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Research Article

Integrated Advanced Ozonation Technologies for Enhanced Total Organic Carbon Removal from Secondary Treated Municipal Wastewater: Systematic Optimization and Environmental Analysis

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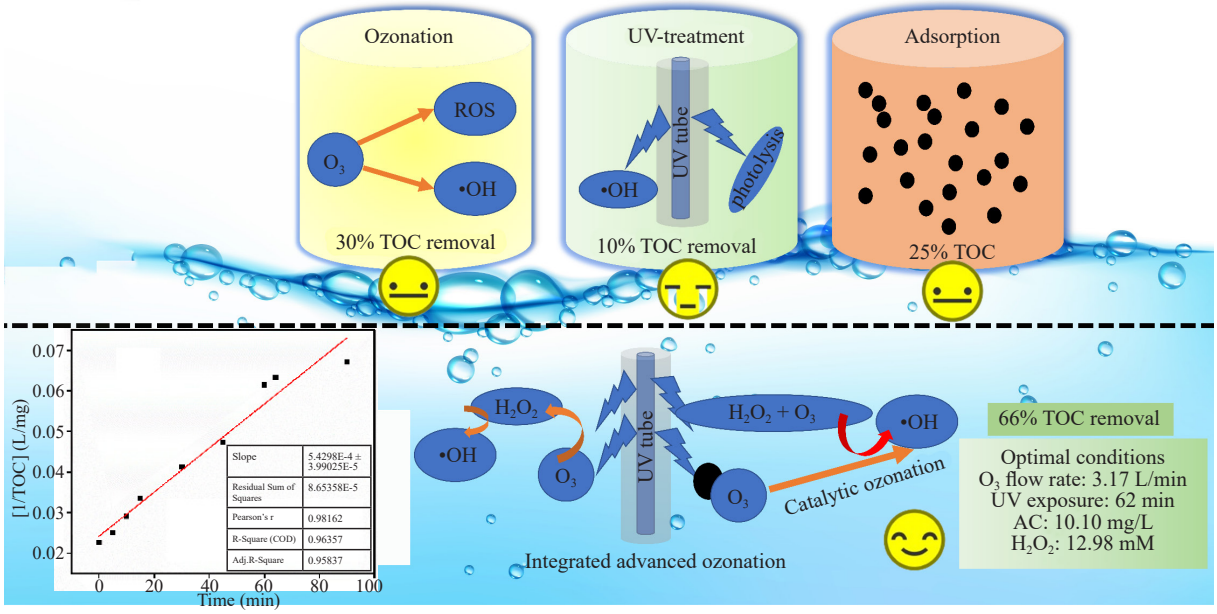
Graphical Abstract



Abstract: Municipal wastewater, characterised by a complex matrix of organic contaminants, poses significant environmental challenges due to residual total organic carbon (TOC), a critical marker of persistent organic pollutants, even after secondary treatment. To address this issue, the investigation evaluates the efficiency of integrated advanced ozonation technologies combining ozone (O_3), ultraviolet (UV) irradiation, hydrogen peroxide (H_2O_2), and activated

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carbon (AC) for TOC removal from secondary-treated effluent. A predictive model optimised the process parameters, achieving a maximum TOC removal efficiency of 65.95% at an O_3 flow rate of 3.17 L/min, H_2O_2 dosage of 12.98 mM, UV exposure duration of 62.04 min, and AC dosage of 10.10 mg/L. In contrast, the lowest TOC removal of 39.55% ± 2.15% occurred under sub-optimal conditions, with an O_3 flow rate of 3 L/min, H_2O_2 dosage of 10 mM, UV exposure for 20 min, and 1 mg/L of AC. The economic and environmental analyses revealed the integrated process to be more cost-effective and sustainable compared to conventional single-step treatments. These findings highlight the potential of integrated advanced ozonation technologies for effective TOC removal, providing a pathway for enhanced wastewater treatment practices and improved environmental sustainability.

***Keywords*:** adsorption, peroxone treatment, ozonation, total organic carbon removal, wastewater treatment

1. Introduction

Historically, wastewater has been treated using biological methods to decrease organic matter through microbial metabolism. However, these processes do not eliminate persistent organic compounds (POCs), resulting in total organic carbon (TOC) in treated wastewater.[1-4] These leftover organic compounds after secondary treatment comprise traces of personal care products, antibiotics, painkillers, pesticides, etc. Some of these compounds have endocrine disrupting properties; hence, the presence of these compounds, even at trace concentration, when secondary treated wastewater is released into the water body is a matter of deep concern. In this regard, advanced treatment technologies, including ozonation, UV treatment, adsorption, and peroxide treatment, have gained significant attention for removing TOC from biologically treated effluents.[5-9]

