

Original paper

Advanced oxidation processes treating of Tire Cord production plant effluent: A comparative study

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ABSTRACT

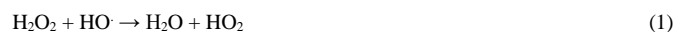
The degradation of an industrial wastewater (Tire Cord factory) with low BOD₅/COD ratio (0.1-0.2) was investigated using advanced oxidation processes (AOPs) (i.e. hydrogen peroxide, UV/H₂O₂, O₃/H₂O₂ and UV/O₃/H₂O₂ treatments). In order to investigate the effects of influential variables on the process performance, four independent factors involving two numerical factors (initial H₂O₂ concentration and initial pH) and two categorical factors (ozonation and UV irradiation) were selected. 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 H₂O₂ concentration (0-20 mM) and initial pH (3-11) boundaries at three levels. For two categorical factors (ozonation and UV irradiation), the experiments were performed at two levels (with and without application of each factor). Two dependent parameters (TCOD removal and BOD₅/COD ratio) were studied as the process responses. As a result, initial H₂O₂ concentration showed a reverse impact on the responses; an increasing effect at low concentrations (0-10 m mol/l) and a decreasing effect at higher concentrations (10-20 m mol/l). The maximum and minimum the responses were obtained at H₂O₂ concentration of 10 and 20 mmol/l and initial pH 3 and 11, respectively. O₃/UV/H₂O₂ system showed better performance with 32 % for TCOD removal efficiency and 0.41 for BOD₅/COD ratio.

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1. Introduction

Industrial effluent is one of the important pollution sources for water resources with unpredictable toxicological and ecotoxicological effects (Shi 2003; Di Marzio et al. 2005). Post treatment systems currently used in wastewater treatment plants include membrane technology, activated carbon adsorption, and sand filters. However, none of these treatment methods is effective enough to generate water with acceptable levels of the most recalcitrant pollutants (e.g., phenols, pesticides, solvents, household chemicals and drugs, etc.). Therefore, a further treatment stage is often necessary to achieve standard levels for the removing persistent chemicals. This stage can entail the application of advanced oxidation processes (AOPs), which are recommended when wastewater components are stable and not biologically degraded. In the AOPs, very reactive species-hydroxyl radicals (OH[•]) is produced which cause a complete mineralization of pollutants to CO₂, water, and inorganic compounds, or at least their transformation into more innocuous products (Shi 2003). There are several different processes which produce hydroxyl radicals; e.g. ozonation (Latifoglu and Guroi 2003; Sanchez-Polo et al. 2007; Lucas et al. 2010), Fenton process (Ghaly et al. 2001; Kusic et al. 2006; Horsing et al. 2012), UV/O₃ (Shen and Ku 1999; Garoma et al. 2008), O₃/H₂O₂ (Qiang et al. 2010), photocatalytic process (Keller et al. 2003; Lin et al. 2012) and etc. Ozone has an ability to oxidize various organic contaminants in water and wastewater such as naphthalene, anthracene and hydroxylated aromatics like phenols (Latifoglu and Guroi 2003). However, ozone reaction with saturated organic compounds is very slow. In a research work, using direct ozonation, 12% COD reduction after 180 min has been reported for treatment of

winery wastewater with COD content of 4650 mg/l (Lucas et al. 2010). Ozonation process combined with H₂O₂ has been also examined and found to be one of the most practical AOPs because of its simplicity (Katsoyiannis et al. 2011). It is noted that an appropriate range of H₂O₂ concentration must be applied because H₂O₂ acts not only as a HO[•] generator, but also as a HO[•] scavenger through generating peroxy radical (HO₂[•]) during the O₃/H₂O₂ process as follows:



It was also reported that the appropriate range of H₂O₂ concentration depends upon the type of solutes and their concentrations (Crittenden et al. 1999). O₃/H₂O₂ process was used for degradation of various compounds such as methyl-tert-butyl ether (MTBE) (Safarzadeh-Amiri 2001), 17β-estradiol and 17α-ethinylestradiol (Guedes Maniero et al. 2008) and humic acid Kosaka et al. 2001).

Simultaneous application of ozone with ultraviolet radiation (O₃/UV) is another AOP tested. It showed to be more effective compared with ozone alone. Application of the O₃/UV for the treatment of winery wastewater with COD content of 4650 mg/l, could remove 21% of COD after 180 min of reaction (Lucas et al. 2010). A very effective mineralization of TOC (94%) with a UV radiation of 96 W and an ozone dosage of 3.8 g/h was obtained (Poyatos et al. 2010). Although UV radiation itself has ability to destroy organic molecules, the efficiency of direct photolysis of organic matter is somewhat difficult and it depends on the compound's reactivity and photosensitivity. Moreover, most of the commercially used dyes are usually designed to be light resistant

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(Kusic et al. 2006). The direct photolytic effect on the compounds dissolved in the winery wastewater was insignificant (Lucas et al. 2010). However, when UV irradiation is combined with some powerful oxidant, such as H_2O_2 , organic matter degradation efficiency can be significantly enhanced because H_2O_2 absorbs UV light, and breaks down into OH radicals, degrading the contaminant via OH radical oxidation (Kusic et al. 2006; Rosenfeldt et al. 2006). UV/ H_2O_2 process has been used for degradation of various organic compounds such as p-chlorophenol (Ghaly et al. 2001), methyl orange (Haji et al. 2001), naphthalenesulfonic acids (Sanchez-Polo et al. 2007) and cyclohexanoic acid (Afzal et al. 2012). In a study, the UV/ H_2O_2 process examined for removing naproxen from surface water and more than 93% removal efficiency was obtained at pH 6 after 3 min (Poyatos et al. 2010).

Another combined AOP is O_3 /UV/ H_2O_2 process which is able to oxidize organic matters faster than ozone, showing an enhanced photochemical oxidation effect. This is principally due to the photolysis of ozone and the enhanced mass transfer of ozone for generation of hydroxyl radicals that react rapidly with the organic matter in the target wastewater. Treatment of winery wastewater with COD content 4650 mg/l using the O_3 /UV/ H_2O_2 process showed a COD removal of 35% after 180 min (Lucas et al. 2010). An O_3 /UV/ H_2O_2 process under UV irradiation of 6.4 mW cm^{-2} and an initial H_2O_2 concentration of 7 mg L^{-1} has been used for removal of carbamazepine (CBZ) and 96.5% removal efficiency achieved (Im et al. 2012).

Tire cord manufacturing plant uses polyesters and polyamides as the basic material for production of required textiles to be used in tire. The compounds found in Tire Cord wastewater (TCW) are mostly recalcitrant and non-biodegradable. It is noted that some of the chemicals, i.e. pyridine compounds, are not even detected in COD test. Up to the date, no study on degradation of TCW by the AOP processes has been reported. The present study was therefore undertaken to examine the degradation of TCW by combination of advanced oxidation processes.

