures survey on combined chemical oxidation and biological processes shows that O_3 , O_3/H_2O_2 , H_2O_2/UV , UV-light, wet air and natural sunlight have been combined with biological treatment processes to oxidize various organic compounds in the chemical oxidation step. However, very little information has been cited in the literature regarding the applications of combined AOPs with biological treatment to eliminate pesticides. Parra et al. [20] used photo-Fenton pretreatment process to oxidize the herbicide Isoproturon before the biological treatment step and they reported that in this coupled system, 100% of the initial concentration of Isoproturon and 95% of the TOC were removed. Thus, the purpose of this study is to apply integrated chemical–biological oxidation processes to pesticides effluents. O_3 and O_3/UV systems will be used to degrade both halogenated and unhalogenated pesticides found in the effluent wastewater of Veterinary and Agricultural Products Mfg. Co. Ltd. (VAPCO, Amman, Jordan) and the biological treatment step will be applied to reduce the COD load in the resulted treated wastewater to the acceptable levels.

2. Experimental

2.1. Chemicals

The three pesticides used in this investigation were kindly provided by VAPCO (Amman, Jordan). The chemical structures of these pesticides are shown in Table 1. The choice of these pesticides was motivated by two reasons. First, their concentration in the water effluents of the factory is relatively high. Secondly, they are both halogenated and unhalogenated compounds and their treatment by only one treatment method seems to be relatively difficult. These pesticides are Triadimenol, Lambda-Cyhalothrin and Deltamethrin. 2.5% solutions of these pesticides are usually prepared using organic solvent (Solnesso 150).

A 1000 mg/L stock solution of each pesticide was prepared by dissolving the suitable amount of the pesticide concentrate in 200 mL of distilled water in a stirred beaker. For example, 40 mL of 2.5% Deltamethrin were dissolved in 500 mL distilled water. After the complete dissolution, the volume of the solution was completed to 1 L by the addition of distilled water. The weak solutions used in the further experiments were prepared by appropriate dilutions of the stock solution.

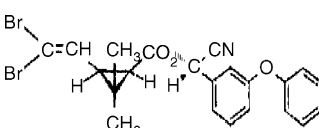
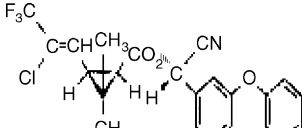
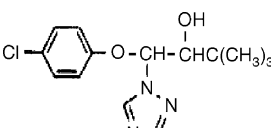
2.2. Analytical methods

High performance liquid chromatography HPLC (LACHROM, Germany) was used to determine the pesticide concentrations in the sample before and after the degradation process. The KI-starch titration method [22] was used to determine O_3 concentration in the feed gas and in the off gas. pH was measured using 3151 WTW pH meter (WTW GMBH, Germany). COD was determined according to Standard methods [22].

2.3. AOPs experiments

Fig. 1 shows the apparatus used to conduct the AOPs experiments. The chemical oxidation process is carried out in a 5 L working volume covered tank (1), while a magnetic stirrer was used for agitation. The UV emitting device (5) typically consisted of a stainless steel tube with a coaxial mercury vapor lamp (14 W low-pressure, AQOAPRO, USA) inside the running length of the tube. The lamp emits radiation basically at 253 nm. Ozone was produced from air by an Ozone generator (SPA, USA) (4). Ozone production rate was of 1.2 g O_3/h at 1 atm and 25 °C. The produced ozone gas was continuously fed

Table 1
Chemical structure of three investigated pesticides

Pesticide	Deltamethrin	Lambda-Cyhalothrin	Triadimenol
Chemical structure			
Mol. mass (g/mol)	505.2	449.9	294.5