The ozonation process eliminates POCs from wastewater and breaks down diverse organic pollutants through direct ozone (O_3) attack or the production of hydroxyl radicals (•OH), which initiate chain reactions decomposing complex organic compounds into simpler and less toxic by-products.[10,11] However, the effectiveness of direct ozonation is limited due to its slow reaction rate constants ($1.0\text{-}10^6$ $M^{-1}s^{-1}$).[12] Therefore, incorporating UV treatment and Hydrogen peroxide (H_2O_2) as an oxidant into the ozonation process enhances the degradation of POCs by increasing •OH production and direct photolysis.[13] Additionally, integrating catalysts like activated carbon (AC) into the ozonation process enhances removal efficacy.[14] The extensive surface area and porous structure of AC provide numerous active sites for O_3 absorption and subsequent degradation reactions.[15,16]

The removal of TOC from wastewater, particularly from secondary treated effluents, remains a persistent challenge due to the complex matrix of organic contaminants. Advanced treatment methods, including ozonation, UV irradiation, H_2O_2, O_3/H_2O_2, AC, and catalytic ozonation, have demonstrated significant potential for addressing this issue.[17,18] Integrating these processes within a single reactor is proposed to exploit synergistic effects, potentially achieving greater TOC removal efficiency compared to individual applications. Recent investigations have focused on optimising integrated approaches to enhance treatment performance. For instance, Ren et al. demonstrated the benefits of combining O_3, H_2O_2, and UV irradiation for enhanced antibiotic removal, achieving a 33% higher efficiency compared to standalone ozone treatment.[18] Similarly, Yang and co-researcher investigated the combined application of UV, ozone, and peroxydisulphate for tetracycline removal, reporting a 2.3-folds improvement over UV/O_3 and a 3.2-fold increase compared to UV alone.[19] Moreover, catalytic ozonation has been extensively studied; Gong and co-researcher achieved 96% of dye removal within 40 min using modified activated carbon as a catalyst in ozonation.[17] However, a significant lacuna persists in the literature, as no studies have synergistically integrated activated carbon as a catalyst with the $O_3/UV/H_2O_2$ system, underscoring a critical gap in the optimisation of these advanced oxidation technologies for maximising TOC abatement.

The present investigation addresses a critical lacuna in wastewater treatment research by systematically evaluating the efficacy of an integrated ozonation system comprising O_3, UV irradiation, H_2O_2, peroxone, AC, and catalytic ozonation for tertiary treatment applications. Through the utilisation of response surface methodology (RSM), operational parameters were rigorously optimised to achieve maximal TOC removal efficiency. A detailed kinetic analysis elucidated the underlying reaction dynamics, while comprehensive economic and environmental evaluations affirmed the superior sustainability and cost-efficiency of the proposed system relative to conventional single-step

methodologies. These findings make a substantial contribution to the scholarly discourse on advanced wastewater treatment technologies by presenting a paradigm-shifting framework for integrated processes. The outcome furnishes pivotal insights for researchers, policymakers, and industry stakeholders, thereby facilitating decision-making aimed at enhancing environmental sustainability and advancing water resource management strategies.

2. Material and methods

2.1 *Secondary treated sewage sample*

In this investigation, secondary treated effluent from the sewage treatment facility located at the Indian Institute of Technology (IIT) Kharagpur campus was utilised. The treatment facility, with a capacity of 0.3 MLD, employs an up-flow anaerobic sludge blanket (UASB) reactor, anaerobic and aerobic moving bed biofilm reactor (MBBR), and lamella clarifier for sewage treatment. The TOC of the secondary treated effluent was monitored for a month using a TOC Analyzer (TOC-L, Shimadzu, Japan), yielding a consistent TOC value of 44 ± 5 mg/L.

2.2 *Experimental setup and operation*

Initial single-step investigations were conducted to determine boundary conditions for TOC removal using different technologies. A dedicated UV reactor unit with a 1 L glass beaker and an 8 W UV-C lamp (OSRAM, India) was employed for TOC reduction and optimising UV exposure time. For ozonation, a Yuwell 7F-5 oxygen concentrator and a Cecon ozone generator (Chennai, India) unit capable of producing 10 g of ozone per hour were employed. The process was optimised by adjusting the concentrated flow rate between 1 and 5 L/min using a flow controller, with residual ozone safely released into the atmosphere in 1 L glass reactor. Further, AC (Sigma, India) doses were optimised using a 1 L beaker containing the effluent for TOC adsorption. In addition, the H_2O_2 (30%) was also sourced from the local manufacturer (QUALIKEMS, India). For integrated ozonation, a single reactor was designed for UV/H_2O_2/O_3/AC treatment Figure 1.

