Original paper

# Performance of advanced oxidation process (UV/O₃/H₂O₂) degrading amoxicillin wastewater: A comparative study

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## ARTICLE INFO

## ABSTRACT

The degradation of synthetic amoxicillin wastewater (SAW) treated with advanced oxidation process (AOP) including UV/$O_3$/$H_2O_2$ was investigated in the present study. In order to investigate the impacts of effective factors on the process performance, four variables involving two numerical factors, initial $H_2O_2$ concentration, and initial pH, and two categorical factors, ozonation and UV irradiation, were selected. Enhancement of ozonation processes by the addition of $H_2O_2$ and different initial pH was also evaluated. The process was modeled and analyzed using response surface methodology (RSM). The region of exploration for the process was taken as the area enclosed by initial $H_2O_2$ concentration (0-20 mM) and initial pH (3-11) boundaries. For two categorical factors (ozonation and UV irradiation), the experiments were performed at two levels (with and without application of each factor). Ozone was the most effective factor with a direct effect on the response in this research. The variables had a synergistic impact on the response. Maximum chemical oxygen demand (COD) removal efficiency was obtained at $H_2O_2$ concentration 20 mM at initial pH 11. As a result, $O_3$/ $H_2O_2$ system at pH 5 showed better performance in terms of $BOD_5$/COD ratio (0.40). From the HPLC chromatograms, complete degradation of amoxicillin (AMX) was achieved. The $O_3$/$H_2O_2$ process showed to be more effective in comparison with UV/$H_2O_2$ system.

## 1. Introduction

The antibiotics have been known to be presented in the ecosystem for almost 30 years. However, it was only in the mid-1990s. when the use of these compounds was widespread and new analytical technologies were developed, that their presence became an emerging concern (Lissemore et al. 2006; Hernando et al. 2006; Bound and Voulvoulis. 2006). Antibiotics enter the environment from different sources including industrial and domestic wastewaters which may cause resistance in bacterial populations and make them ineffective in the treatment processes (Schwartz et al. 2003; Schwartz et al. 2006; Baquero et al. 2008; Rosenblatt-Farrel. 2009; Martinez. 2009). Most of the WWTPs are not designed to remove highly polar micro pollutants like antibiotics (Xu et al. 2007). Therefore, they can be transported to rivers and reach groundwater after leaching. Therefore, in order to reduce the antibiotics discharged into the environment, practical and economical solutions must be achieved. A wide range of chemical and physical techniques for antibiotics removal can be used, for example, chemical oxidation and biodegradation (destructive methods), adsorption, liquid extraction and membrane techniques (nondestructive processes) (Adams et al. 2002; Putra et al. 2009; Acero et al. 2010; Radjenovic et al. 2008; Jacobsen et al. 2004; Thompson and Doraiswamy. 2000).

The non-biodegradable nature of the effluents containing antibiotics residues interferes with the removal of these compounds by conventional biological treatments. In these cases, one solution is to apply advanced oxidation processes (AOPs). In antibiotic wastewater treatment, advanced processes can be applied to increase the BOD/COD ratio, degrading non-biodegradable wastewater. Several laboratory studies have been performed to investigate the ability of different wastewater treatment methods in removing antibiotics and other pharmaceuticals from wastewater with increasing biodegradability (Elmolla and Chaudhuri. 2010; Elmolla and Chaudhuri. 2011; Elmolla and Chaudhuri. 2012; Halling-Sorensen et al. 2000; Ternes et al. 2002; Perez et al. 2005). One of the antibiotic classes is β-Lactams that are narrow spectrum antibiotics, which are highly effective against the gram-positive genera viz. Streptococcus, Gonococcus, and Staphylococcus. These antibiotics act as bacteriostatics by inhibiting the synthesis of the bacterial peptidoglycan cell wall (Marzo and Dal Bo. 1998). The degradation of β-lactam antibiotics such as amoxicillin (AMX), takes place under acidic and alkaline conditions or by reactions with weak nucleophiles, such as water or metal ions (Aksu and Tunc. 2005). And they are not very stable due to hydrolysis of the β-lactam ring (Langin et al. 2009).

Advanced oxidation processes (AOPs) are quite efficient novel methods and effective in the degradation of most pollutants in wastewater (Pera-Titus et al. 2004; Ahmed et al. 2010). Ozonation like the other AOPs is based on the generation of intermediate radicals, the hydroxyl radicals (OH·), which are extremely reactive and less selective than other oxidants (e.g. chlorine, molecular ozone…). Chemical mineralization can occur by direct reaction with the applied oxidant and/or via the generation of highly oxidative secondary species, most commonly, hydroxyl radicals (OH·), which is one of the most powerful oxidants known (Metcalf. 2007). Processes that promote the enhanced formation of OH· are generally referred to as AOPs. UV radiation is commonly used to enhance the formation of OH·. This can be achieved by a number of methods such as O3/H2O2 and UV/O3 are also considered AOPs since they promote the formation of hydroxyl radicals. One of the most widely used antibiotics is amoxicillin. In this study, an advanced oxidation process including UV radiation, ozonation at different dosage of $H_2O_2$ was examined for the treatment of SAW in a batch experiment. The process performance was evaluated in terms of COD removal efficiency and final $BOD_5$/COD.

## 2. Materials and methods
### 2.1. Wastewater preparation

The synthetic antibiotic wastewater (SAW) was prepared by dissolving two capsules of amoxicillin (AMX 500 mg) in tap water in the laboratory scale. The stock SAW was prepared in CODin 2000 mg/L. Other solutions were prepared by dilution the main solution. Furthermore, the actual COD values have been verified each time

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before initiation of experimental work. pH and BOD5/COD ratio were about 7.5 0.1 and 0.18- 0.2, respectively.