2. Materials and methods

2.1. Wastewater characteristics

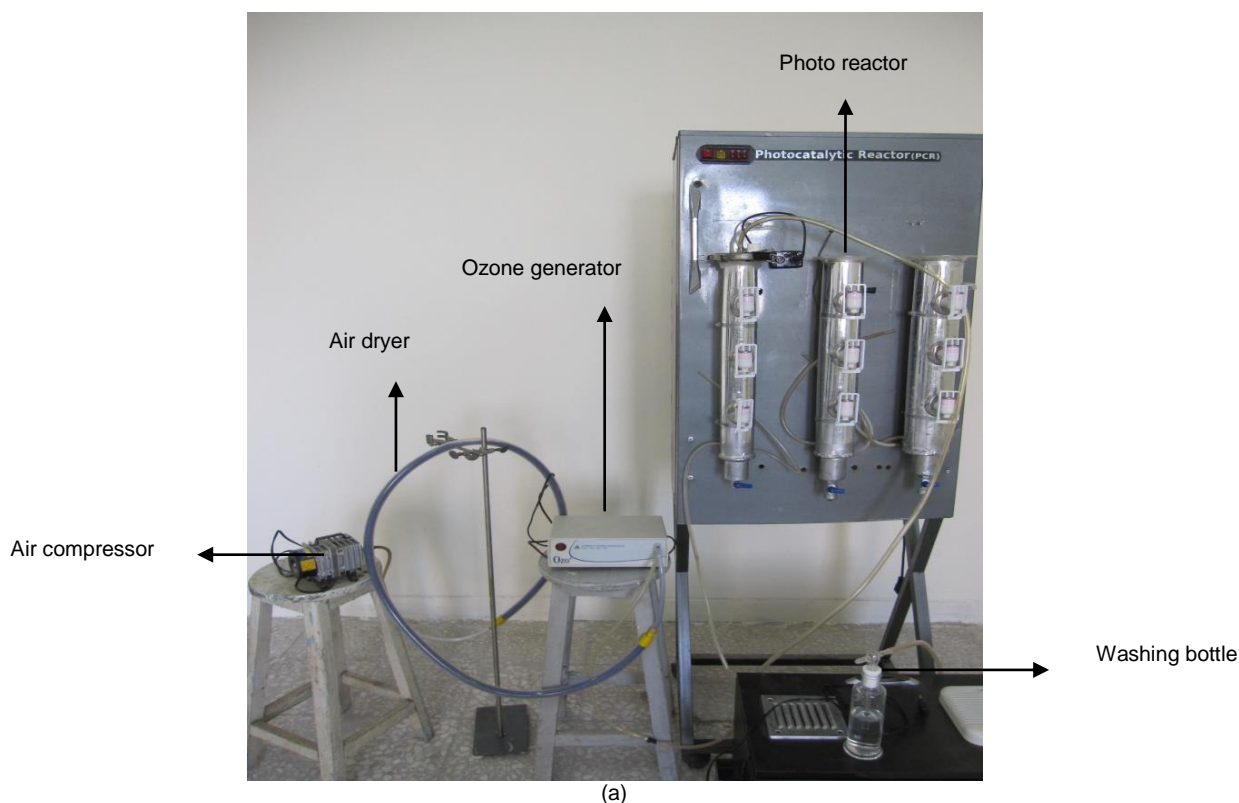
Tire Cord production wastewater (TCW) was taken from a working Co. Producing Tire Cord, Kermanshah, Iran. The characteristics of the TCW are shown in Table 1.

Table 1. Characteristics of Tire Cord manufacturing wastewater

Parameters	Unit	Amount
TCOD	(mg/l)	450-500
BOD ₅	(mg/l)	80-100
TSS	(mg/l)	120-360
pH	-	7-7.8

2.2. Experimental set-up

The experimental set-up used for treatment of tire cord wastewater (TCW) by the advanced oxidation processes consists of an air compressor, air dryer, ozone generator, photo reactor and a washing bottle (Figs. 1a and b). Fig. 1a represents an image of the experimental setup used in this study. The air dryer consisted of a column which was filled with a high adsorptive molecular sieve (silica). Ozone was generated using a laboratory ozonizer, Model COG, 1G/L. 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). The air flow rate was adjusted at 5 L/min. The ozone content of the input air stream was measured as $0.27 \text{ g O}_3/\text{h}$. The cylindrical steel reactor had a 5 cm diameter with a total volume of 1450 ml (with lamp) in which the solution was introduced at the bottom. The irradiation in the photo reactor was obtained by a 15 W UV 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 3.5 cm. The reactor was followed by a washing bottles, containing 250 ml of acidified 2 % KI solution for determining of unreacted ozone at influent and effluent in several times.



(a)

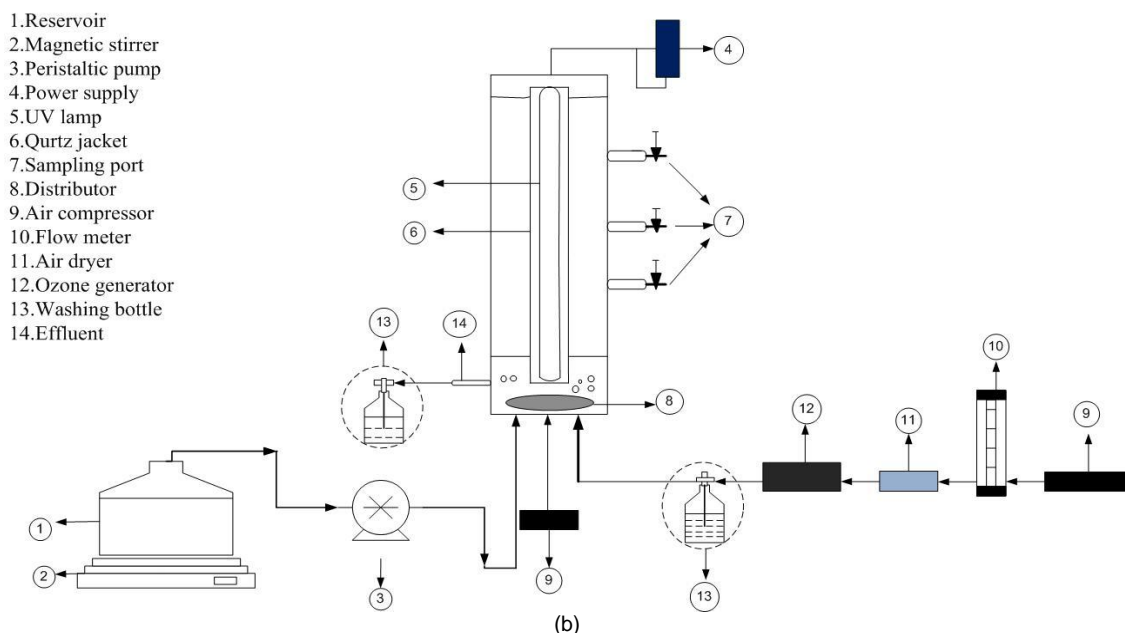


Fig. 1. Laboratory-scale experimental set-up (a) photo reactor, (b) Schematic diagram of the experimental set-up.

2.3. Photo reactor operation

In experimental runs, 1450 mL of TCW with COD concentration 500 mg/L was loaded in the photo reactor. The experiments were performed at selected solution pH which was left uncontrolled during the reaction. The selected solution pHs were 3, 5, 7, 9 and 11. For those runs where the initial pH had to be adjusted, this was done by adding the appropriate amount of 1M NaOH or 1M HCl solutions, as necessary. Concentration of H_2O_2 was selected to be 0, 5, 10, 15 and 20 mM. Categorical variables (ozonation and UV irradiation) were used in several runs by turned on the UV lamp and injection of the ozone in the photo reactor. Air was continuously sparged in the reaction mixture with flow rate of 5 L/min. The ozone content of the input air stream was measured as 0.27 g O_3 /h. The ozone of offgas was also measured and the consumed ozone was obtained (3.68 g ozone_{consumed}/ gCOD_{removed}).

2.4. Experimental design

Effects of four independent factors (initial H_2O_2 concentration and initial pH, ozonation and UV irradiation) on the process performance were investigated. The response surface methodology (RSM) used in the present study was a general factorial design involving two 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 is shown in Table 2. The experimental conditions are presented in Table 3. All experiments were carried out in batch mode in terms of wastewater input. COD removal and BOD₅/COD ratio were dependent responses. The results were completely analyzed using analysis of variance (ANOVA) which was performed by Design Expert Software (version 6.0, State-Ease, Inc., Minneapolis, MN).