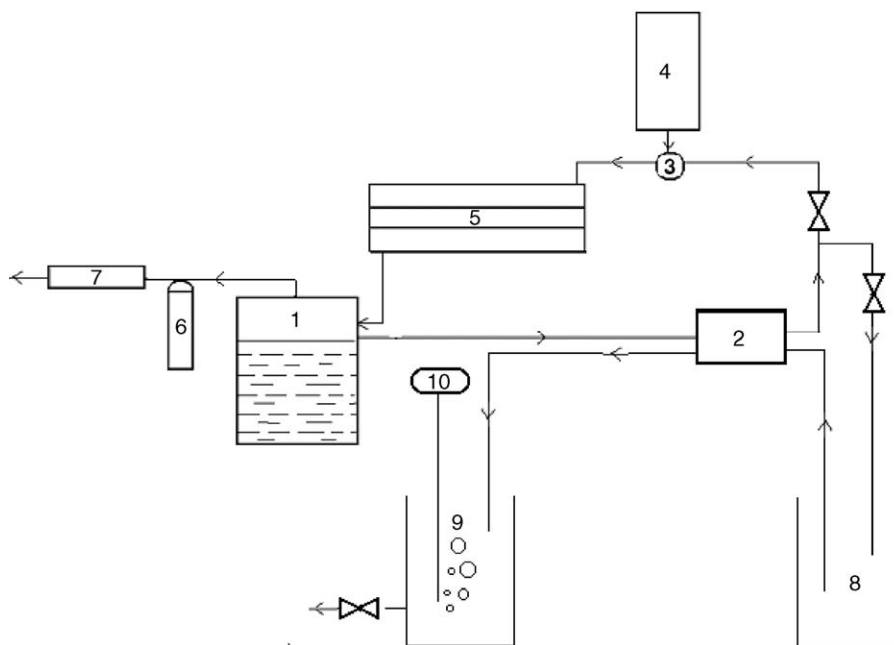


Fig. 1. Experimental setup: (1) chemical oxidation tank, (2) peristaltic pump, (3) diffuser valve, (4) ozone generator, (5) UV emitting device, (6) excess KI trap, (7) ozone destruction device, (8) neutralizer, (9) biological treatment tank, (10) air sparger.

to the oxidation tank via silicon tubing at a rate of 240 mg/h/L. The excess ozone was passed to an ozone destruction device (7) via a KI trap (6). A two-line peristaltic pump (2) (GallenKamp, UK) with a maximum flow rate 0.5 mL/min was used to circulate the solution between the oxidation vessel and the UV unit. The pH in the oxidation vessel was controlled by pH-controller (GallenKamp, UK) to keep the pH value around 7 by subsequent addition of 0.1 M NaOH solution.

After the chemical oxidation process by O_3 or O_3/UV systems the solution was fed to the neutralizer (8) and left for 1 h in order to reduce any residual ozone before neutralization with 0.1 M NaOH solution. After neutralization to a pH of 7 the treated water was fed to the biological treatment tank (9) which is equipped with air sparger (10).

2.4. Biodegradation experiments

This aerobic biological oxidation step is designed to reduce the COD load of the treated wastewater in the first chemical oxidation step. Experiments in this step were conducted in a 6 L stirred tank (Figs. 1–9). The working liquid volume in the tank was 5 L. Air was continuously fed to the bioreactor through a gas sparger with a constant flow rate of 200 L/h. In addition to its role in the aerobic biodegradation step, the air acts to improve the mixing of the tank contents. The feed solution to the bioreactors was fed from the neutralizer. Activated sludge from wastewater treatment plant (Amman, Jordan) was used as biomass. Initially, 4.9 L of a the cell suspension containing 1.5 g/L biomass, 0.01 L of the ozonated wastewater and amounts of 0.1 M solutions of K_2HPO_4 , NH_4Cl , $CaCl_2$, $MgSO_4$ and $NaNO_3$ were charged to the stirred tank vessel in order to maintain the ratio COD:N:P at around 100:5:1. This ratio is necessary to keep the biomass activity in the reactor [23]. During the first 10 days of continuous

mixing 0.1 L of the reactor content was withdrawn each day and replaced by a fresh 0.1 L of the pretreated water solution with O_3/UV system. In the next four 10-day periods, the amounts of the replacements increased to 0.2, 0.3, 0.4 and 0.5 L, respectively. During this total period of 50 days, the biomass density was monitored to make sure that biomass growth and concentration was normal. It was assumed that after the 50 days period that the process had reached a new steady state and biomass had been acclimated the pretreated wastewater of the first step. After that, the reactor was fed by this pretreated wastewater only.

3. Results and discussion

3.1. O_3 , O_3/UV oxidation processes

Ozone is considered as a powerful oxidant having electrochemical oxidation potential of 2.0 V versus 2.8 V for hydroxyl radical. Consequently, oxidation by ozone have usually been used as an effective method for removing residual pollutants such as pesticides and other hazardous chemicals from raw water used for drinking and for wastewater treatment. For this reason, oxidation by ozone is used in this investigation to oxidize pesticides found in industrial wastewater. Fig. 2 shows the normalized concentration of the three different pesticides used against the oxidation time. The initial concentration of all pesticides was 100 mg/L and the initial COD was 6500, 6300 and 6500 mg/L for Deltamethrin, Lambda-Cyhalothrin and Triadimenol, respectively. The ozonation time for each pesticide continued for 3.5 h. During this oxidation time, 4200 mg ozone entered the oxidation reactor. It is evident from Fig. 2 that pesticide concentration decreases in the first 45 min at a relatively high rate compared to that after 120 min of the reaction time. The concentration of Deltamethrin for example decreases with

