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RESEARCH ARTICLE

Turbidity and COD removal from leather processing effluents using TiO_2–assisted photocatalytic-ozonation by response surface methodology

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ABSTRACT

In the present study, concurrently removal of COD and turbidity from leather processing effluents (LPE) using TiO_2–assisted photocatalytic-ozonation were investigated by utilization of Box-Behnken design (BBD) in planning experiments. Effects of ozone dose (OD, mg L^{-1}), catalyst dose (CD, g L^{-1}), and aeration (A, mL min^{-1}) were performed as explanatory variables. An increase both in doses of ozone and catalyst and a decrease in aeration leaded increases both in removals of COD and turbidity. Values of 96.77% and 95.37% were obtained as the highest COD and turbidity removal efficiencies, respectively. This showed that TiO_2-assisted photocatalytic-ozonation process was significantly effective for the treatment of LPE. By using BBD, 2.95 g L^{-1} of CD, 19.99 mg L^{-1} of OD, and 1.63 mL min^{-1} of A were determined as BBD-optimized operating conditions. BBD suggested removals of 96.77% and 94.93% for COD and turbidity, respectively at these optimized conditions. Validation experiments at BBD-optimized conditions were resulted as 95.52%±1.28 and 94.36%±2.52 for COD removal and turbidity removal, respectively. Good agreement between predicted values and experimental results demonstrated the accuracy of BBD in optimization of explanatory variables of TiO_2-assisted photocatalytic-ozonation process. Finally, multiple non-linear regression (MNLR) studies were performed to state the variation in responses and also to predict the responses. The proposed models predicted COD and turbidity removals with regression coefficients of 99.99% and 99.97%, respectively. These findings also showed that MNLR was an efficient way to model and to predict the response variables of photocatalytic-ozonation process.

Keywords: Leather processing effluents, Photocatalytic-ozonation, COD, Turbidity, Empirical modeling

1. INTRODUCTION

Increase in human population in recent years has triggered the technological developments in all fields in industries. Leather as a developing industry, uses a lot of chemical compounds to process leather before their product is presented to customers' satisfaction. While leather is being processed, tons of effluents including toxic and hazardous chemicals are being occurred. Discharging these effluents before a complete treatment will cause a serious environmental problem. Thus, treatment of leather effluent before discharging has gained an importance to be addressed [1-5].

A lot of various methods for treatment of industrial effluents have been extensively investigated by researcher such as adsorption, coagulation, activated carbon, and etc. Although some good results have been obtained by these traditional methods, some negative situations are generally come together with them like desorption and long time to reach equilibrium. Unlike, advanced oxidation processes (AOPs) such as photocatalytic degradation, ultrasound, Fenton, and etc. can remove effluents in a short time period. Ozone can be also added into AOPs due to its advantages of highly effective and easy operating conditions. So, treatment of leather processing effluents (LPE) by incorporating photocatalytic degradation and ozone may contribute to related literature significantly in terms of novelty. By this way, a hybrid process is created and its effects on removal efficiency may be compared [6-10]. For example, ultrasonic degradation was incorporated with mineralization and detoxification for removal of diclofenac from wastewater [6]. Similarly, dielectric

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barrier discharge plasma process was utilized in some kind of advanced oxidation processes [7]. Additionally, sonolysis was used in both homogeneous and heterogeneous medium with various catalysts [10].

Designing experiments, determination of levels of operating conditions, and decreasing cost can be stated as ones of the most important steps in data-driven studies. To meet this criteria, design of experiments (DOEs) can be utilized. Response surface methodology (RSM) as a kind of DOEs provides a cost-effective way to investigate the related system with minimum runs. Box-Behnken design (BBD) as a kind of RSM is generally chosen for operating conditions without fraction. It is mostly set with three of four explanatory variables with three levels, three replicates, and one duplicate. By this way, response variable(s) can be predicted by regression analyses, the effects of explanatory variables can be compared by ANOVA, and operating conditions can be optimized by numeric techniques. Considering the advantageous sides of BBD, incorporating ozone-based photocatalytic treatment of LPE with BBD can contribute to related literature significantly [11-14].