Table 2. Experimental range and levels of the independent variables

Type of variables	Variables	Range and levels				
		-1	-0.5	0	+0.5	+1
Numerical	A-Initial pH	3	5	7	9	11
	B- H_2O_2 Conc.	0	5	10	15	20
Categorical	C-Ozonation	Without	-	-	-	With
	D-UV irradiation	Without	-	-	-	With

2.5. Analytical methods

The samples analyzed by GC/MS using an Agilent 6890N (0.25 lm, 30 m) capillary column. Oven conditions: 110 °C (2 min), 200 °C (4 min), 20 °C /min, 250 °C (2 min), 40 °C /min. Injector temperature set up to 180 °C, source temperature 250 °C. Helium (Infra, chromatographic purity) was used as carrier gas at 1 psi of pressure. Main products were identified by comparing their mass spectra with those in NIST library. All the chemicals used in the analysis were analytical grade (Merck, Darmstadt, Germany). Chemical oxygen demand (COD) was measured according to the Standard Methods. A colorimetric method with closed reflux method was developed. Spectrophotometer (DR 5000, Hach, Jenway, USA) at 600 nm was used to measure the absorbance of COD samples. A pH meter (JENWAY 3510) was used for pH measurement. Biodegradability was measured by 5-day biochemical oxygen demand (BOD₅) test in a BOD meter (OxiTop IS 6) according to the Standard Methods (American Public Health Association 1999).

In the runs with H_2O_2 , MnO_2 powder was used for elimination of the interference of residual H_2O_2 in COD test. Then, the sample was centrifuged to remove MnO_2 powders; the supernatant was used for COD test (Sousy et al. 2007).



The ozone dosage was determined by an iodometry method using a washing bottle containing 2 wt % KI solution (Nyangiro 2003).

3. Results and discussion

3.1. Process performance

3.1.1. Statistical analysis

In this study, relationship between the two numerical independent variables (initial H_2O_2 concentration and initial pH) and two categorical factors (ozonation and UV irradiation) and two process responses (COD removal efficiency and BOD₅/COD ratio) for the TCW photo oxidation process were determined using response surface methodology (RSM). The ANOVA results for all responses have been summarized in Table 4. In order to quantify the curvature effects, the data from the experimental results were fitted to higher degree with cubic model. The model terms in the equations are after elimination of insignificant variables and their interactions. Based on the statistical analysis, the models were highly significant with very low probability values (<0.0001). It was shown that the models terms of independent

variables were significant at the 99% confidence level. The square of correlation coefficient for each response was computed as the coefficient of determination (R^2). It showed high significant regression

at $\geq 90\%$ confidence levels. The value of the adjusted determination coefficient (adjusted R^2) was also high to prove the high significance of the model.

Table 3. Experimental conditions for advanced oxidation process

Run No.	Factor1 A: Initial pH	Factor2 B: H ₂ O ₂ concentration, mmol/l	Factor3 C: Ozonation	Factor4 D: UV irradiation	Run No.	Factor1 A: Initial pH	Factor2 B: H ₂ O ₂ concentration, mmol/l	Factor3 C: Ozonation	Factor4 D: UV irradiation
1	3	0	1*	1	27	7	10	1	2
2	3	0	2*	2	28	7	10	1	2
3	3	0	1	2	29	7	10	1	2
4	3	0	2	1	30	7	10	1	2
5	3	20	1	1	31	7	10	1	2
6	3	20	2	2	32	7	10	2	1
7	3	20	1	2	33	7	10	2	1
8	3	20	2	1	34	7	10	2	1
9	5	10	1	1	35	7	10	2	1
10	5	10	2	2	36	7	10	2	1
11	5	10	1	2	37	7	15	1	1
12	5	10	2	1	38	7	15	2	2
13	7	5	1	1	39	7	15	1	2
14	7	5	2	2	40	7	15	2	1
15	7	5	1	2	41	9	10	1	1
16	7	5	2	1	42	9	10	2	2
17	7	10	1	1	43	9	10	1	2
18	7	10	1	1	44	9	10	2	1
19	7	10	1	1	45	11	0	1	1
20	7	10	1	1	46	11	0	2	2
21	7	10	1	1	47	11	0	1	2
22	7	10	2	2	48	11	0	2	1
23	7	10	2	2	49	11	20	1	1
24	7	10	2	2	50	11	20	2	2
25	7	10	2	2	51	11	20	1	2
26	7	10	2	2	52	11	20	2	1

1* without applying the categorical variable 2* with applying the categorical variable

Adequate precision is a measure of the range in predicted response relative to its associated error or, in other words, a signal-to-noise ratio. Its desired value is 4 or more. The value was found more than 30. Simultaneously, low values of the coefficient of variation (CV) ($>5\%$) indicated good precision and reliability of the experiments as suggested

by Kuehl (2000), Khuri and Cornell (1996). The predicted versus actual plots for the two responses, COD removal and BOD₅/COD ratio is shown in Figs. 2a and b, respectively. These plots indicate an adequate agreement between real data and the ones obtained from the models.

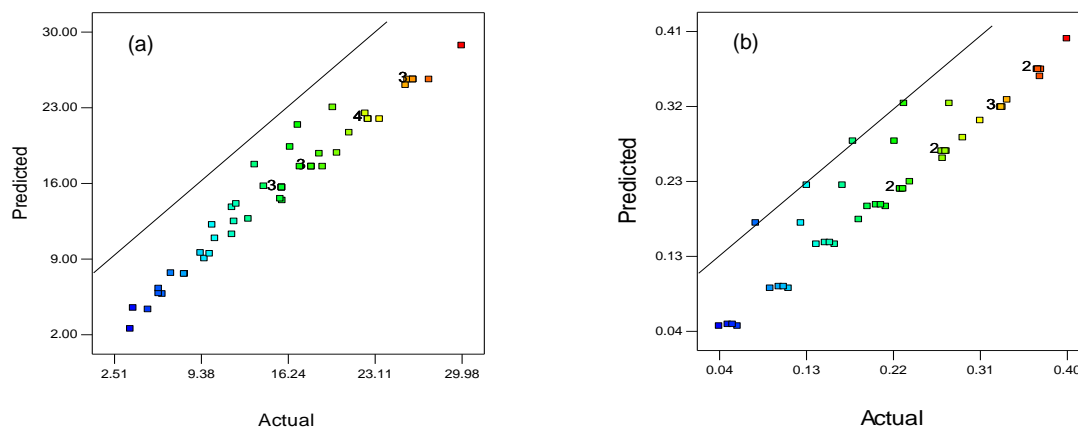


Fig. 2. Predicted vs. actual values plots for (a) COD removal, (b) BOD₅/COD ratio.