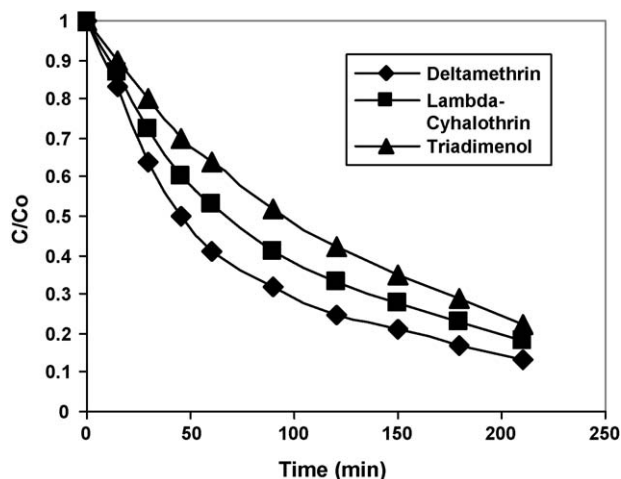


Fig. 2. The variation of the normalized concentration of the three different pesticides used against the oxidation time using O_3 oxidation, $C_0 = 100$ mg/L, $T = 25^\circ C$, pH 7.

a rate of 1.1 mg/L min in the first 45 min, while the rate falls to 0.12 mg/L min in the last 60 min. This is an expected behavior since pesticide concentration is continuously decreases and part of the ozone is utilized in oxidizing the solvent of the pesticides. In addition, Deltamethrin oxidation was more severe than Lambda-Cyhalothrin and Triadimenol. The final normalized concentration C/C_0 of these pesticides was 0.13, 0.18 and 0.22, respectively. These results indicate that ozonation of pesticides solution successfully reduces the pesticide concentration more than 80% in 210 min. It is possible to reduce this concentration of pesticides to lower values if the oxidation time increases or by coupling this step by another method of oxidation to enhance the oxidation power of ozone.

In this ozonation process, two possible pathways of oxidation could be considered. The first is the direct pathway through the reaction between ozone and the dissolved compounds and the second is the radical pathway through the reaction of radicals generated from the reaction between ozone and dissolved compounds. The combination of both pathways for the elimination of pesticides molecules depends on the nature of the compounds themselves, the pH of the medium and the ozone dose. In the present case, the pesticide solution is slightly basic, thus the reaction of ozone with pesticides molecule primarily occurred by means of the ozonation of the double bond of the nucleophilic center. The other mechanism consists of the decomposition of ozone to other secondary oxidant, mainly hydroxyl radical which reacts quickly with the pollutants. These mechanisms predominate, with low reactive molecules such as hydrocarbons, benzene, or halogenated compounds [18] as those under investigation. Consequently, the oxidation mechanism in this step is complex.

However, the global decomposition of organic compounds such as pesticides by ozone can be represented by the following simple irreversible reaction [4]:



with k_o as a rate constant.

According to profiles shown in Fig. 2 the kinetics of the ozonation reaction can be assumed to be pseudo-first-order with respect to the pesticides concentration. Accordingly, the following differential equation can describe the decomposition process:

$$-\left(\frac{dC_p}{dt}\right) = k_o C_p \quad (2)$$

Integrating this equation leads to:

$$\ln\left(\frac{C_{p0}}{C_p}\right) = k_o t \quad (3)$$

where C_{p0} and C_p are the pesticide concentrations at $t = 0$ and t , respectively.

This model assumes that the ozone concentration was constant during each experiment. Experimental measurements of ozone concentration in the reactor showed that this concentration was constant in each run and its value depends on the temperature, pH and the concentration of ozone in the gaseous phase. For instance, ozone concentration at $15^\circ C$ and pH 7 was about 16.5 mg/L, whereas its value at was about $20^\circ C$ and pH 7 was about 12.5 mg/L. Consequently, a plot of $\ln(C_{p0}/C_p)$ versus t will give a straight line with k_o as a slope. Such a plot is shown in Fig. 3 for the three pesticides. It is evident from Fig. 3 that the pseudo-first-order satisfactorily fits the data of the three pesticides. The values of R^2 and k_o for the three pesticides Deltamethrin, Lambda-Cyhalothrin and Triadimenol are shown in Table 2. The relatively high values of R^2 confirm the applicability of this model to the pesticides oxidation process by ozone.

The treatment with ozone can also be enhanced by the use of ultraviolet radiation to generate more hydroxyl radicals. Fig. 4 depicts the variation of the normalized concentration of the three pesticides using the combined O_3/UV radiation which was conducted at $25^\circ C$ and pH 7. It is clear from Fig. 4 that the rate as

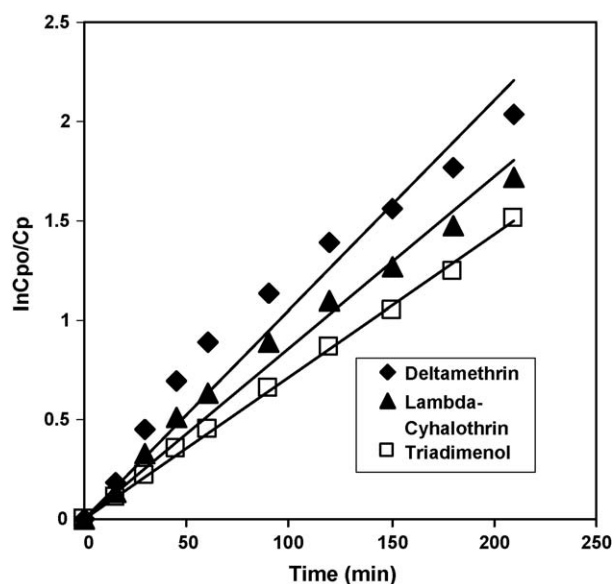


Fig. 3. $\ln(C_{p0}/C_p)$ vs. t for the three pesticides using O_3 oxidation, $C_0 = 100$ mg/L, $T = 25^\circ C$, pH 7.