The purpose of the present study can be summarized considering the literature survey given above as follows: (1) investigation of performance of TiO_2–assisted photocatalytic-ozonation process in treatment of LPE, (2) quantification of the effects of catalyst dose, ozone dose, and aeration, (3) prediction of COD and turbidity removals using multiple non-linear regression models, and (4) optimization and validation of explanatory variables.

2. MATERIALS AND METHOD

2.1. Leather processing effluents

Leather processing effluents (LPE) were provided from the discharge point of a local leather processing plant in Gerede, Bolu, Turkey. Its properties were listed in Table 1. Any pretreatment procedure was not applied to the effluents and they were directly used in the experiments.

2.2. Photocatalytic ozonation process

This process was formed incorporating a cylindrical photoreactor made from stainless steel with an ozone generator coupled to an oxygen tube. Additionally, a UV lamb, an air pump and a magnetic stirrer with heater were also utilized. Photoreactor with a certain volume of 1.25 L was put onto magnetic stirrer vertically and UV-C lamb (235 nm, Philips, 20 cm, 11 W) was put in it. Air pump that could pump up to 50 mL min^{-1} was connected to process using a glass-tube. Detailed information on photocatalytic process could be reached from the related paper [14]. By this way, air was sent to system from below to above. Likewise, ozone generator that could produce an ozone amount from 8 mg L^{-1} to 32 mg L^{-1} by decreasing flow rates from 5 mL min^{-1} to 0.5 mL min^{-1} was adopted to photoreactor. Schematic illustration of the related process was given in Fig 1.

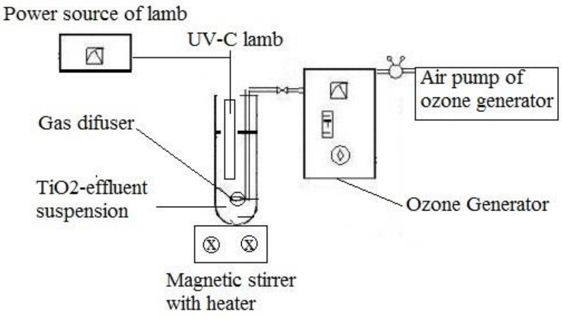


Fig 1. Schematic presentation of photocatalytic-ozonation process.

2.3. Catalyst

Although TiO_2 could be synthesized by various simple ways, it was purchased from Merck in anatase form with a purity of 99% and it was used in the experiments without any purification. Because, synthesis of a novel catalyst and characterization and/or comparison of it with other catalysts were out of scopes of the present study.

2.4. Response surface methodology

Box-Behnken design (BBD) as a kind of response surface methodology (RSM) was used to decrease both error probability and cost, and to predict both the COD and turbidity removals. It was set up with three explanatory variables of ozone dose (OD, mg L^{-1}), catalyst dose (CD, g L^{-1}), and aeration (A, mL min^{-1}) with three replicates and one duplicate. This approach suggested 15 experiments to investigate the variations in response variables. Levels of explanatory variables and the experimental schedule were concurrently given in Table 2. For all statistical approaches, Design Expert 9.0.6 (Statease) software was utilized. Additionally, Minitab 17 (Minitab, PA) was used to correlation calculations.

2.5. Turbidity and COD analyses

A similar procedure for COD analysis was followed that Buyukada (2017) performed [14]. COD removal was analyzed using COD measuring kits (Hach LCI 400, 0-1000 mg L^{-1} O_2). 2 mL of effluent was added into kit and then it was heated at 150oC for 2 hours in a digester (Hach 200). After it, it was left to get cool at room temperature. Blank sample was obtained by following the same procedure with 2 mL of destile water and it was used to calibrate UV-spectrophotometer. Finally, a UV spectrophotometer (Hach 2000) based on a barcode system was utilized to determine the COD values of each samples. Difference between the COD values of initial and treated samples were divided to initial COD values for converting the results to percentage. Turbidity (T, NTU) was analyzed using a turbidimeters (Micro TPI, Scientific Inc.) and the same percentage procedure that was used for COD was applied to data.