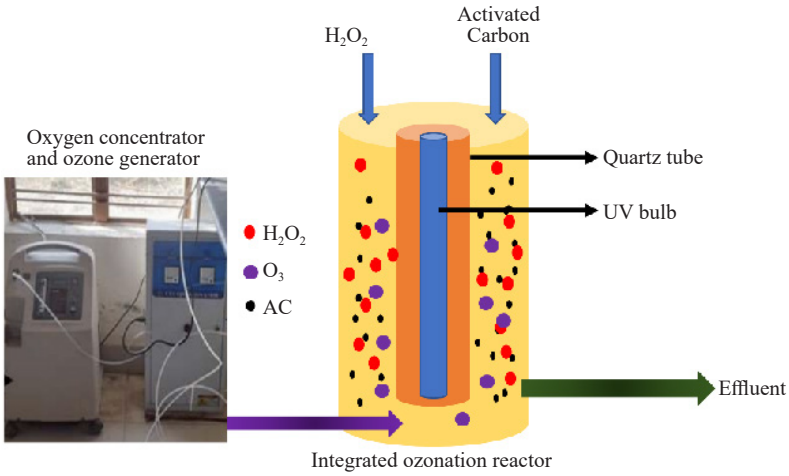

Figure 1. Schematic representation of the integrated ozonation reactor

The RSM was employed to optimise and analyse the treatment processes, and four factors were considered: O_3 flow, H_2O_2 concentration, UV exposure time, and AC dose for optimisation. The range of these factors for the RSM analysis was selected based on the initial investigation with a focus on TOC removal. The RSM was used to establish a mathematical relationship between these factors and experimental results for optimum TOC removal by fitting them to a second-order polynomial model (Eq. (1)).

$$\text{TOC Removal } = \alpha_1 + \alpha_2 A + \alpha_3 B + \alpha_4 C + \alpha_5 D + \alpha_6 A^2 + \alpha_7 B^2 + \alpha_8 C^2 + \alpha_9 D^2 + \alpha_{10} AB + \alpha_{11} AC + \alpha_{12} AD + \alpha_{13} BC + \alpha_{14} BD + \alpha_{15} CD \quad (1)$$

Where, α_n represents the coefficient of regression, A indicates the dose of O_3 (L/min), B designate the time (min) for UV exposure, C specifies the dose of AC (mg/L), and D is denoting to the dose of H_2O_2.

2.3 *Life cycle analysis*

The primary objective of the life cycle analysis (LCA) was to assess and compare the environmental footprint of the TOC removal technologies discussed in this investigation by adopting 1 g of TOC removal as the functional unit. The gate-to-gate system boundary for the assessment considers the energy and material consumption during the wastewater treatment. The primary data for compiling the life cycle inventory (LCI) was based on the experimental values, while the secondary data was adopted from the EcoInvent 3.8 database. Finally, the environmental impacts were estimated based on the ReCiPe 2016 (H) methodology and using SimaPro v9.4.0.2.

3. Results and discussion

3.1 *Step-wise optimisation*

3.1.1 *Ozonation*

The O_3, as an oxidising agent, selectively reacts with different organic compounds through direct oxidation with molecular ozone or indirectly via •OH.[20] Thus, in order to visualise the impact of the O_3 flow rate on the degradation of TOC, the experiment was performed by increasing the O_3 flow rate from 1 L/min to 5 L/min, which resulted in TOC removal rising from 21.27 ± 2.1% to 30.04 ± 1.5% within 60 min of reactor operation, respectively (Figure S1a in Appendix). These findings align with previous investigations; for instance, Dantas and co-researcher reported 18% TOC removal from synthetic wastewater with an O_3 dose of 1.5 L/min over 60 min.[21] Furthermore, the laboratory results were consistent with ANOVA one-way analysis of variance for the ozonation flow rate, observing less than a 10% variation in TOC removal from 1 L/min to 5 L/min of O_3 flow rate (Figure S1d in Appendix).

Higher O_3 concentrations facilitated by increased gas flow rates led to more TOC removal due to enhanced mass transfer and reaction kinetics, with the degradation rate constant increasing from 0.00436 to 0.00636 min^{-1}. The initial rapid TOC removal (19.19% in 20 min) followed by a plateau suggests O_3 saturation in the solution, where a further increase in O_3 concentration yielded diminishing returns. Thus, the results underscore the importance of optimising gas flow rates to enhance TOC removal efficiency in wastewater treatment.