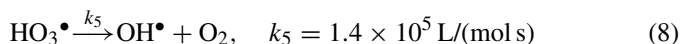
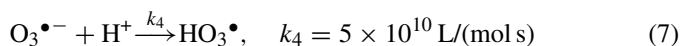
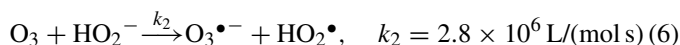
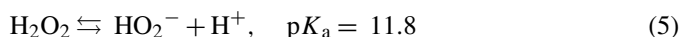
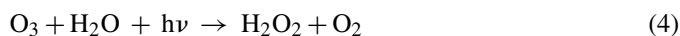
Table 2

Pseudo-first-order constants for the decomposition of the three pesticides by O₃ and O₃/UV systems

Oxidation system	Pesticide					
	Deltamethrin		Lambda-Cyhalothrin		Triadimenol	
	R ²	Rate constant (min ⁻¹)	R ²	Rate constant (min ⁻¹)	R ²	Rate constant (min ⁻¹)
O ₃	0.9457	0.0105	0.9776	0.0086	0.998	0.0071
O ₃ /UV	0.981	0.0233	0.9896	0.0163	0.9962	0.0121

well as the extent of pesticide oxidation increases by combining the effect of UV radiation to that of ozone. The rate for the pesticides Deltamethrin, Lambda-Cyhalothrin and Triadimenol in the first 45 minutes was 1.42, 1.29 and 0.98 mg/L min and the extent of oxidation after 210 min reaches 100, 96 and 92%, respectively. These results indicate that UV radiation accelerates the oxidation process and eliminates most of the pesticides molecules from the solution. Since the aim of this step is to reduce the pesticides load in the wastewater to a low value where no pesticide inhibition occurs to the biological treatment step, this combined system of relatively low capita and operational cost will be used in the following experiments prior to the biological treatment step designed to reduce the COD load.

The enhancement effect of UV illumination could be attributed to the production of more OH• radicals which can be illustrated in the following sequence of chemical reactions [24]:



The kinetics of the combined oxidation reaction by O₃/UV illumination can similarly be assumed to be pseudo-first-order with respect to the pesticides concentration. Accordingly, a plot

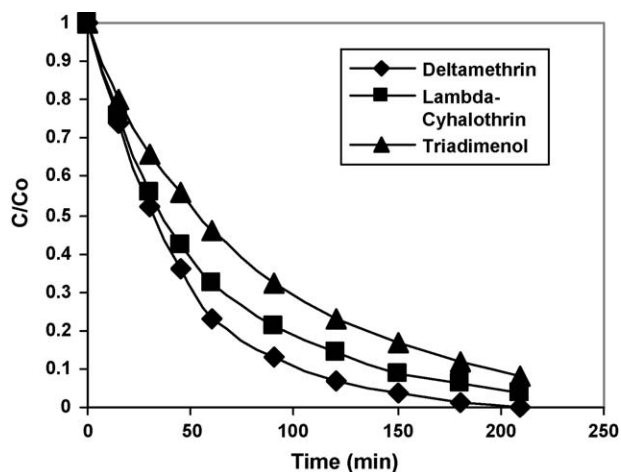


Fig. 4. The variation of the normalized concentration of the three pesticides using the combined O₃/UV system, C₀ = 100 mg/L, T = 25 °C, pH 7.

of ln(C_{p0}/C_p) versus *t* will give a straight line with the rate constant *k*_{O₃UV} in this case as a slope. This plot is shown in Fig. 5 for the decomposition of the three pesticides. The values of the rate constants *k*_{O₃UV} and the correlation coefficient *R*² are tabulated in Table 2. It is clear from Table 2 that the values of the decomposition rate constant *k*_{O₃UV} for all pesticides are almost twice as much as those of *k*_o. This result confirms the enhancement effect of UV in the oxidation process and agrees with the results reported by Benitez et al. [4] for the degradation of carbofuran. In addition, the relatively high values of *R*² confirm the applicability of this pseudo-first-order model to the pesticides oxidation process by the combined system.