3.1.2. COD removal

In this process, COD was measured as a response representing the organic content of the TCW. Figs. 3a and b illustrate the COD removal as a function of initial pH and H₂O₂ concentration at the conditions with and without the categorical variables, respectively. Relationship between the response and the variables is described by the Eq. 4.

$$\text{COD removal} = 20.15 - 6.27A + 1.63B + 3.60C + 1.40D - 0.917AB + 0.431CD - 12.07B^2 + 6.25AB^2 - 1.525B^2C \quad (4)$$

where, A is initial pH, B is H₂O₂ concentration, C is ozonation and D is UV irradiation. From the Eq. 4, terms B, C and D had a positive effect on the response while term A had a negative effect on the response. As can be seen in the Figs., H₂O₂ concentration showed a reverse impact on the response; an increasing effect at low concentration (0-10 mmol/l) and a decreasing effect at higher concentration (10-20 mmol/l). While for initial pH; a decreasing effect on the process response was found except at the conditions with the lowest and highest levels of H₂O₂ concentration which showed no effect. As seen in the Fig. 3 a (UV/O₃/H₂O₂), maximum COD removal efficiency was found to be about 32% for the H₂O₂ concentration 10 mmol/l and initial pH 3. In other side,

minimum COD removal obtained 13% at H_2O_2 concentration 20 mmol/l and initial pH 11. Whereas, under conditions with no ozonation and UV irradiation, the range of changes in the response was 6 to 20 % at H_2O_2 concentration 20 mmol/l and initial pH 11 and H_2O_2 concentration 10 mmol/l and initial pH 3, respectively (Fig. 3 b). In the both systems, minimum efficiency was found at the highest level of H_2O_2 concentration (20 mmol/l). This may be due to auto-decomposition of H_2O_2 to oxygen and water and the recombination of OH^\cdot radicals. Since OH^\cdot radicals

react with H_2O_2 , H_2O_2 itself contributes to the OH^\cdot scavenging capacity. Therefore, H_2O_2 should be added at an optimal concentration to achieve the best degradation (Crittenden et al. 1999; Ghaly et al. 2001; Im et al. 2012). According to the Fig. 3 a, an enhancement of the COD removal was achieved by adding ozone and UV to the hydrogen peroxide in the solution under the $\text{O}_3/\text{UV}/\text{H}_2\text{O}_2$ process with a COD/ H_2O_2 (w/w) ratio equal to 1.5.

Table 4. ANOVA for response surface models applied.

Response	Modified Equations with significant terms	Probability	R^2	Adj. R^2	Adeq. precision	S.D.	CV	PRESS
Advanced oxidation process								
COD removal	20.15-6.27A+1.63B+3.60C+1.40D-0.917AB+0.431CD-12.07B ² +6.25AB ² -1.525B ² C	<0.0001	0.9611	0.9528	40.48	1.48	9.24	121.37
BOD ₅ /COD	0.289-0.076A+0.050C+0.023D-0.168B ² +0.077AB ²	<0.0001	0.9030	0.8925	31.77	0.03	14.22	0.06

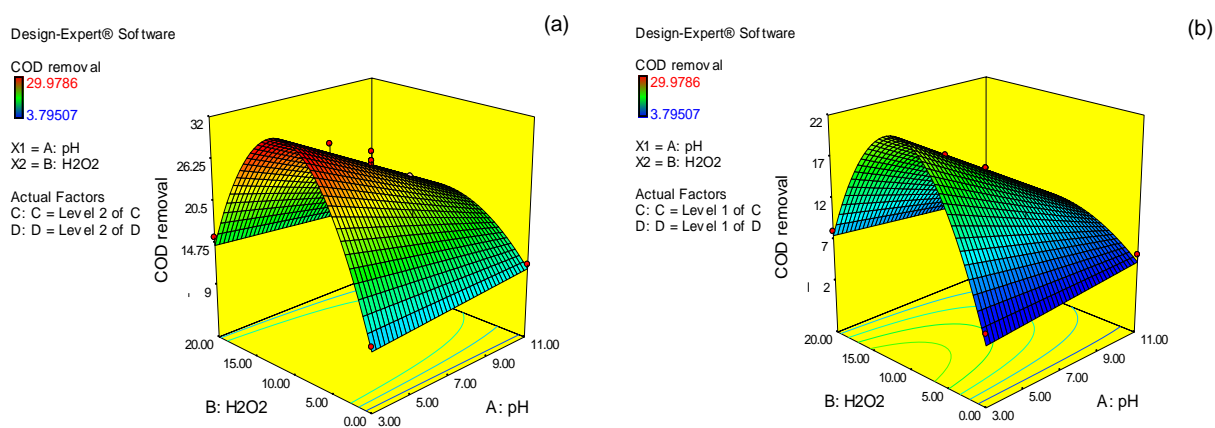


Fig. 3. Response surface plots for COD removal in (a) with and (b) without ozonation and UV irradiation.

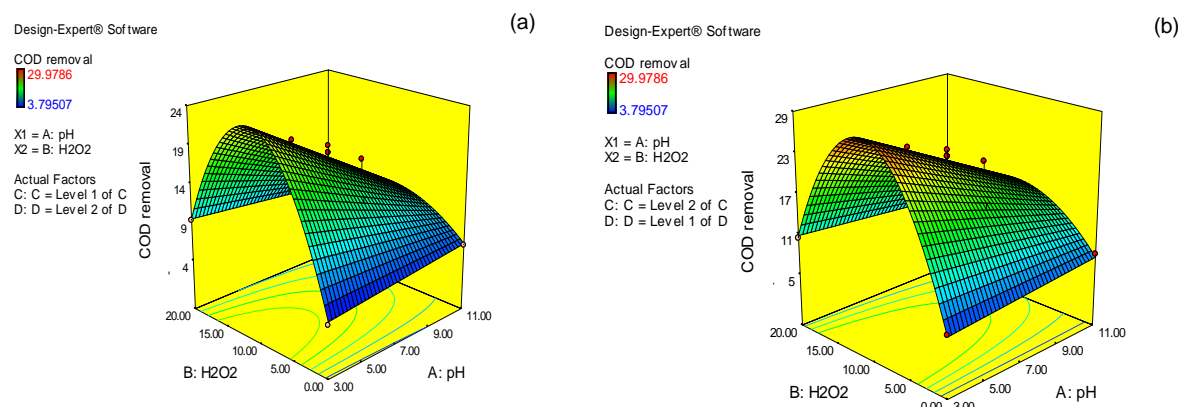


Fig. 4. Response surface plots for COD removal (a) without ozonation and with UV irradiation (b) with ozonation and without UV irradiation.

Figs. 4a and b illustrate the COD removal as a function of initial pH and H_2O_2 concentration at different conditions of ozonation and UV irradiation. As is seen in the Figs., ozonation showed to be a bit more effective in comparison with UV irradiation. In the $\text{UV}/\text{H}_2\text{O}_2$ system, the

COD removal efficiency can be considered to occur mainly through its reaction with highly oxidizing OH^\cdot which is produced by the photolysis of H_2O_2 (Safarzadeh-Amiri 2001). More studies were performed with $\text{O}_3/\text{H}_2\text{O}_2$ and $\text{UV}/\text{H}_2\text{O}_2$ processes for degradation of different

compounds. As a result, O_3/H_2O_2 process showed to be more effective than the UV/H_2O_2 process in terms of COD removal efficiency (Ghaly et al. 2001; Safarzadeh-Amiri 2001; Sanchez-Polo et al. 2007; Guedes Maniero et al. 2008).

In order to clarify the interactive effects of the variables studied, interactive graphs were prepared as shown in Figs. 5a-f and 6a-d. Figs. 5a-f depict interactive effects of DC (UV irradiation-ozonation) on COD removal at different values of pH and H_2O_2 concentration. As illustrated in the Figs., in all conditions, D (UV irradiation) had a slight constant

increasing interaction on C effect. It proves this fact that O_3/H_2O_2 system increases the kinetics of ozone decay and accelerates its transformation into OH (Katsoyiannis et al. 2011). The principal species reacting with and oxidizing compounds in the O_3/H_2O_2 process are molecular ozone and hydroxyl radicals. The decomposition of ozone catalyzed by hydroperoxide (HO_2) generates hydroxyl radicals (Safarzadeh-Amiri 2001). By comparing the Figs., the synergistic effect of the combined system ($O_3/UV/H_2O_2$) showed the maximum COD removal at pH 3 and H_2O_2 concentration 10 mmol/l.