3. RESULTS AND DISCUSSION

3.1. Effects of operating parameters

3.1.1. Effect of catalyst dose (CD, g L^{-1} TiO_2)

A positive correlation between CD and COD removal ($p = 0.007$; $r = 0.120$; $n = 15$) and turbidity removal ($p = 0.005$; $r = 0.762$; $n = 15$) was determined according to results. Thus, increasing CD resulted an increase in both COD and T removals. Increasing CD from 1 g L^{-1} to 3 g L^{-1} increased COD and T removal from 52% to 63% and 40% to 48%, respectively under the experimental conditions of 15 mg L^{-1} of OD and 20 mL min^{-1} of A. These results showed the positive effect of CD on both COD and turbidity removals. The effect of CD on removal of COD and turbidity was visually given in Fig 2. Similarly, oxidation of a drug with ozone in aqueous media was studied in related literature and removal efficiency of 85% was obtained [17]. Furthermore, diclofenac removal was aimed in another study using photocatalytic ozonation and 89% was obtained as COD removal efficacy [15]. These findings were in good agreement with related literature [15-18].

Table 1. Chemical properties of leather effluents

COD (mg L^{-1} O_2)	TNb (mg L^{-1})	TOC (mg L^{-1})	Abs (IU)	pH	Conductivity (μS cm^{-1})	Turbidity (NTU)	Color (m^{-1})
384.3	12.1	216.5	0.968	6.8	1265	9.6	452

Table 2. Levels of explanatory variables and experimental schedule

		Explanatory variables			Response variables	
	Levels of variables	OD (mg L^{-1})	CD (g L^{-1})	A (mL min^{-1})	COD removal (%)	Turbidity removal (%)
	Min. (-1)	10	1	0	0	0
	Med. (0)	15	2	5	-	-
	Max. (+1)	20	3	10	100	100
Standard run	Randomly run	OD (mg L^{-1})	CD (g L^{-1})	A (mL min^{-1})	COD removal (%)	Turbidity removal (%)
8	1	20	2	20	58.81	47.27
3	2	10	3	10	90.85	78.76
15	3	15	2	10	93.53	76.43
11	4	15	1	20	52.09	40.01
5	5	10	2	0	94.45	88.86
4	6	20	3	10	93.58	81.99
14	7	15	2	10	93.40	76.41
12	8	15	3	20	62.63	48.26
1	9	10	1	10	85.00	73.90
7	10	10	2	20	55.19	45.69
9	11	15	1	0	96.03	89.86
6	12	20	2	0	96.77	95.37
13	13	15	2	10	93.49	76.39
2	14	20	1	10	88.61	78.78
10	15	15	3	0	95.90	89.96

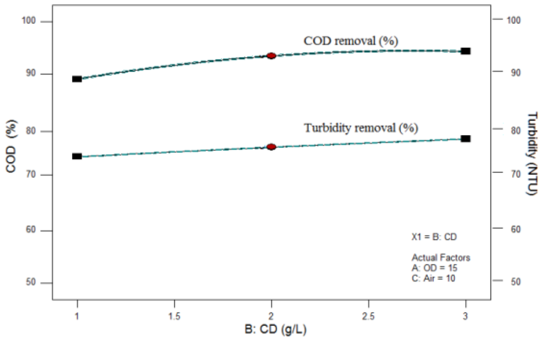


Fig 2. The effect of CD on COD and turbidity removal

3.1.2. Effect of ozone dose (OD, mg L^{-1} O_3)

Similar findings of CD were obtained for the effect of OD on removal of COD and turbidity. A positive correlation between OD and COD removal ($p = 0.009$; $r = 0.806$; $n = 15$) and turbidity removal ($p = 0.004$; $r = 0.765$; $n = 15$) was determined according to results. Thus, increasing OD triggered an increase in both COD and turbidity removals. Increasing OD from 10 g/L to 20 g L^{-1} increased COD and turbidity removal from 90% to 94% and 78% to 81.8%, respectively under operating conditions of 3 g L^{-1} of CD and 10 mL min^{-1} of A. These results showed the positive effect of OD on both COD and turbidity removal. This synergistic effect was figured out in Fig 3. In a similar study, ultrasound assisted ozonation was utilized for wastewater treatment and COD removal of 70% was obtained [19]. Additionally, UV–assisted hydrogen peroxide was used for the treatment of pharmaceutical effluents and an approximate COD removal of 80% was obtained [20]. Results of related literature showed a fairly similarity with the results of present study [19, 20].