## 2.2. Experimental set-up

The experimental rig is shown in Fig. 1. The reactor was of stainless steel with 70 mm in diameter, 456 mm in height, and 1 L in volume. The influent air to the ozone generator (COG, 1G/H) supplied by an air pump ($Q = 0.075$ $m^3$.$min^{-1}$) and air dryer. The air dryer consisted of a column which was filled with a high adsorptive molecular sieve (silica). Ozonation experiments were carried out by continuously feeding an ozone gas stream in a mixed semi-batch bubble reactor (continuous for gas and batch for liquid). Influent ozone concentration in the gas phase

was adjusted to 112.5 mg/L at a flow rate of 5 L/min for all the experiments. The irradiation in the photoreactor was obtained by a 15 W UV/A lamp (HITACHI, emission: 365 nm, constant intensity 60 mW/$cm^2$) that protected by a quartz jacket, and positioned and immersed in the solution in the center of the reactor. The lighted length of the lamp was 452 mm with a quartz sleeve diameter of 3 cm. The reactor was followed by a washing bottle, containing 250 mL of acidified 2 % wt. KI solution for determining of inject and unreacted ozone at influent and effluent in several times. The air flow rate was adjusted 5 L/min. The ozone content of the input air stream was measured as 0.27 g $O_3$/h. The ozone in off-gas was also measured and the consumed ozone was obtained 3.68 as g ozone$_{consumed}$/g COD$_{removed}$.
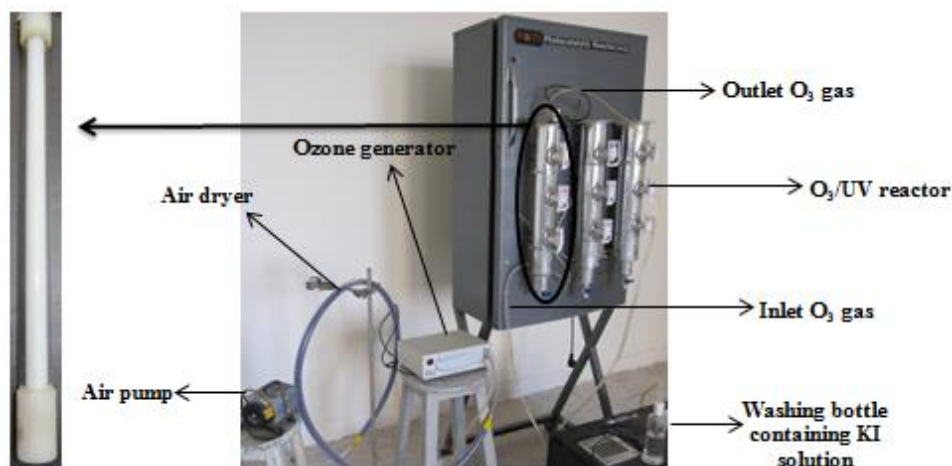


**Fig. 1.** Laboratory-scale experimental set-up for advanced oxidation reactor ($O_3$/UV).

## 2.3. Experimental Design

In order to investigate the effects of influential variables on the process performance, four independent factors (initial $H_2O_2$ concentration and initial pH, ozonation and UV irradiation) were considered to design the experiments. The experiments were designed using RSM. The RSM used in the present study was a general factorial design involving two different numerical factors, initial $H_2O_2$ concentration and initial pH, and two categorical factors, ozonation and

UV irradiation. The experimental range and levels of the independent variables are shown in Table 1. All experiments were carried out in batch mode in terms of wastewater input. The results were completely analyzed using analysis of variance (ANOVA) automatically performed by Design Expert software (Stat-Ease Inc., version 6.0). The results can be obtained as 3D presentations for visualization and also as contours to study the effect of system variables on responses. From these three-dimensional plots, the simultaneous interaction of the two factors on the responses was studied.

**Table 1.** Experimental range and levels of the independent variables.

| Numerical Variables | | | | | |
|---|---|---|---|---|---|
| Variables | -1 | -α | 0 | +α | +1 |
| pH | 3 | 5 | 7 | 9 | 11 |
| $H_2O_{2\ mM}$ | 0 | 5 | 10 | 15 | 20 |
| Categorical Variables | | | | | |
| Variables | | Level 1 | | Level 2 | |
| Ozonation | | Without | | With | |
| UV Irradiation | | Without | | With | |

## 2.4. Analytical methods

Antibiotic concentration was determined by a high performance liquid chromatograph (HPLC) equipped with a micro-vacuum degasser (m), quaternary pump, diode array and multiple wavelength detector (DAD) (m) at wavelength 254 nm. The column was ECLIPSE XDD-C18 (4.6 mm×150 mm, 5 µm) and its temperature was 60 °C. The content of the mobile phase was potassium dihydrogen phosphate and acetonitrile in the ratio (98:02 v/v). The flow rate of the mobile phase was maintained at 1.0 mL/min. Chemical oxygen demand (COD) was measured according to the Standard Methods (APHA. 1992). The entire chemicals used in the analysis were analytical grade (Merck, Darmstadt, Germany). A pH meter (JENWAY 3510) and a pH electrode

were used for pH measurement. Biodegradability was measured by 5-day biochemical oxygen demand (BOD$_5$) (OxiTop IS 6) test according to the Standard Methods [28].

## 3. Result and discussion
## 3.1. Statistical analysis of the model developed

A mathematical equation was developed to describe this relationship based on the results obtained. The results obtained were then analyzed by ANOVA to assess the "goodness of fit". Equation from the first ANOVA analysis was modified by eliminating the terms found statistically insignificant. Table 2 illustrates the reduced cubic model in terms of coded factors and also shows other statistical parameters.