Fig. 6 shows the effect of pH on the decomposition of Triadimenol solution of initial concentration of 100 mg/L and at 25 °C. It is clear from Fig. 6 that as pH increases above 7, both the rate and extent of pesticide oxidation increase. The normalized pesticide concentration after 210 min after start up at pH values of 7, 9.2 and 11.3 are 0.08, 0.01 and 0.0, respectively. Furthermore, the rates of decomposition in the first 45 min for the same pH values are 0.98, 1.33 and 1.37 mg/min. On the other hand, at relatively low values of pH the rate of oxidation and the extent of oxidation decrease. For example, at pH 4, the normalized pesticide concentration after 210 min from start up reaches 0.57 and the rate of decomposition in the first 45 min = 0.422 mg/min.

The effect of pH on the decomposition of pesticides by the combined system can be attributed to the effect of OH⁻ ion

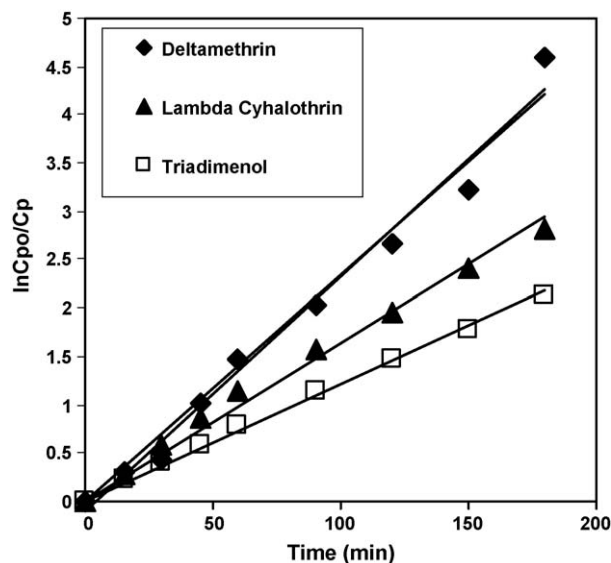


Fig. 5. ln(C_{p0}/C_p) vs. *t* for the three pesticides using the combined O₃/UV system, T = 25 °C, pH 7.

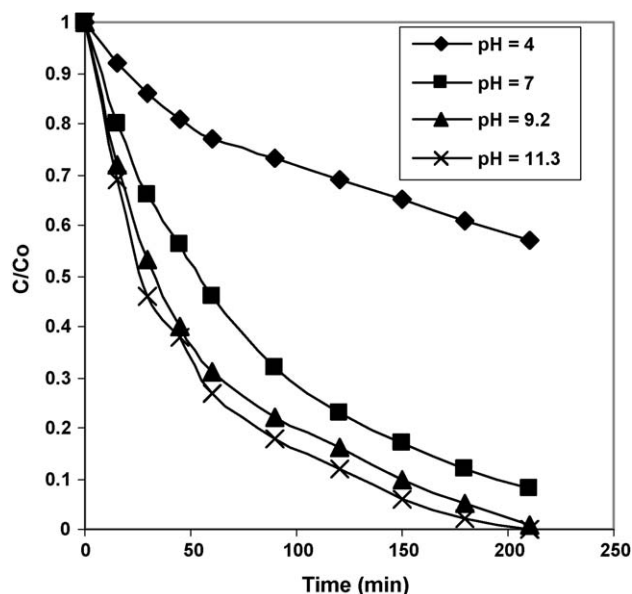


Fig. 6. The effect of pH on the decomposition of Triadimenol, $C_0 = 100 \text{ mg/L}$, $T = 25^\circ \text{C}$.

concentration in the solution. Reaction (5) is a reversible reaction and it usually reaches equilibrium at certain conditions. In addition, this reaction has a very low equilibrium constant as indicated by the value of pK_a . Consequently, it could be considered as the rate-determining step for the production of free radicals in reaction 8. For this reason increasing the pH by the addition of OH^- ions will shift reaction (5) to the right because it reacts with H^+ ions. This leads to the production of more HO_2^- , which in turn accelerates reaction (4) and then reaction (5) thus producing more free radicals.

As mentioned above, the aim of this step was to eliminate the pesticides present in the wastewater rather than to reduce the COD load which will primarily take place during the biological stage of this study. However, the oxidation systems of O_3 as well as of O_3/UV are able to oxidize some of the organic matter present in the solution. Fig. 7 shows the variation of the normalized COD with time at different values of pH using the combined O_3/UV oxidation system. Fig. 7 depicts that the value of the normalized COD after 210 min from startup decreases to 0.64, 0.70, 0.78 and 0.88 for pH values of the solution of 11.3, 9.2, 7 and 4, respectively. The effect of pH can be explained in the same manner as before.

COD removal rates are assumed to follow the pseudo-first-order kinetics during the ozonation and the combined ozonation/UV systems [25]. As a consequence, the COD value at any time can be calculated using the following equation:

$$\ln\left(\frac{\text{COD}_0}{\text{COD}}\right) = k_{\text{COD}}t \quad (9)$$

where k_{COD} (min^{-1}) is the first-order rate constant for the COD removal.