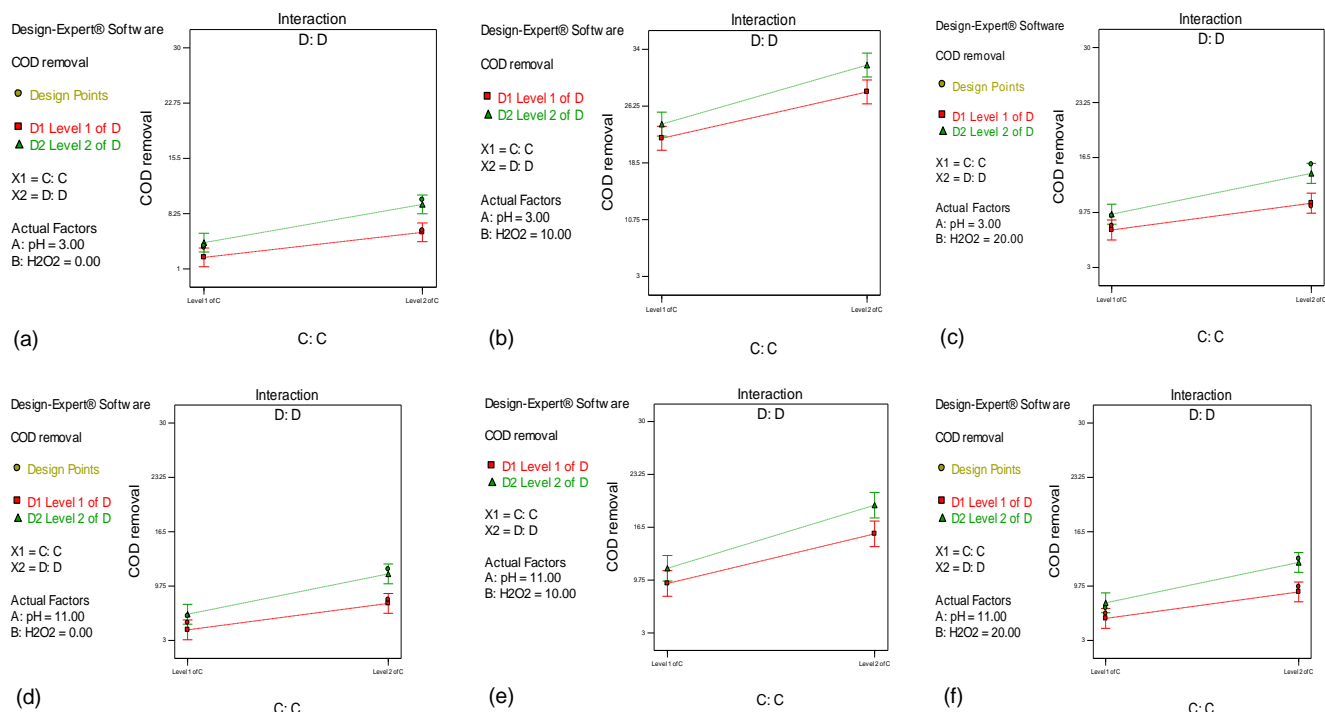


Fig. 5. Interactive effects of DC (UV irradiation-ozonation) on COD removal at different pH and H_2O_2 concentration.

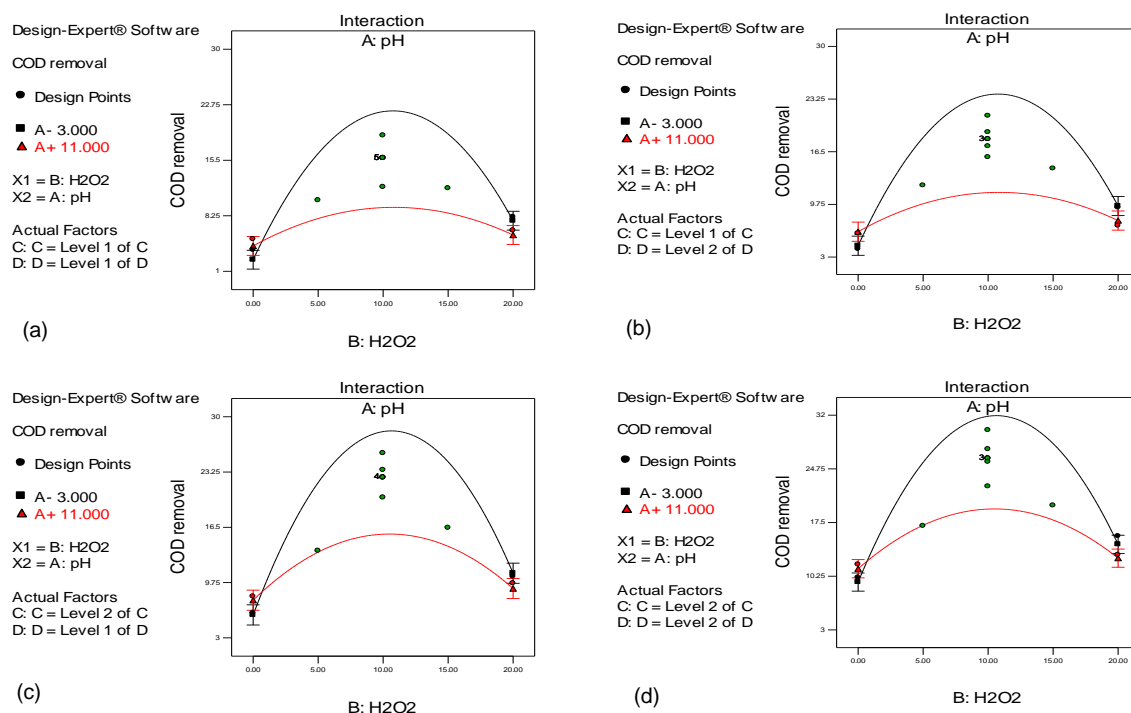


Fig. 6. Interactive effects variable AB (initial pH- H_2O_2 concentration) on COD removal at different conditions of ozonation and UV irradiation.

Figs. 6a-d represent the interactive effect of pH- H_2O_2 on the response in the different conditions studied. As mentioned earlier, pH had a significant effect on the process performance in terms of COD removal which the interactive effect of AB (pH- H_2O_2) proves this matter

as shown in the Figs. The dissociated form of hydrogen peroxide (HO_2) in alkaline media reacts with hydroxyl radicals more than two orders of magnitude faster than hydrogen peroxide does. Higher pH values slightly enhance the decomposition of hydrogen peroxide for the same

reason. Furthermore, the molar extinction coefficient of HO_2^- is more than ten times greater than that H_2O_2 (with the same quantum yield as H_2O_2), and thus increases the hydrogen peroxide decomposition (Crittenden et al. 1999). Therefore, best degradation efficiency was obtained at acidic condition.

In summary, the effectiveness of the different AOPs examined removing COD content of TCW at neutral pH is shown in Fig. 7. As presented in the Fig., the order of the processes in terms of COD removal efficiency is as follow: $(\text{H}_2\text{O}_2/\text{O}_3/\text{UV}) > (\text{H}_2\text{O}_2/\text{O}_3) > (\text{H}_2\text{O}_2/\text{UV}) > (\text{H}_2\text{O}_2)$. Maximum COD removal efficiencies obtained 26.16, 22.59, 18.11 and 14 %, respectively at 10 mM of H_2O_2 . The best COD/ H_2O_2 (w/w) ratio was determined 1.5.