Data given in this Table demonstrates that all the model terms were significant at the 5 % confidence level since P values were less than 0.05 (Table 2). The $R^2$ coefficient gives the proportion of the total variation in the response predicted by the model, indicating the ratio of sum of squares due to regression (SSR) to the sum of squares (SST). A high $R^2$ coefficient ensures a satisfactory adjustment of the model to the experimental data. A value of 0.86 for $R^2$ indicates that some other variables might have interaction on the response and have not

considered in this study. Adequate precision (AP) compares the range of the predicted values at the design points to the average prediction error. Ratios greater than 4 indicate adequate model discrimination (Mason et al. 2003). Diagnostic plots such as the predicted versus actual values (Fig. 2) help us judge the model satisfactoriness. The predicted versus actual values plot of COD removal is presented in Fig. 2.
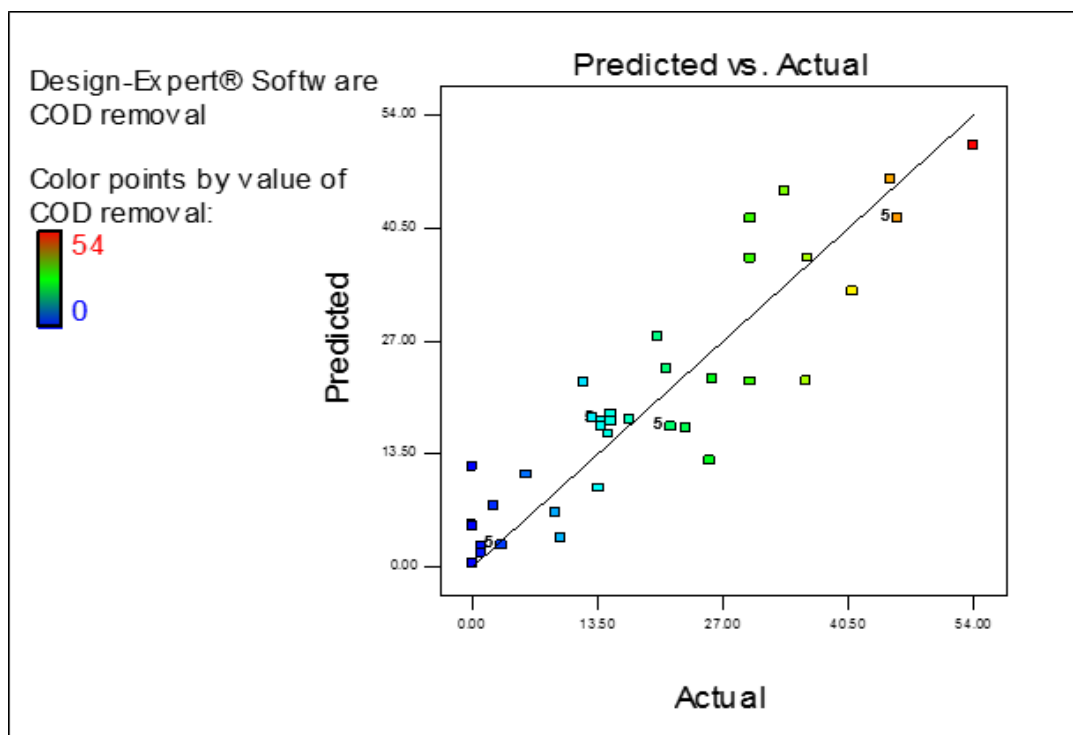


**Fig. 2.** Actual vs. predicted values of COD removal.

**Table 2.** ANOVA for response surface model applied.

| Response | Model type | ANOVA | | | | | |
|---|---|---|---|---|---|---|---|
| | | source | Sum of Squares | Degrees of freedom (DF) | Mean square | F value | P value |
| COD removal (%) | Reduced cubic model | Model | 9914.2 | 8 | 1239.3 | 32.4 | <0.0001 |
| | | A | 408.9 | 1 | 408.9 | 10.7 | 0.0021 |
| | | B | 557.78 | 1 | 557.8 | 14.6 | 0.0004 |
| | | C | 5121.1 | 1 | 5121.1 | 134.0 | <0.0001 |
| | | D | 2969.4 | 1 | 2969.4 | 77.7 | <0.0001 |
| | | AB | 250.6 | 1 | 250.6 | 6.5 | 0.0140 |
| | | BC | 262.1 | 1 | 262.1 | 6.8 | 0.0121 |
| | | CD | 325.2 | 1 | 325.2 | 8.5 | 0.0056 |
| | | $A^2D$ | 902.6 | 1 | 902.6 | 23.6 | <0.0001 |
| | | Residual | 1643.1 | 43 | 38.2 | - | - |

($R^2$ = 0.8578, Adj. $R^2$ = 0.8314, Adeq. Precision = 19.41, Std. Dev. = 6.12, C.V % = 31.62, PRESS = 2637.23)

## 3.2. Process performance of AOP (UV/$O_3$/$H_2O_2$) treating SAW

In this study, AMX content is expressed as COD. As this investigation deals with the effect of advanced oxidation processes removing the 16-C organic molecule-AMX, the compound may be degraded to various intermediates. So, in order to assess the performance of the processes studied, different possible intermediates are classified into four categories of COD as (1) COD degraded into bCOD or BOD, (2) COD mineralized (in the form of $CO_2$ + $H_2O$), (3) COD broken down to intermediate compounds but in non-biodegradable form (nbCOD) and (4) COD as parent form.

### 3.2.1. COD removal

TCOD concentration was monitored throughout the experiments representing the organic content of SAW at initial and final samples. The contribution of aeration in COD removal efficiency was determined in an experiment with aeration alone and no effect was observed. The process performance was monitored in terms of COD removal every 30 min up to 180 min. The data obtained after 180 min were selected for the process analysis and modeling. TCOD removal variation as a function of the variables was described by a reduced cubic model in the coded form as below:

TCOD removal, % = 19.55 + 4.77 A + 5.57 B + 9.92C
+ 9.57D  + 3.96 AB + 3.82 BC + 2.50 CD – 9.4 A$^2$D  (1)