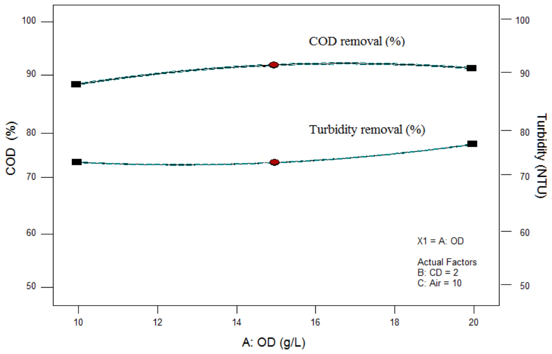


Fig 3. The effect of OD on COD and turbidity removal

3.1.3. Effect of aeration (A, mL min^{-1})

A powerful and also negative correlation between A and COD removal ($p < 0.001$; $r = -0.872$; $n = 15$), and turbidity removal ($p < 0.001$; $r = -0.952$; $n = 15$) were obtained according to experimental results. These findings pointed out a certain decrease in COD and turbidity removals while A was increasing. A decrease from 94.5% to 55.2% in COD removal and from 88.9% to 45.7% in turbidity removal were obtained by increasing A from 0 mL min^{-1} to 20 mL min^{-1} under 10 mg L^{-1} of OD and 2 g L^{-1} of CD. These results were also illustrated in Fig 4. Fenton process was utilized in related literature for diclofenac removal and this resulted in terms of COD removal of 70% [21]. A similar study of [21], photo–assisted Fenton process was utilized for the same aim and 80% of COD removal was obtained [22]. Similar results were obtained by various studies [21-23].

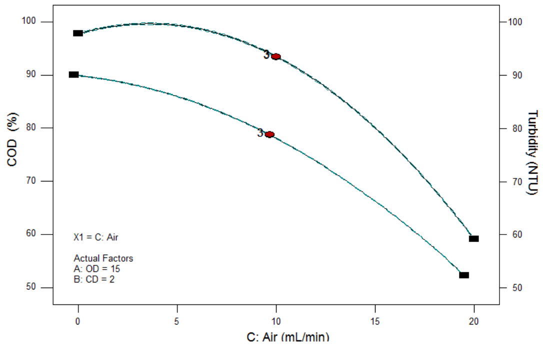


Fig 4. The effect of A on COD and turbidity removal

3.2. Characteristic findings on Box Behnken design (BBD)

To determine the optimum model type, sequential model sum of squares, lack of fit test, and model summary statistics were concurrently incorporated. All the obtained results were given in Table 3. Model type showed that the quadratic model was the best way to predict the response variables considering the choosing criteria of p [11]. As much as lower p could be stated as a better p. Thus, quadratic model was firstly suggested by the results of sequential model findings (Table 3) [12]. Lack of fit could be stated as an indicator that showed the sustainability and it demonstrated the reasonable and significant sides of proposed model. To meet this criteria, lack of fit must be greater than 0.05, in another terms it must be insignificant [13]. It was totally clear that only quadratic model had a lower p value than 0.05 (Table 3). Summary statistics were generally used to take general information about predictive power of suggested models. The highest regression coefficients could guide for selection of the optimum model type. Table 3 showed that the highest regression coefficient of 99.99% was obtained for quadratic model. Thus, quadratic model was selected to identify the variation in response variables and also to predict the response variables [11-13].

3.3. Diagnostic findings based on ANOVA results

Some assumption such as there was no autocorrelation and data had a normal probability were also tested before statistical modeling. To test these criteria, externally studentized predicted vs. actual graph (Fig 5) and normal probability plot (Fig 6) were drawn, respectively [13, 14]. As seen from Fig 5 and 6, there was no autocorrelation and experimental data showed a normal distribution.