The plot of $\ln(\text{COD}_0/\text{COD})$ against t for the removal of Triadimenol by the combined oxidation system at 25°C and various pH is shown in Fig. 8 and the corresponding values of k_{COD} and

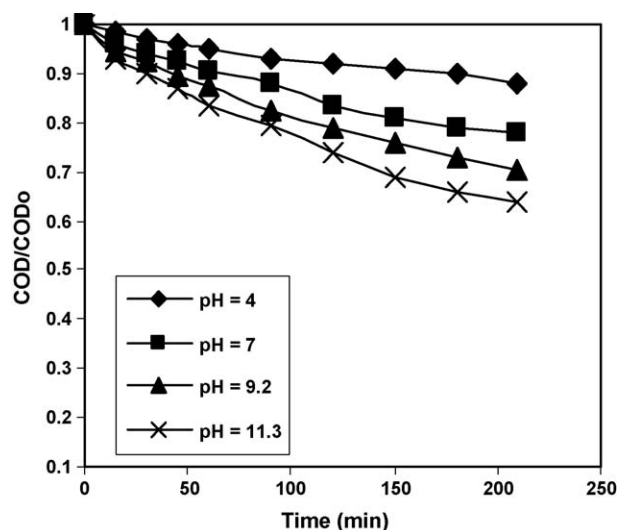


Fig. 7. The variation of the normalized COD with time at different values of pH using the combined O_3/UV oxidation system.

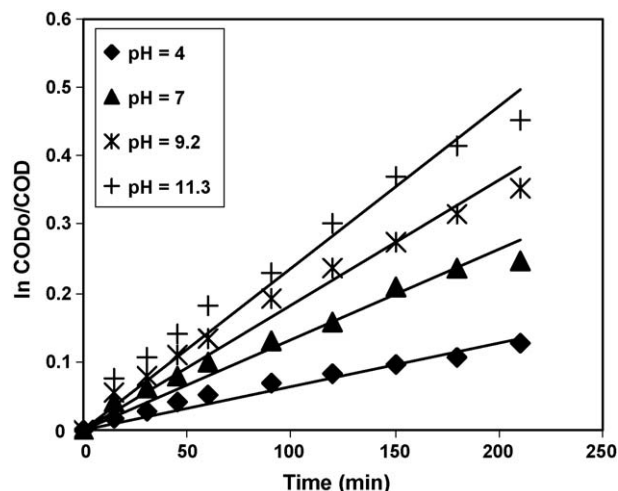


Fig. 8. $\ln(\text{COD}_0/\text{COD})$ against t for the removal of Triadimenol by the combined O_3/UV oxidation system, $T = 25^\circ \text{C}$ and different values of pH.

R^2 are tabulated in Table 3. It is clear that R^2 values are all about 0.95, thus confirming the applicability of the pseudo-first-order model to the COD removal by the combined system. Additionally, k_{COD} increases about four times as the pH increases from 4 to 11.3. These results are in agreement with those of Alaton et al. [25] for the treatment of penicillin and those of Benitez et al. [23], for the degradation of olive mill wastewaters.

Table 3
Pseudo-first-order constants for the decomposition of Triadimenol O_3/UV systems

	pH			
	4	7	9.2	11.3
k_{COD} (min^{-1})	0.0006	0.0013	0.0018	0.0024
R^2	0.9499	0.954	0.9563	0.9594

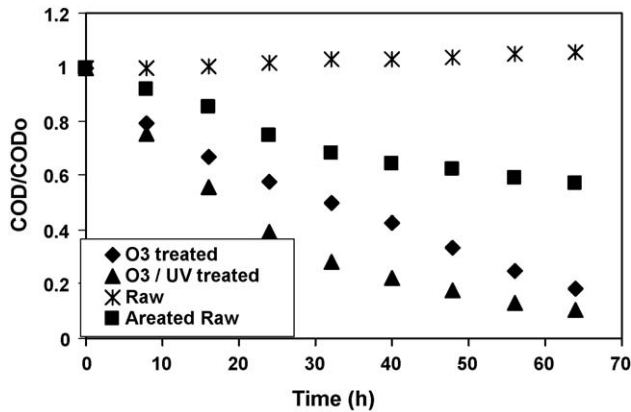


Fig. 9. The normalized COD values of four Triadimenol solutions versus biological treatment time, $T=25^{\circ}\text{C}$, $\text{pH} 7$.

3.2. Biological oxidation process

As mentioned above, the oxidation step by O_3 and O_3/UV system was conducted mainly to eliminate the inhibitory pesticides molecules and to combine this step with the biological treatment step by feeding the treated solution as a substrate to the biomass in the bioreactor. The aim of this integration between the chemical oxidation and biological treatment of industrial wastewater is to combine the best characteristics of these processes including both economical and technical advantages.