From Table 2, A, B, C, D, AB, BC, CD and A$^2$D are selected as the effective terms with P value less than 0.05. Where, A is initial pH, B is $H_2O_2$ concentration, C and D are respectively, ozonation and UV irradiation. AB, BC, CD and A$^2$D also indicate the interactive terms. All the model terms in the Eq. except A$^2$D, had a positive effect on the COD removal efficiency. From the Eq., term C (O$_3$) was the most effective factor with direct effect on the response with the largest coefficient.
Figs. 3a-d represent three dimensional graphs for COD removal as a function of pH and $H_2O_2$ concentration at different combination of O$_3$ and UV. In all of the Figs pH showed an inverse effect on the response. in the condition with no UV irradiation, by increasing pH from 3 to7, the COD removal was decreased. But by increasing pH up to 11, it had a positive effect on the response. On the other hand, in the experiment with UV irradiation, by increasing pH from 3 to about the neutral value, the COD removal was increased. But by increasing pH from about 7 to 11, the response was decreased.
Fig. 3a shows a three dimensional graph for COD removal as a function of pH and $H_2O_2$ with no ozonation and UV irradiation. As can be seen in the Fig., pH showed almost no effect at its low levels (3-7) and a remarkable increasing effect on the response at the high values (7-11). $H_2O_2$ concentration also showed no impact at the low levels of pH while by increasing pH from 7 to 11 an increasing effect on the response was observed (Arslan-Alaton et al. 2011). Maximum COD removal efficiency was obtained to be about 20 % at the highest value of the variables.
The effect of the numerical variables at the condition with UV irradiation and without ozonation is illustrated in the Fig. 3b. From the Fig., The effect of $H_2O_2$ concentration was slight in the range studied for the variables (a slight decreasing effect at low pH and an increasing effect at high values of pH). pH had an inverse effect on the response. Comparing the results presented in the Fig. 3b with Fig. 3a showed that UV irradiation caused an inverse curvature, so that, the maximum response was found at neutral pH (about 21 %). However, it did not have a significant change in the response.

Fig. 3c illustrates the effect of pH and $H_2O_2$ under ozonation on the COD removal. By comparing the results with those presented in the Fig. 4a, the results (Fig. 3c) showed an improvement in the COD removal efficiency with almost the same trend when O$_3$ is applied. The addition of high concentrations of $H_2O_2$ will not improve the process efficiency, it might be due to $H_2O_2$ deforming to hydroxyl radicals under ozonation conditions or it may act as a free radical scavenger (Homem and Santos. 2011). As can be seen in the Fig. 3c, $H_2O_2$ concentration showed a linear increasing impact on the response in the range of pH examined. But this effect was more in alkaline condition. Minimum to maximum of the efficiency obtained was varied between 15 to 45 %.
Fig. 3d depicts three dimensional graphs for COD removal as a function of pH and $H_2O_2$ under ozonation and UV irradiation. The maximum efficiency of COD removal was obtained to be 54 % at the high value of pH and $H_2O_2$ (11 and 20 mM, respectively), where both categorical variables (O$_3$ and UV) are applied. It showed a synergistic effect of the factors studied. Under this condition, the initiation of ozone decomposition is accelerated by increasing the pH value (more changes are observed in the range of pH from 3 to 7). It should be mentioned that according to the actual data, the maximum efficiency was found at pH 11. Based on the modeled data, the optimum condition was determined to be pH 7 and $H_2O_2$ 20 mM under ozonation and UV irradiation (Esplugas et al. 2007). Comparing Figs 3b and d, showed that when ozonation be applied, the COD removal efficiency was improved about 30 %. It should be due to O$_3$ was a strong oxidizing relative to UV irradiation.
In general, From the Fig., the oxidation rate is $H_2O_2$< ($H_2O_2$/UV) < O$_3$ < (O$_3$/UV/ $H_2O_2$).
In a research work performed by Andreozzi et al. (2003), removal of AMX ($C_0$= 401.5 mg/L) in an ozonation process was investigated and low mineralization was reported. In the purpose of comparison with the present work, 36 % COD removal was achieved at the initial concentration of 1100 mg/L. The authors also examined UV/$H_2O_2$ process for treatment of AMX in their work and not clear finding on the process performance is reported. Another study carried out on the effect of ozonation (2.96 g/L. h) on human antibiotic removal (450 mg/L COD) which a 74 % COD removal was reported (Balcıoglu and Otker. 2003).
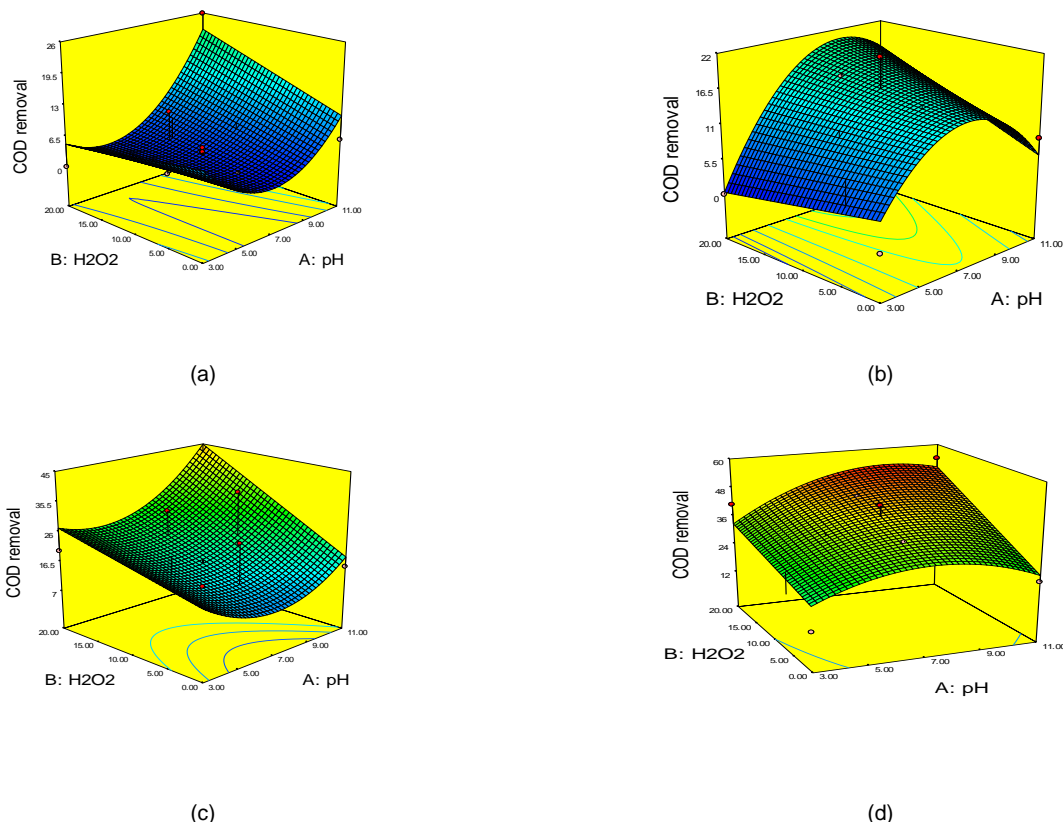