Table 3. Characteristic findings on Box Behnken design

Sequential model sum of squares for COD removal

Source	Squares	df	Square	Value	Prob > F	Decision
Mean vs. Total	104,200,000	1	104,200,000			
Linear vs. Mean	3056.27	3	1018.76	12.94	0.0006	
2FI vs. Linear	29.08	3	9.69	0.093	0.9620	
Quadratic vs. 2FI	836.65	3	278.88	27948.77	< 0.0001	Suggested
Cubic vs. Quadratic	0.041	3	0.014	3.08	0.2544	Aliased
Residual	0.008867	2	0.004433			
Total	108,100,000	15	7209.58			

Lack of fit tests for COD removal

Source	Squares	df	Square	Value	Prob > F	
Linear	865.77	9	96.20	21698.39	< 0.0001	
2FI	836.69	6	139.45	31454.41	< 0.0001	
Quadratic	0.041	3	0.014	3.08	0.2544	Suggested
Cubic	0.000	0				Aliased
Pure Error	0.008867	2	0.004433			

Model summary statistics for COD removal

Source	Std. Dev.	R2	R2adj	R2pred	PRESS	
Linear	8.87	0.7793	0.7191	0.6051	1548.96	
2FI	10.23	0.7867	0.6267	0.1910	3172.75	
Quadratic	0.100	1.0000	0.9999	0.9998	0.68	Suggested
Cubic	0.067	1.0000	0.9999			Aliased

Sequential model sum of squares for turbidity removal

Source	Squares	df	Square	Value	Prob > F	
Mean vs. Total	78907.56	1	78907.56			
Linear vs. Mean	4244.40	3	1414.80	42.35	< 0.0001	
2FI vs. Linear	23.36	3	7.79	0.18	0.9063	
Quadratic vs. 2FI	344.13	3	114.71	28046.35	< 0.0001	Suggested
Cubic vs. Quadratic	0.020	3	0.006550	16.38	0.0581	Aliased
Residual	0.0008	2	0.0004			
Total	83519.48	15	5567.97			

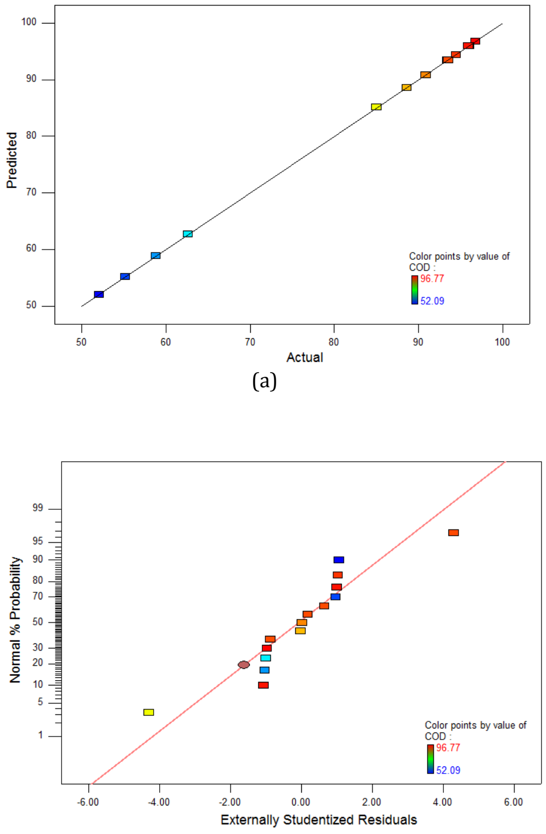
Lack of fit tests for turbidity removal

Source	Squares	df	Square	Value	Prob > F	
Linear	367.51	9	40.83	102,100,000	< 0.0001	
2FI	344.15	6	57.36	143,400,000	< 0.0001	
Quadratic	0.020	3	0.0006550	16.38	0.0581	Suggested
Cubic	0.000	0				Aliased
Pure Error	0.0008	2	0.0004			

Model summary statistics for turbidity removal

Source	Std. Dev.	R2	R2adj	R2pred	PRESS	
Linear	5.78	0.9203	0.8986	0.8391	742.16	
2FI	6.56	0.9254	0.8694	0.6435	1644.01	
Quadratic	0.064	0.9999	0.9999	0.9999	0.32	Suggested
Cubic	0.020	0.9999	0.9999			Aliased