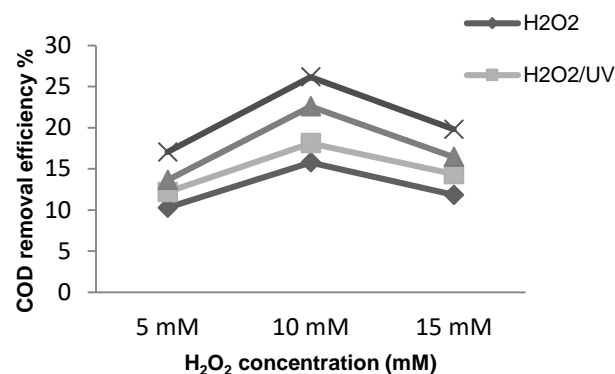
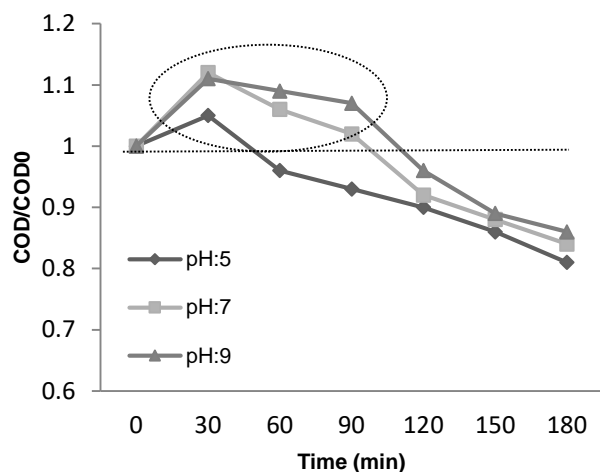
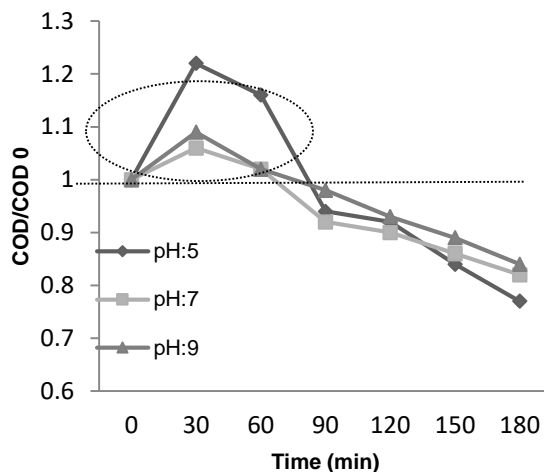


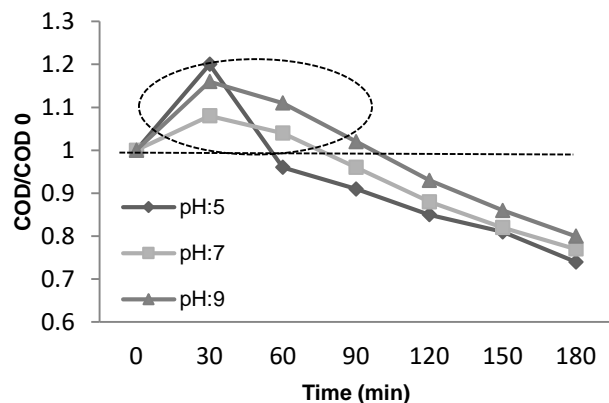
Fig. 7. Performance of different AOPs treating TCW.



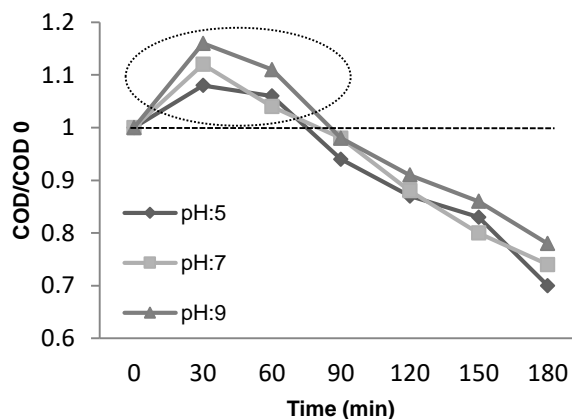
(a)



(b)



(c)



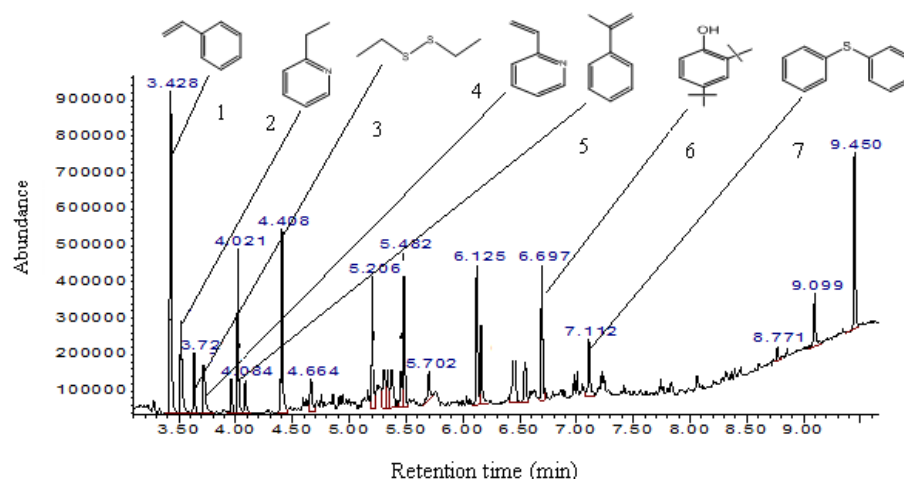
(d)

Fig. 8. Changes in COD/COD₀ versus reaction time at (a) H_2O_2 alone, (b) $\text{H}_2\text{O}_2/\text{UV}$, (c) $\text{H}_2\text{O}_2/\text{O}_3$ and (d) $\text{H}_2\text{O}_2/\text{O}_3/\text{UV}$

COD concentration was measured every 30 min up to 180 min for all the experiments. In order to investigate the trend of COD reduction during the reaction time, the COD to COD₀ ratio versus reaction time was drawn for few selected conditions (at 10 mM of H_2O_2 and different pH) as shown in Figs. 8a-d. Increase in the ratio at the beginning times indicates the presence of some recalcitrant and refractory organic compounds in TCW which probably are not detected in the COD test (e.g. pyridine 2-ethyl, styrene, pyridine 2-ethenyl and etc.). So that, by progressing the time the compounds are broken to intermediates that observed in the COD test and caused a decrease in the COD removal

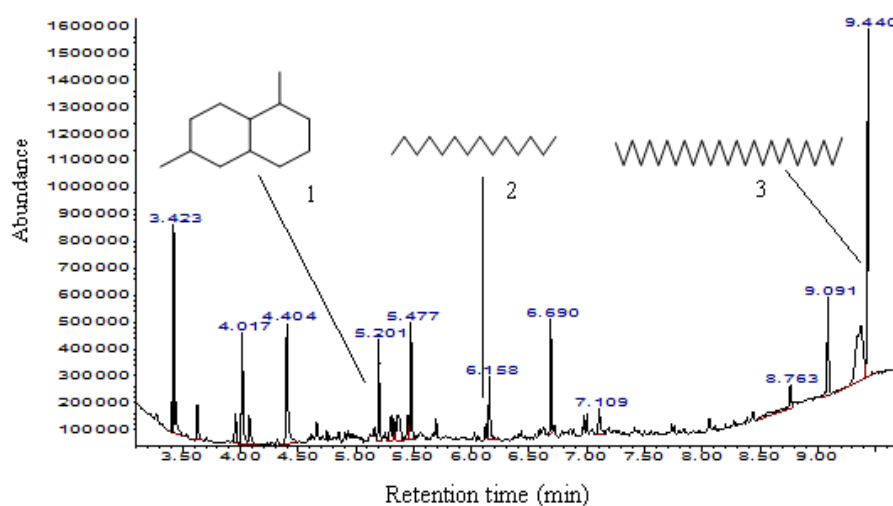
efficiency. As observed in the Figs., thereafter degradation of the refractory compounds, the COD/COD₀ was decreased, implying increase in COD removal efficiency. The abovementioned claim was approved by results obtained from GC-MS analysis of the samples.