(a)



(b)



(c)



(d)

**Fig. 3.** Three dimensional graphs for COD removal as a function of pH and $H_2O_2$ at (a) without O$_3$ and UV, (b) with UV and without O$_3$, (c) with O$_3$ and without UV, and (d) with O$_3$ and UV.

### 3.3. Interactive effects of the variables studied
### 3.3.1. Effect of H₂O₂

Figs. 4a-c show the interactive effects of $H_2O_2$ concentration-ozone on the COD removal efficiency at different levels of initial pH without UV irradiation. As shown in the Figs., at the condition with ozonation, asimilar trend is observed when ozone is applied which is increasing. The Figs. 4a-c illustrate that the effect of ozone is more significant than initial pH and $H_2O_2$ concentration. Synergistic interactive effects of the three variables are seen in the Figs., so that by increasing the numerical variables (initial pH and $H_2O_2$ concentration) under ozonation, the response was increased.

The Figs. show that $H_2O_2$ had a slight effect on the response at the condition without ozone while showed a positive impact in the presence of ozone. Fig. 4 showed that perozonation ($O_3/H_2O_2$) enhances the ozonation performance. Similar finding about the effect of $H_2O_2$ is reported in the literature (Glaze and Kang. 1989; Witte et al. 2009). Effect of hydrogen peroxide combined by ozone to enhance oxidizing ability has been extensively researched recently and is considered to be a promising alternative for refractory organics removal from aqueous solutions (Masten et al. 1997; Lin et al. 2009). It is important to recognize that OH˙ and related free-radical degradation pathways occur readily even in treatment with $O_3$ alone. Where a wastewater containing contaminants that warrant enhanced treatment via degradation by OH˙, $H_2O_2$ should be applied sparingly as to promote the generation of free radicals but not so high as to consume and deplete aqueous $O_3$ or even scavenge the resultant OH˙ rapidly that would end up with no benefits in treatment (Lin et al. 2009). The maximum degradation rate occurred at $H_2O_2$ concentration of 20 mM. Increasing hydrogen peroxide concentration up to an optimum concentration enhanced about 15 % increase in the oxidation rate in the case of the antibiotic wastewater (Esplugas et al. 2007).

From the result, the effect of $H_2O_2$ on AMX degradation was obtained that by increasing $H_2O_2$, COD removal was increased (Fig. 5). These results confirmed that the oxidation of AMX proceeded mainly by hydroxyl radicals in accordance with the results obtained at initial pH 3, 7 and 11.

The trend and interactive effects of $H_2O_2$ Concentration-Ozone on of the COD removal are the same under UV irradiation at different initial pH but with higher values when UV irradiation is applied.
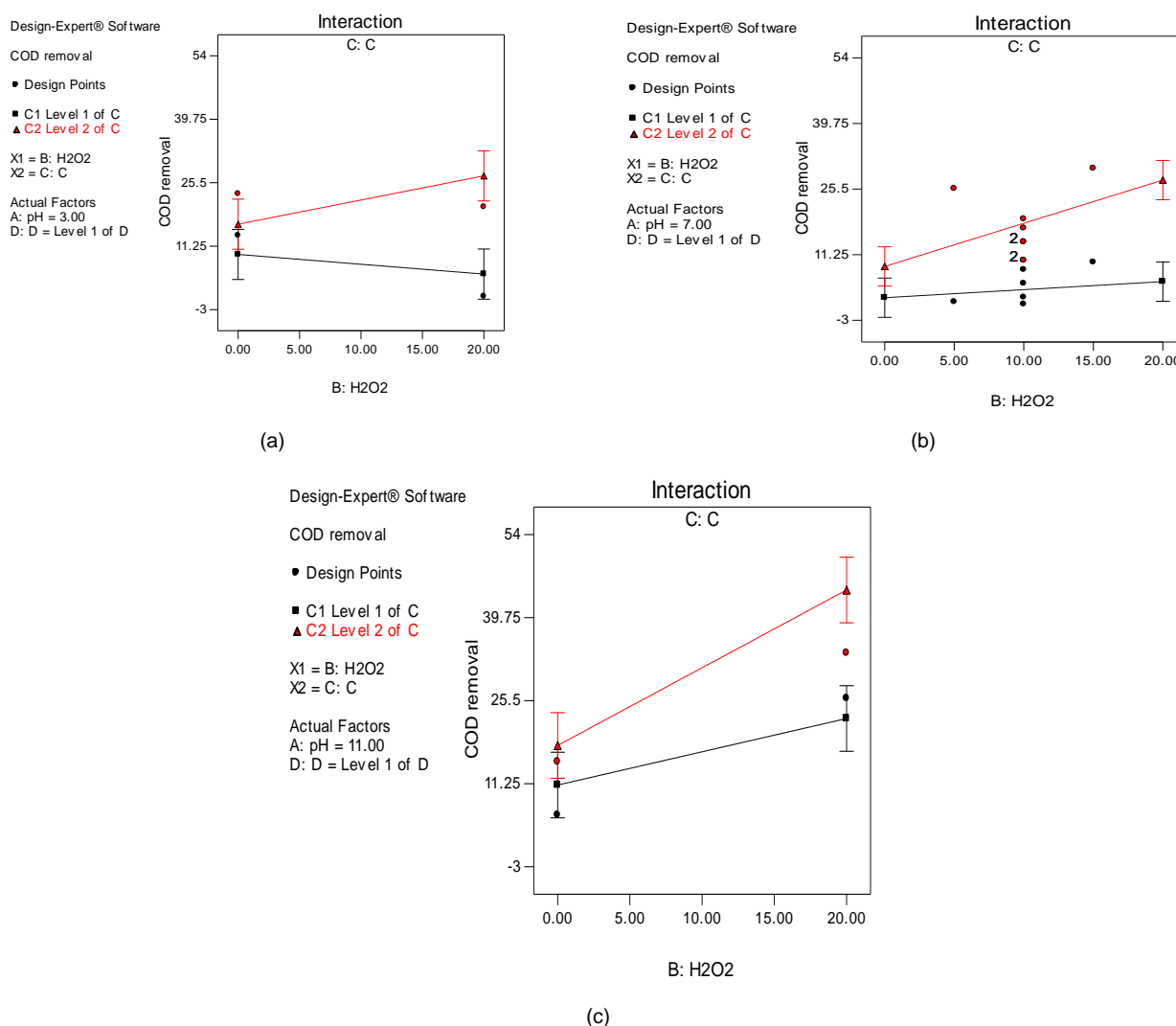