ANOVA results were given in Table 4. According to Table 4, all the linear effects of CD, A, and OD were found significantly effective on both COD and turbidity removals ($p < 0.001$). Additionally quadratic effects of all explanatory variables were also significantly effective on COD removal ($p < 0.001$) and turbidity removal ($p < 0.0044$). Furthermore, three significant binary interaction between A and OD ($p = 0.0013$ for COD and $p < 0.001$ for turbidity), A and CD ($p < 0.001$ for COD and $p < 0.001$ for turbidity), and OD and CD ($p < 0.0070$ for COD and $p < 0.001$ for turbidity) were found as significantly effective parameters. The visual presentation of these binary interactions were given in Fig 7 and Fig 8 for COD and turbidity removals, respectively.



(a)

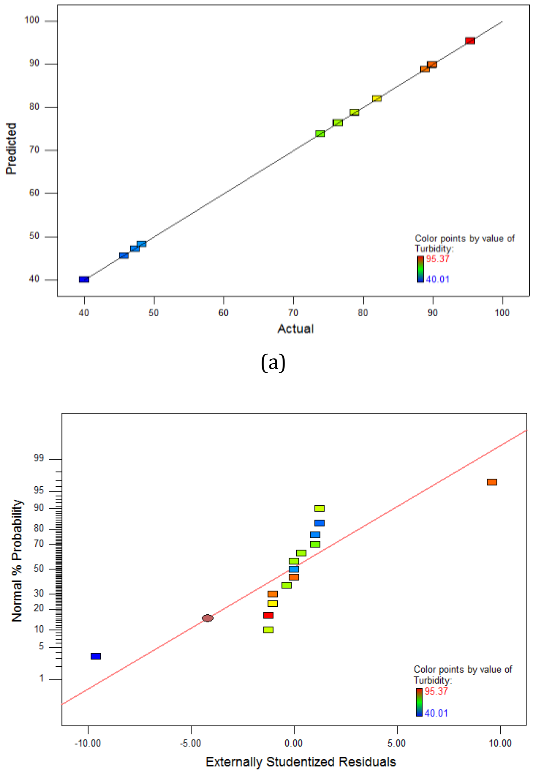
(b)

Fig 5. Externally studentized graph for (a) COD removal (b) turbidity removal

3.4. *Optimization and validation*

To maximize the COD and turbidity removals, a numeric optimization procedure was followed. Considering the results obtained for linear effects of explanatory variables, “in range” section was selected for OD and CD unless “minimize” was selected for A. At the same time “maximize” function was also selected for both COD and turbidity removal considering interpolation (not extrapolation of experimental results). 19.99 mg L^{-1} of OD, 2.95 g L^{-1} of CD, and 1.63 mL min^{-1} of A were determined as RSM-optimized operating conditions. RSM suggested COD removal of 96.77% and turbidity removal of 94.03% at this conditions.

Finally, proposed multiple non-linear regression models were given in Table 5. Adjusted and predicted regression coefficients of 99.99% for COD and turbidity removals demonstrated the powerful side of proposed model in statement of variation and in prediction.



(a)

(b)

Fig 6. Normal probability plot of (a) COD removal (b) turbidity removal

Validation experiments were performed under RSM-optimized conditions for three times to prevent experimental error and also to calculate standard deviation. 95.52%±1.28 for COD removal and 94.36%±2.52 for turbidity removal were obtained. The findings of this part of present study seemed to be in good accordance with related literature [11-14]. These results demonstrated that RSM was a successful method for optimization of operating parameters of TiO_2-assisted photocatalytic ozonation process. Good accordance between predicted values and experimental results justified the accuracy of RSM in optimization.