The first biological experiment was conducted to investigate the effect of pretreatment on COD removal. Fig. 9 shows the normalized COD removal values of four Triadimenol solutions versus biological treatment time. These four solutions were: pretreated by O_3 , pretreated by O_3/UV system, aerated for one week, and the final solution was raw or untreated solution. It can be seen from Fig. 9 that COD removal when using untreated solution was zero because of the complete inhibition of the biomass with the pesticides present. The slight increase in the COD content after 24 h is attributed to the decomposition of the biomass itself to produce more COD. On the other hand, when using one week previously aerated solution the COD removal was fair and reaches 32% after two days. This indicates that aeration of the pesticides solution oxidizes the pesticides present in the solution, while the activity of the biomass was not affected. When using pretreated solution with O_3 and the O_3/UV system the COD removal rate and extent increase. In the first 24 h, the rate was 90 and 120 mg/L h for O_3 and O_3/UV pretreated solutions, respectively. The final values of COD after 64 h of the biological treatment using raw, aerated, O_3 treated and combined O_3/UV treated were 6800, 3705, 1000 and 260 mg/L, respectively. Based on these results O_3/UV pretreated solution was used in the further biological treatment experiments.

Fig. 10 shows normalized COD values of the three pesticides pretreated solutions with O_3/UV system against time in the biological treatment unit. It is evident that COD removal rate of the three pesticides solutions is significant. For instance, in the first 24 h from startup these rates were 150, 123 and 117 mg/L h for Deltamethrin, Lambda-Cyhalothrin and Triadimenol, respectively. The final values of the normalized COD

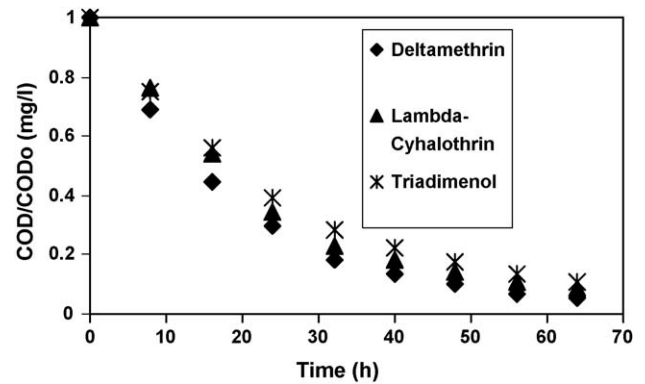


Fig. 10. The normalized COD of the three pesticides pretreated solutions with O_3/UV system against time in the biological treatment unit, $T=25^{\circ}\text{C}$, $\text{pH}=7$.

for these solutions after 64 h were 0.052, 0.09 and 0.107 for Deltamethrin, Lambda-Cyhalothrin and Triadimenol, respectively. This indicates that the biological treatment process was able to remove 95, 91 and 90%, respectively of the initial COD load within this period. The residual COD in the biologically treated solution which is less than 10% of the initial COD could be considered as non-biodegradable organic matter and can be removed by other methods such as coagulation.

The decomposition rate of COD in the biological process could be described by the model proposed by Grau et al. [26]. This model can be expressed by the following power equation:

$$q = K_2 \left(\frac{\text{COD}}{\text{COD}_0} \right)^n \quad (10)$$

where K_2 and n are the kinetic parameters of the decomposition process and q is the specific COD decomposition rate given by the expression:

$$q = -\frac{1}{X} \left(\frac{d\text{COD}}{dt} \right) \quad (11)$$

where X is the biomass mass (g). To evaluate these kinetic parameters equation (10) can be linearized to the following form:

$$\ln q = \ln K + n \ln \left(\frac{\text{COD}}{\text{COD}_0} \right) \quad (12)$$

A plot of $\ln q$ against $\ln(\text{COD}/\text{COD}_0)$ will give a straight line of slope n and intercept $\ln K$.

Table 4 shows sample data of the variation of COD (g/L), biomass density X (g/L), q (g COD/g biomass h) with time (h) for Deltamethrin at $\text{pH} 7$, 25°C and $\text{COD}_0 = 5050$ mg/L. Based on these data for Lambda-Cyhalothrin and Triadimenol a plot of $\ln q$ against $\ln(\text{COD}/\text{COD}_0)$ is shown in Fig. 11. High values of R^2 indicate the applicability of Grau model to the data obtained in this investigation. The values of the model parameters for the three pesticides Deltamethrin, Lambda-Cyhalothrin and Triadimenol are 0.9335, 1.0342 and 1.1039 for n and 0.089, 0.052 and 0.041 for K , respectively. These parameters are usually affected by the initial COD load and the initial biomass density. This effect will be the subject of further investigations in our labs (Table 5).