(a)



(b)



(c)

**Fig. 4.** Interactive effect of $H_2O_2$ concentration-Ozone on the COD removal without UV irradiation at (a) pH 3, (b) pH 7, and (c) pH 11.

### 3.3.2. Effect of pH

Initial pH is an important parameter that can affect advanced oxidation reactions (Andreozzi et al. 2005). In overall, when OH˙ is scarce (i.e., low pH), the depletion reaction is slow allowing for accumulation of dissolved $O_3$ to a high level, whereas when OH˙ is abundant (i.e., high pH), the depletion reaction is rapid thus prohibiting dissolved $O_3$ to accumulate (e.g., dissolved $O_3$ rarely exceeds 1 mg/L at pH 11 or higher). With the increment of the solution pH from 3 to alkaline pH, overall COD abatement is enhanced for most wastewaters as expected. In general, ozone reacts with organic compounds found in water and wastewater via two different pathways namely direct

molecular and indirect radical chain type reaction depending upon pH and composition of water (Andreozzi et al. 2005). It is expected that molecular ozone is the major oxidant at acidic pH, whereas less selective and faster radical oxidation (mainly hydroxyl radical) becomes dominant at pH > 7 as a consequence of OH˙ accelerated ozone decomposition (Beltran et al. 2001). Since the oxidation potential of hydroxyl radicals is much higher than that of ozone molecule, direct oxidation is slower than radical oxidation and furthermore, causes incomplete oxidation of organic compounds as observed in this study. However, low pH is known to suppress the formation of hydroxyl radicals from ozone and ozone is reacting directly by an electrophilic attack that led to 13 % lower COD removal than that obtained in the highest initial pH. In other words, at optimum values of the variables with the lowest initial pH, the COD removal achieved 41 %.

Figs. 5a and b also show the effect of different levels of initial pH applied on the degredation of AMX relative to reaction time at different oxidation conditions. It was found that by increasing in initial pH, the response ($C/C_0$) was decreased, corresponding to the improvement in COD removal efficiency.
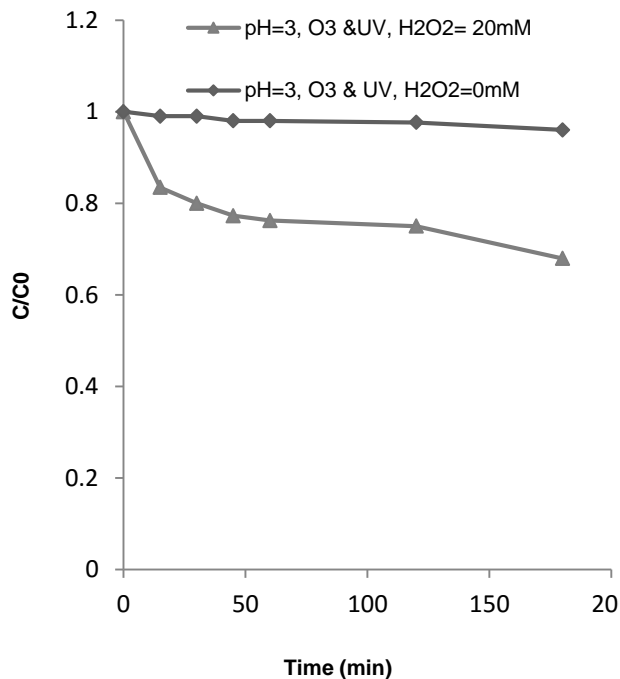
### 3.3.3. BOD₅/COD ratio

Further investigations to determine the bioactivity of the observed unknown by-products produced in the AOPs processes would be necessary after application of the advanced oxidation processes. The $BOD_5$/COD ratio indicates the biodegradable fraction of the remaining COD content in the treated wastewater. However, $BOD_5$ measurements do not mirror the actual situation in biological treatment units and hence