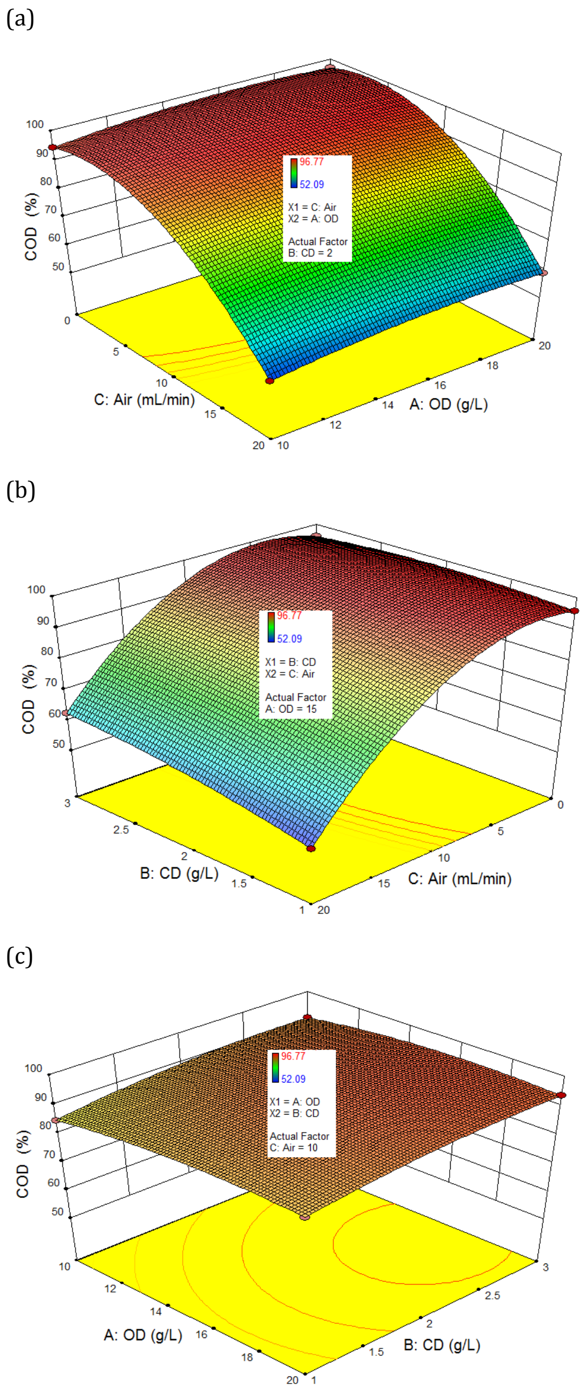


Fig 7. Binary interactive effects of (a) A and OD, (b) A and CD, and (c) OD and CD on COD removal