Table 4

Variation of COD, biomass density, specific COD degradation with time for Deltamethrin O₃/UV system treated solution, of COD₀ = 5050 mg/L

Time (h)	Deltamethrin			
	COD	X	ln(COD/COD ₀)	ln q
0	5.05	1.9	0	-2.5
8	2.58	2.1	-0.67	-2.71
16	1.97	2.2	-0.94	-3.2
24	1.52	2.4	-1.14	-3.67
32	1.14	2.5	-1.52	-3.96
40	0.84	2.6	-1.84	-4.23
48	0.6	2.7	-2.13	-4.5
56	0.4	2.8	-2.54	-4.72
64	0.26	2.8	-2.97	-5.08

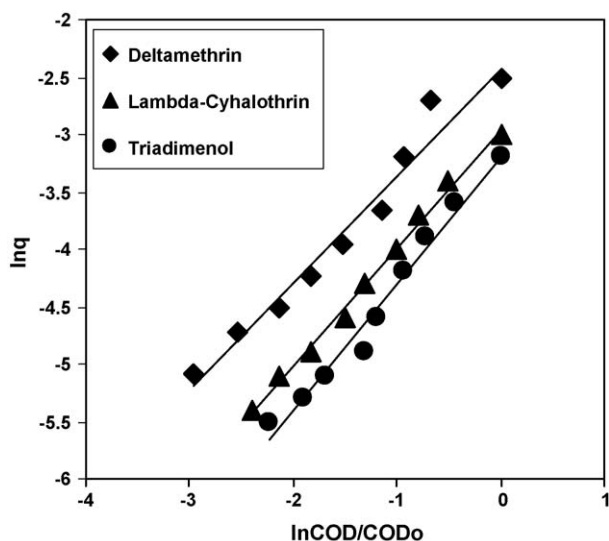


Fig. 11. $\ln q$ against $\ln(\text{COD}/\text{COD}_0)$ of the three pesticides pretreated solutions with O₃/UV system against time in the biological treatment unit.

Fig. 12 shows the COD variation with time for the biological treatment of Triadimenol at different temperatures. It is clear that the rate of COD removal as well as the extent of COD removal increase as the temperature increases. For instance, the rates of COD removal after 16 h from start up for the temperatures 16, 25, 31 and 37 are 78, 119, 131 and 146 mg/h, respectively. On the other hand, the COD values after 64 h from start up corresponding to the same temperatures are 1560, 696, 494 and 390 mg/L, respectively. This indicates as expected that temperature variations during the day or during the whole year will affect the stability of the process. The temperature effect necessitates using an isothermal biological process in order to eliminate the temperature effect on the rate and extent of the bioprocess.

Table 5

Parameters of Grau model for the three pesticides

Pesticide	<i>n</i>	<i>K</i>	<i>R</i> ²
Deltamethrin	0.9335	0.089	0.967
Lambda-Cyhalothrin	1.0342	0.052	0.99
Triadimenol	1.1039	0.041	0.978

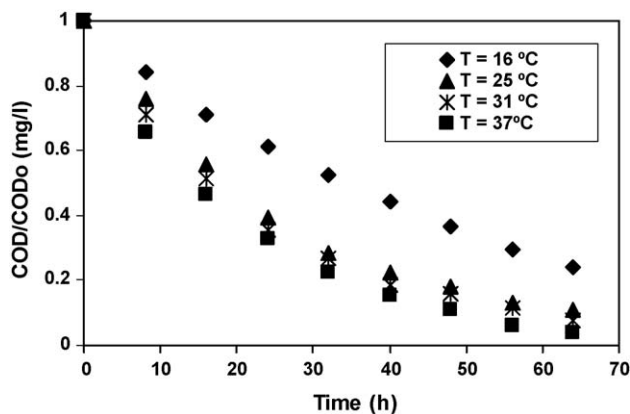


Fig. 12. The COD variation with time for the biological treatment of Triadimenol at different temperatures.

4. Conclusions

In this study, combined chemical oxidation with biological treatment processes were applied to treat pesticides from aqueous solutions. Based on experimental results the following conclusions can be drawn:

- (1) Ozone oxidation process using ozone dose of 240 mg/h/L was able to reduce the concentration of both halogenated and unhalogenated pesticides to about 80%.
- (2) The use of UV radiation in the combined O₃/UV system enhances pesticides degradation and the residual pesticide reaches zero in the case of Deltamethrin.
- (3) More than 20% removal of the COD content was achieved by the combined O₃/UV system using ozone dose of 240 mg/h/L and a UV emitting mercury vapor lamp with a power of 14 W and at pH 7.
- (4) Both pesticide degradation and COD removal in the combined O₃/UV system follow the pseudo-first-order kinetics.
- (5) Increasing the pH was found to increase the pesticide removal rate and the extent of removal.
- (6) The application of the biological treatment was more effective in the case of O₃/UV system treated water where more than 90% of the COD was removed after 64 h of biological treatment at pH 7 and temperature of 25 °C.
- (7) The biological treatment was affected by temperature variation and reaches 96% at 37 °C at pH 7.
- (8) The parameters of the pseudo-first-order model for the degradation of pesticides and COD in addition to those of Grau model were estimated according to the experimental conditions.

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