Fig. 9 represents GC-MS chromatogram of raw TCW sample. The GC-MS analysis confirmed the aforementioned points, so that, the raw wastewater samples contained some recalcitrant and refractory organic compounds which are not detectable in COD test. Table 5 presents these compounds and peak area obtained from the GC-MS analysis.



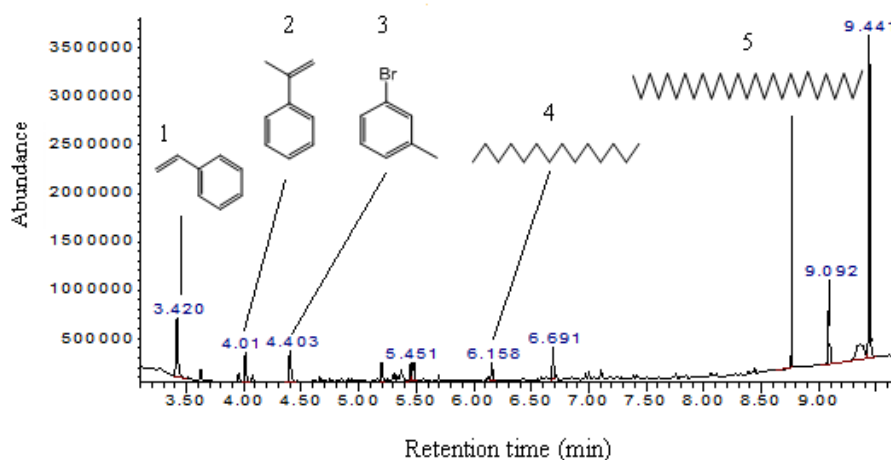
Peak identities are as follows: 1: Styrene, 2: Pyridine 2-ethyl 3: Diethyl disulfide, 4: Pyridine 2- ethenyl, 5: Alpha-methyl styrene, 6: Phenol, 2,4-bis (1,1-dimethylethyl, 7: Diphenyl sulfide

Fig. 9. GC-MS analysis of raw TCW.



Peak identities are as follows: 1: Naphthalene decahydro-1,6-dimethyl, 2: Tetradecane, 3: Heptacosane.

(a)



Peak identities are as follows: 1: Styrene, 2: Alpha methyl styrene, 3: Benzene, 1-bromo-3 methyl, 4: Tetradecane, 5: Heptacosane.

(b)

Fig. 10. GC-MS analysis of organic contaminants in the oxidized TCW by (a) H_2O_2/O_3 at pH 9 and (b) H_2O_2 at pH 5.

Table 5. Details of GC-MS chromatogram of raw TCW.

Type of component	Peak height	Corr. Area
Styrene	902125	9816363
Pyridine 2-ethyl	230586	3142783
Pyridine 2-ethenyl	168635	2336464
Diethyl disulfide	145155	1484417
Alpha methyl styrene	425891	4157105
n-Decane	86184	942783
Benzene, 1-bromo-3 methyl	511086	5637735
Naphthalene,decahydro-1,6-dimethyl	400884	4166187
Naphthalene,decahydro-2,3-dimethyl	140133	2175645
Cyclo undecene,1.methyl	204772	1837840
7-Heptadecene,17-chloro	98631	1062907
Tetradecane	209160	2190089
Phenol,2,4-bis(1,1-dimethylethyl)	378149	3412067
Diphenyl sulfide	147090	1878328
1-monolinoleoylglycerol trimethylsilyl ether	36928	429615
Heptacosane	487483	4861025

Table 6. Details of GC-MS chromatogram of two treatment processes.

Type of treatment	Type of component	Peak height	Corr. Area	Degradation %
H ₂ O ₂ /O ₃ at pH 9	Diethyl disulfide	136294	1404791	5.36
	Alpha methyl styrene	383321	4155120	0.048
	Benzene, 1-bromo-3 methyl	430634	5482166	2.76
	Naphthalene,decahydro-1,6-dimethyl	94245	1307860	68.61
	Tetradecane	93926	1281441	41.49
	Heptacosane	321369	3212407	33.92
	Styrene	596855	7460985	23.99
H ₂ O ₂ at pH 5	Alpha methyl styrene	286660	3066820	26.23
	Benzene, 1-bromo-3 methyl	316744	3783160	32.90
	Cyclo undecene,1.methyl	180367	1666486	9.32
	Naphthalene,decahydro-1,6-dimethyl	346351	3470103	16.71
	Tetradecane	185331	1725886	21.20
	Phenol,2,4-bis(1,1-dimethylethyl)	313331	2710295	20.57
	Heptacosane	173604	980132	79.84

In order to trace the fate of the components, two samples after 180 min were analyzed by GC-MS and the results were compared with the raw TCW. Fig. 10a and b shows the GC-MS chromatogram for these samples. Table 6 presents the peak area obtained from the GC-MS analysis. From the Table, the ratio of peak area for a specific compound showed degradation percentage achieved. As observed, some of recalcitrant compounds (e.g. Pyridine 2-ethyl, and Pyridine 2-ethenyl) were disappeared after the photo oxidation process. The other compounds were relatively degraded as shown in the Table.

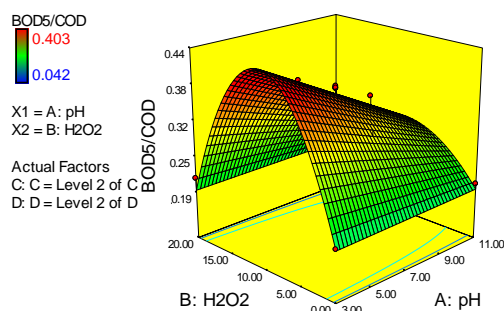
3.1.3. BOD₅ to COD ratio

Since one of the aims to apply the photo oxidation process is to increase the BOD₅/COD ratio, the ratio was determined to indicate biodegradable fraction of COD at the end of each experiment (after 180 min) as another response. Relationship between the response and the variables is described by the Eq. 5.

$$\text{COD removal} = 0.289 - 0.076A + 0.050C + 0.023D - 0.168B^2 + 0.077AB^2 \quad (5)$$

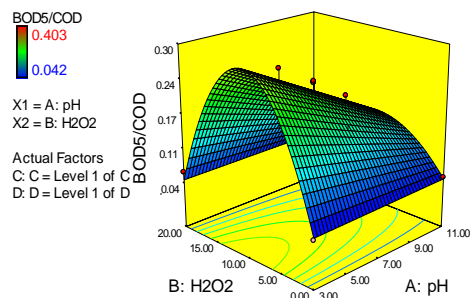
From the Eq. 5, terms C and D had a positive effect on the response while term A had a negative effect on the response. Figs. 11a and b represent the changes in the BOD₅/COD ratio as a function of the initial pH and H₂O₂ concentration at the conditions with and without the categorical variables, respectively. As can be seen in the Figs., similar trends as obtained for COD removal were observed for the BOD₅/COD ratio. As seen in the Fig. 11a, maximum BOD₅/COD ratio was found to be 0.41 at the conditions with H₂O₂ concentration of 10 mmol/l and initial pH of 3. Minimum ratio of BOD₅/COD determined 0.21 for the H₂O₂ concentration 20 mmol/l and initial pH 11. Figs. 12a and b illustrate the BOD₅/COD ratio as a function of initial pH and H₂O₂ concentration at the conditions without ozonation, with UV irradiation and with ozonation, without UV irradiation, respectively. Similar trends but with different amount were found. It showed effect of ozonation was more compared to UV irradiation. As be seen in the Fig. 12 b, maximum BOD₅/COD ratio was found to be 0.37, where ozonation was applied at H₂O₂ concentration of 10 mmol/l and initial pH of 3.