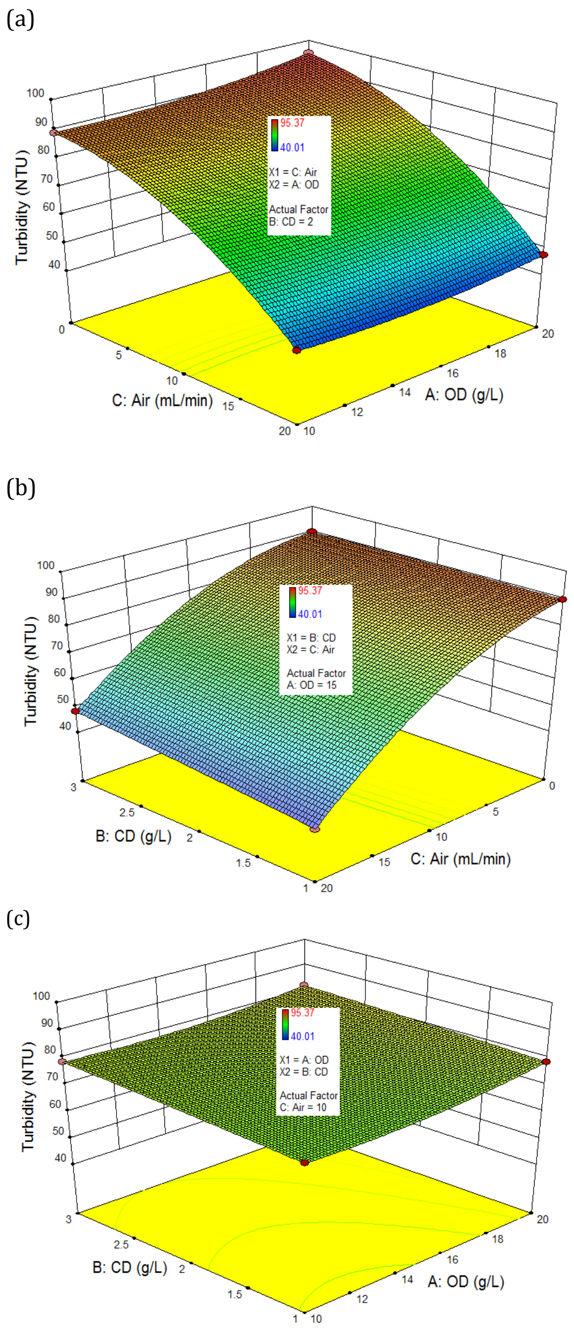


Fig 8. Binary interactive effects of (a) A and OD, (b) A and CD, and (c) OD and CD on turbidity removal

Table 4. ANOVA results based on Box Behnken design

COD removal						
Source	Squares	df	Square	Value	Prob > F	
Model	3921.99	9	435.78	43672.31	< 0.0001	significant
A-OD	18.85	1	18.85	1889.07	< 0.0001	
B-CD	56.34	1	56.34	5646.14	< 0.0001	
C-Air	2981.08	1	2981.08	298,800,000	< 0.0001	
AB	0.19	1	0.19	19.40	0.0070	
AC	0.42	1	0.42	42.34	0.0013	
BC	28.46	1	28.46	2852.40	< 0.0001	
A^2	17.23	1	17.23	1727.09	< 0.0001	
B^2	12.00	1	12.00	1202.79	< 0.0001	
C^2	831.65	1	831.65	83345.22	< 0.0001	
Residual	0.050	5	0.009978			
Lack of Fit	0.041	3	0.014	3.08	0.2544	not significant
Pure Error	0.008867	2	0.004433			
Cor Total	3922.04	14				
Turbidity removal						
Model	4611.89	9	512.43	125,300,000	< 0.0001	significant
A-OD	32.80	1	32.80	8020.78	< 0.0001	
B-CD	33.70	1	33.70	8240.11	< 0.0001	
C-Air	4177.89	1	4177.89	1,021,000,000	< 0.0001	
AB	0.68	1	0.68	166.41	< 0.0001	
AC	6.08	1	6.08	1485.63	< 0.0001	
BC	16.61	1	16.61	4060.06	< 0.0001	
A^2	16.46	1	16.46	4023.96	< 0.0001	
B^2	0.099	1	0.099	24.21	0.0044	
C^2	314.13	1	314.13	76805.02	< 0.0001	
Residual	0.020	5	0.00409			
Lack of Fit	0.020	3	0.00655	16.38	0.0581	not significant
Cor Total	4611.91	14				

Table 5. Predictors of proposed MNLR models

Predictors	COD removal		Turbidity removal	
	Coded	Actual	Coded	Actual
Intercept	93.47	66.19	96.11	76.41
A-OD	1.53	2.92	2.02	1.72
B-CD	2.65	7.86	2.05	1.91
C-Air	-19.30	-0.44	-22.85	-0.48
AB	-0.22	-0.04	-0.41	-0.083
AC	-0.33	-0.007	-1.23	-0.025
BC	2.67	0.267	2.04	0.20
A^2	-2.16	-0.086	-2.11	-0.084
B^2	-1.80	-1.80	-0.16	-0.16
C^2	-15.01	-0.15	-9.22	-0.092

4. CONCLUSIONS

TiO_2-assisted photocatalytic ozonation process was used to remove COD and turbidity from LPE. Maximum COD removal of 96.77% and turbidity removal of 95.37% were obtained under the experimental conditions of 2 g L^{-1} TiO_2, 20 mg L^{-1} of O_3 and no aeration. These findings showed that this process was efficient for treatment of LPE. MNLR models predicted COD removal and turbidity removal with a regression coefficient of 99.99%. This demonstrated the powerful side of proposed models in predictions of removal efficiencies. Accuracy of RSM–based optimization process was justified by the results of validation experiments. RSM was found significantly effective in optimization of operating variables.

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