is only used as an approximate estimation of biodegradability improvement. Fig. 6 demonstrates the $BOD_5$ and different form of COD in selected runs carried out by $O_3$/UV/$H_2O_2$. Fig. 6 has been drawn according to the selected experiments number as presented in Table 3. From the Fig., the $BOD_5$ fractions in the most oxidized samples were increased in comparison with the value in the raw SAW. It is noted that the ratio of $BOD_5$/COD for the raw SAW was determined to be less than 0.2. As observed in the Fig., the maximum ratio of $BOD_5$/COD was found 0.40 under run no. 1 (ozonation, $H_2O_2$ 10 mM and initial pH of 5). From the Table 3, various advanced oxidation processes have increased the ratio from 0 to 0.4 for different antibiotics. Balcıoglu and Otker (2003) reported an increase in the ratio from 0 to 0.27 for the treatment of human antibiotic containing penicillin (Balcıoglu and Otker. 2003).
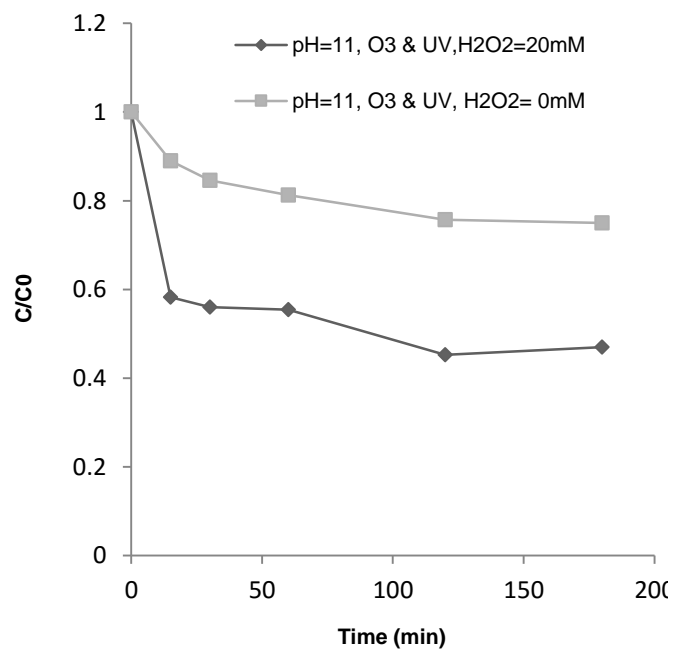
It is figured out from the Fig. 6 that 54 % of COD could be removed and 25 % of the COD contents in the treated sample could be converted into the biodegradable form ($BOD_5$) under optimum conditions (run no. 1, 5). However, about 42 % of total COD has still remained as the non-biodegradable form that may have been changed during the oxidation process, but this is unknown so far and need more investigation. In order to clarify this point, the compounds content of the selected samples was analyzed by HPLC. Figs. 7 show the HPLC chromatogram for the sample and the HPLC analysis results are presented in Table 3. As specified in the illustrations (the Figures. and Table), in all the samples except run no. 3 and 4, AMX could not be detected. It implies that the residual COD (e.g. 42 % at optimum condition) has been degraded into secondary non-biodegradable intermediates.

**Table 3.** Order of experiments number according to operating conditions.

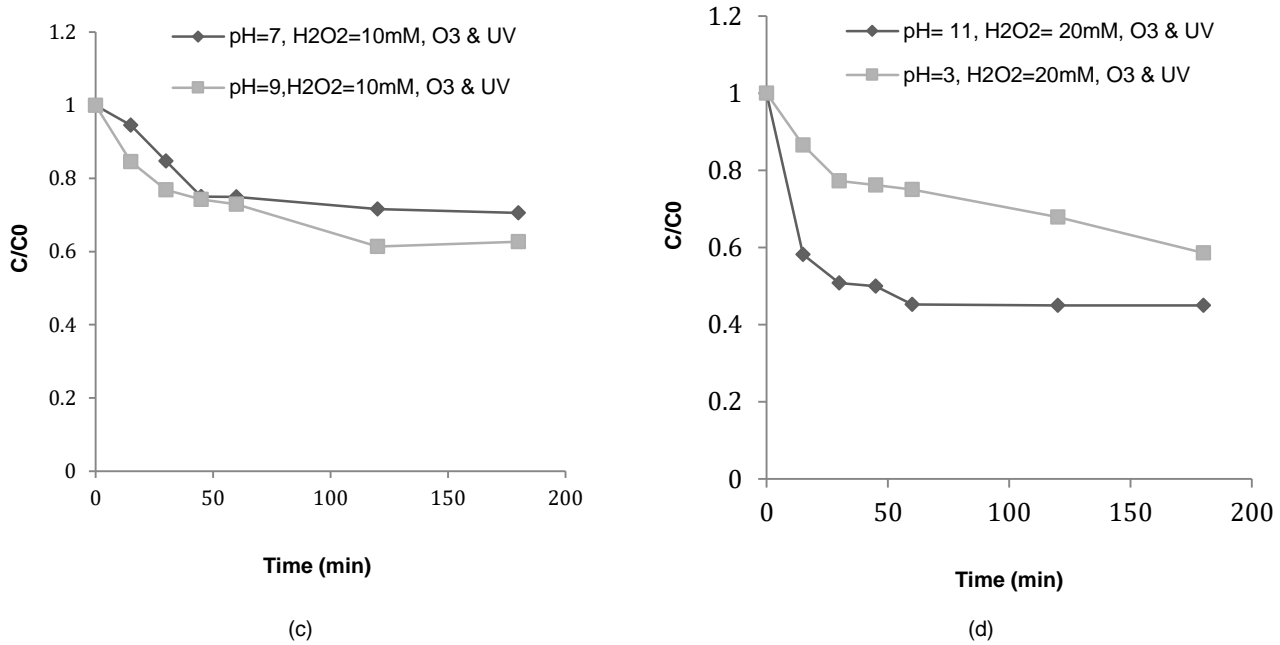| Run No. | Type of process | $H_2O_2$ concentration(mM) | Initial pH | $BOD_5$/COD ratio | Area peak | Degradation percent (%) |
|---|---|---|---|---|---|---|
| 1 | $O_3$/ $H_2O_2$ | 10 | 5 | 0.40 | 0 | 100 |
| 2 | UV/ $H_2O_2$ | 10 | 5 | 0.32 | 10.5 | 96 |
| 3 | | 20 | 11 | 0.23 | 0 | 100 |
| 4 | $O_3$/UV/$H_2O_2$ | 5 | 7 | 0.20 | 0 | 100 |
| 5 | | 20 | 11 | 0.25 | --- | --- |
| - | Raw SAW | --- | 7.5 | 0.2 | 266.5 | --- |



(a)



(b)

(c)

(d)