Design-Expert® Software



(a)

Design-Expert® Software



(b)

Fig. 11. Response surface plots for BOD₅/COD ratio at (a) with (b) without of ozone and UV irradiation.

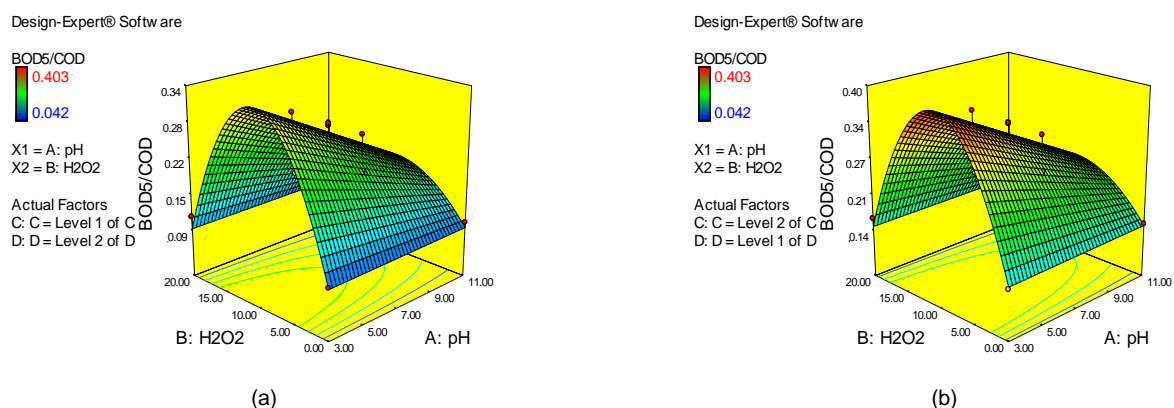


Fig. 12. Response surface plots for BOD₅/COD ratio at (a) without ozonation and with UV irradiation (b) with ozonation and without UV irradiation.

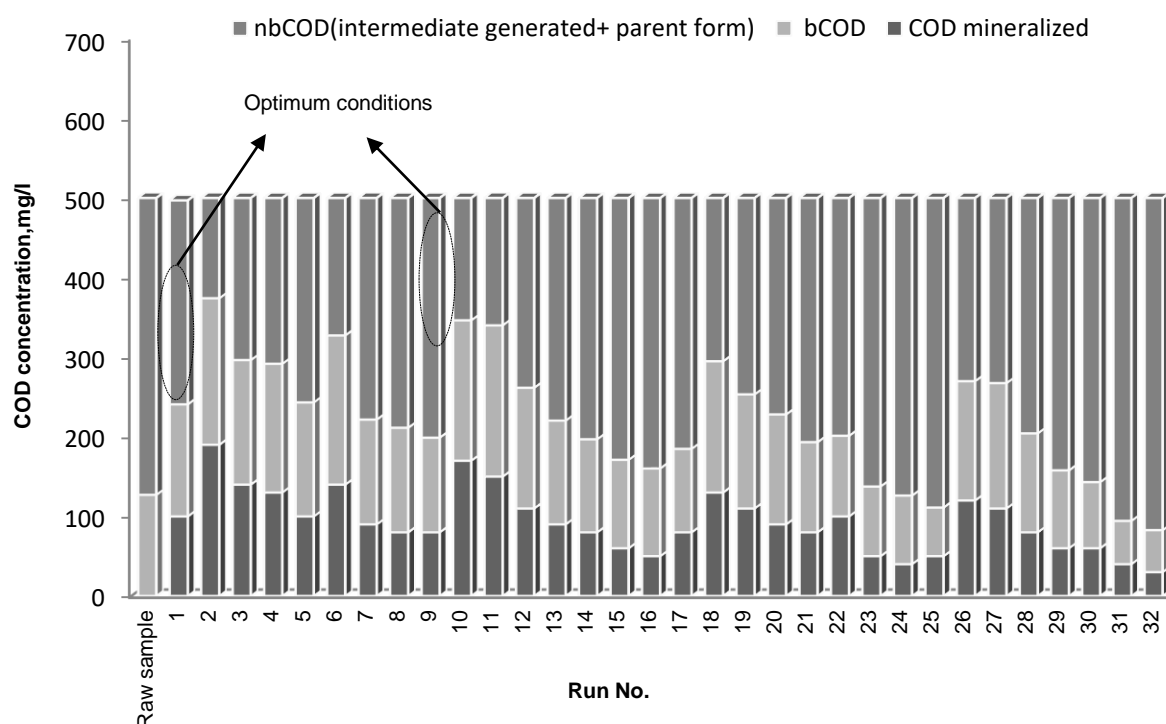


Fig 13. COD fractionation for the samples after the treatment process.

As the ratio of BOD₅/COD for the raw TCW was determined to be about 0.1-0.2. In order to monitor the fate of COD contents in the samples after the treatment processes, different fractions of the COD is represented in Fig. 13. Fig. 13 has been drawn according to the experiments number as presented in Table 7. As specified in the Fig., maximum mineralization and bCOD fraction were observed at experiments no. 2 and 10 (the operating conditions are presented in the Table 7).

4. Conclusions

This research work showed that the advanced oxidation processes could be applicable for treatment of Tire Cord wastewaters. However, it needs more studies in details to introduce the best practice. The main aims in use of advanced oxidation processes for treatment of refractory wastewaters can be COD mineralization and/or COD to BOD conversion which could be well achieved in this study. It is noted that the when UV irradiation or ozonation were combined with hydrogen peroxide, the process performance in terms of COD removal efficiency increased compared to that of hydrogen peroxide alone treatment. O₃/H₂O₂ process showed to be a bit more effective in comparison with UV/H₂O₂ process. As a result, higher performance was obtained at

H₂O₂ concentration 10 mM and initial pH 3 with 25% COD removal efficiency. The best result was obtained by using O₃/UV/H₂O₂ system at same condition with 32%. At low H₂O₂ concentration, UV/O₃/H₂O₂ combination improved the oxidation performance slightly, but showed an inhibitory effect at H₂O₂ concentrations higher than 10 mM. The maximum ratio of BOD₅/COD was found 0.41 in the UV/O₃/H₂O₂ system. The O₃/H₂O₂ found more economical; nevertheless, its performance is slightly low related to others. In the basis of the results obtained, the photo oxidation processes applied could be used as a pretreatment method prior a biological treatment process. And also, other advanced oxidation processes are recommended to be examined.

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Table 7. Order of experiments number according to operating conditions.

Run No.	Types of treatment	H ₂ O ₂ concentration (m mol/l)	Initial pH
1	H ₂ O ₂ / O ₃ / UV	5	7
2		10	3
3		10	5
4		10	7
5		10	9
6		15	7
7		20	3
8		20	11
9	H ₂ O ₂ / O ₃	5	7
10		10	3
11		10	5
12		10	7
13		10	9
14		15	7
15		20	3
16		20	11
17	H ₂ O ₂ / UV	5	7
18		10	3
19		10	5
20		10	7
21		10	9
22		15	7
23		20	3
24		20	11
25	H ₂ O ₂	5	7
26		10	3
27		10	5
28		10	7
29		10	9
30		15	7
31		20	3
32		20	11

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