**Fig. 5.** (a and b) Effect of various H2O2 concentrations on degradation of AMX as a function of reaction time, (c and d) Effect of various initial pH on COD removal as a function of reaction time at different oxidation conditions.
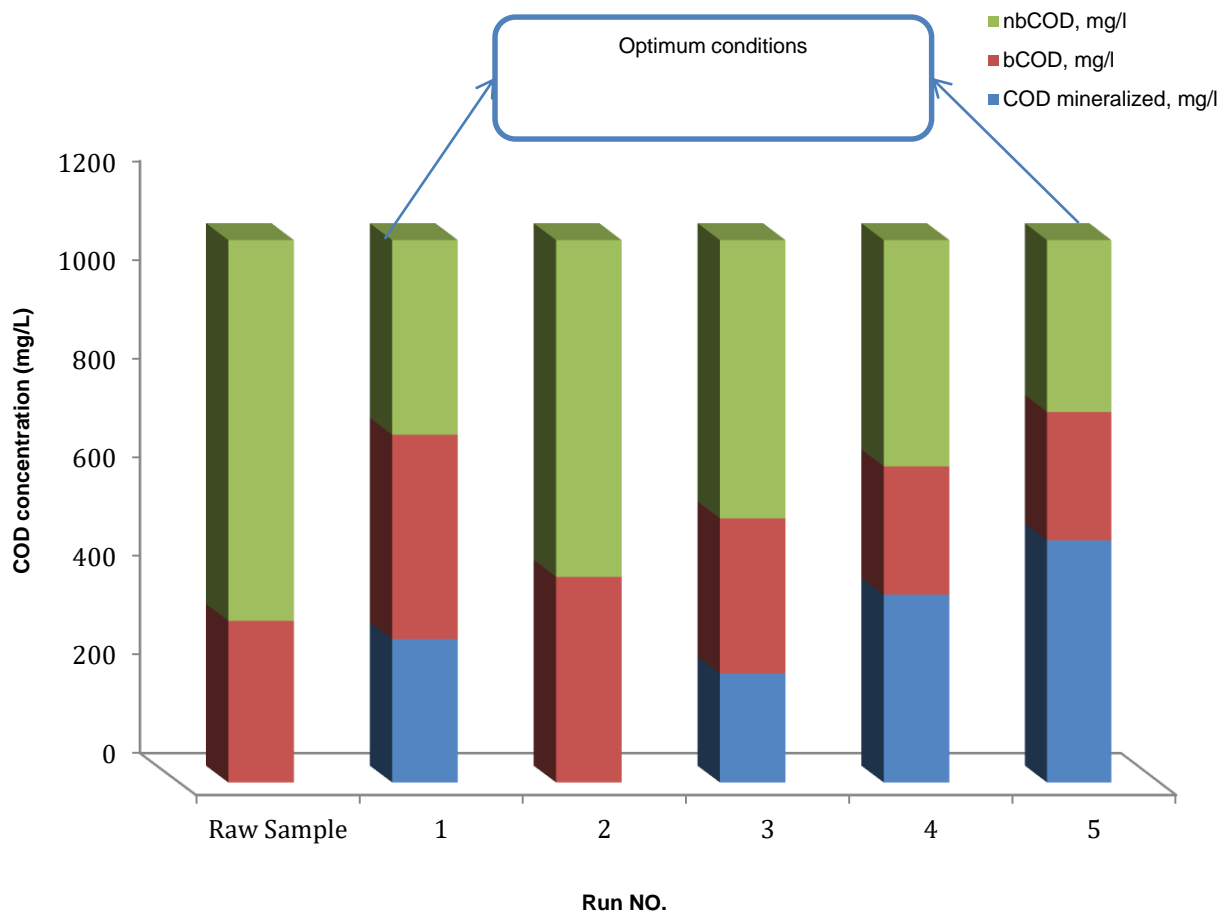


**Fig. 6.** COD fractionation for the raw and treated samples and run no. (1-5), 1) pH= 5, $H_2O_2$= 10, $O_3$, 2) pH= 5, $H_2O_2$= 10, UV, 3) pH= 11, $H_2O_2$= 20, UV, 4) pH= 7, $H_2O_2$= 5, $O_3$ & UV, 5) pH= 11, $H_2O_2$= 20, $O_3$ & UV is present in Table 3.

(a)

(b)

(c)

(d)

(e)

**Fig. 7.** HPLC chromatograms for a) stock SAW, b) pH= 5, $H_2O_2$= 10, $O_3$, c) pH= 5, $H_2O_2$= 10, UV, d) pH= 11, $H_2O_2$= 20, UV, e) pH= 7, $H_2O_2$= 5, $O_3$ & UV.

## 4. Conclusions

The degradation of AMX was investigated via ozone, direct UV photolysis advanced oxidation processes with adding $H_2O_2$ in different initial pH. The results of the present study have clearly delineated that using of ozone and UV with adding $H_2O_2$ at alkalinity pH values provides a promising technique for the treatment of AMX wastewater. (Ozonation was demonstrated to be an effective method in increasing the biodegradability of SAW). From the results, the oxidation rate is $H_2O_2 < (H_2O_2/UV) < O_3 < (O_3/UV/H_2O_2)$ and effect of $H_2O_2$ on AMX degradation was obtained that by increasing $H_2O_2$, COD removal was increased. When UV irradiation was combined with hydrogen peroxide and ozonation, the process performance in terms of COD removal efficiency increased significantly compared to that of single oxidants. The experiment with UV irradiation in neutral pH and experiment without UV irradiation had a significant COD removal in alkaline pH. The best result was obtained at pH 11 with 54 % COD removal efficiency. The maximum ratio of $BOD_5/COD$ was found 0.40 in the $O_3/H_2O_2$ system. From the HPLC results, the run with only UV irradiation and low $H_2O_2$ concentration, residual AMX was found in the solution while complete degradation was achieved in the others. In the basis of the results obtained, the AOP applied could be used as a pretreatment method prior a biological treatment process. And also, other advanced oxidation processes are recommended to be examined.

## Acknowledgements

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