3.1.2 *UV treatment*

Ultraviolet radiation is being utilized in UV treatment to generate •OH, degrading organic compounds in wastewater into simpler by-products.[22] Therefore, the UV treatment process was operated to assess TOC reduction over a period of 120 min. As reported in Figure S1b in Appendix, the first 15 min were particularly effective, with around 8% TOC reduction, highlighting the immediate efficacy of UV-induced photochemical processes. This rapid reduction can be attributed to the immediate impact of UV radiation on organic compounds.[23] However, over 120 min of UV exposure, the TOC concentration only decreased from 46.7 ± 7.5 mg/L to 42.2 ± 2.1 mg/L, indicating UV's inadequacy as a standalone technology for efficient TOC removal from secondary treated effluent. The minimal TOC reduction suggests the presence of refractory organics, necessitating a more potent oxidant or an integrated treatment approach. Further, the ANOVA analysis validates the investigation, as the central design points are distributed within the 95% confidence band, with a 10% difference in TOC removal during the increase in UV exposure from 20 min to 90 min (Figure S1e in Appendix).

3.1.3 *Activated carbon*

The dose of *AC* was optimised, revealing that increasing the *AC* dose from 10 to 20 g/L improved TOC removal, reaching nearly 77.39 ± 5.21% from 28.24 ± 3.72% (Figure S2c in Appendix). However, increasing the *AC* dose from 20 to 30 g/L decreased TOC removal, suggesting agglomeration of the *AC*, thus reducing active sites and effective contact between organic pollutants and *AC*.[24,25] The ANOVA one-way analysis, depicted in Figure S1f in Appendix, also shows the decrease in removal with increasing activated carbon dose. Moreover, the reduction in TOC removal may also be attributed to the oxidation of activated carbon, leading to leaching in the presence of oxidants.

3.2 *Performance of the integrated ozonation process for TOC removal*

To evaluate the efficacy of integrated ozonation technology for TOC removal, an experiment was designed using RSM to examine critical parameters such as O_3 flow rate (L/min), UV exposure (min), activated carbon dose (mg/L), and H_2O_2 dose (Table 1). The parameter ranges for *A*, *B*, and *C* were selected from the initial screening experiment phase, while the H_2O_2 dose was based on previous investigation.[26]

Table 1. Experimental designs and corresponding results (experimental and predicted) of TOC removal by using an integrated ozonation process

Run	Independent variables				TOC Removal (%)	
	A: Ozone dosage (L/min)	*B*: UV duration (min)	*C*: AC dosage (mg/L)	*D*: H_2O_2 dosage (mM)	Experimentally observed	Model predicted
1	5	55	1	10	69.96 ± 2.31	68.96
2	1	55	1	10	52.53 ± 2.87	52.10
3	3	90	10.5	5	68.83 ± 3.52	71.86
4	1	55	10.5	15	60.34 ± 2.14	63.96
5	3	55	10.5	10	64.21 ± 1.85	60.30
6	3	55	1	5	59.50 ± 2.93	62.89
7	3	20	10.5	5	59.42 ± 2.10	57.57
8	3	20	10.5	15	58.82 ± 3.82	55.59
9	5	55	10.5	5	85.49 ± 3.87	80.54
10	3	20	20	10	44.00 ± 2.02	49.51
11	1	55	10.5	5	64.55 ± 3.51	64.18
12	3	90	20	10	60.98 ± 3.54	55.51
13	1	90	10.5	10	63.57 ± 2.05	64.82
14	5	55	20	10	64.00 ± 2.45	64.23
15	1	20	10.5	10	52.29 ± 2.75	47.45
16	3	55	20	15	60.29 ± 3.52	58.45
17	3	90	10.5	15	64.04 ± 2.51	65.69
18	3	90	1	10	68.91 ± 3.43	62.08
19	3	55	10.5	10	55.42	60.30
20	3	55	10.5	10	60.57	60.30
21	3	55	10.5	10	58.28	60.30
22	3	20	1	10	39.55 ± 2.15	43.69
23	3	55	10.5	10	63.01 ± 2.63	60.30
24	3	55	20	5	61.66 ± 3.91	62.45
25	5	90	10.5	10	65.75 ± 2.61	72.15
26	3	55	1	15	57.98 ± 1.74	58.75
27	1	55	20	10	55.27 ± 3.44	56.08
28	5	20	10.5	10	64.83 ± 2.91	65.13
29	5	55	10.5	15	73.56 ± 3.15	72.61

3.2.1 *Model fitting and regression analysis*

The model fit summary statistics provided in Table 2 give insights into the performance of the integrated ozonation process for TOC removal. From different models available in the RSM, the quadratic model stands out with an R^2 value of 84.12%, indicating it explains a significant portion of the response variable's predictability. In addition, a low sequential *p*-value (0.0026) supports its statistical significance and suitability as a predictive model. According to the literature, R^2 values above 0.75 are acceptable,[27] and the R^2 value of 0.84 for TOC removal with the suggested quadratic model prioritises it for further investigations. This model accurately describes the sensitivity of responses to parameter variations within the operating range. Adequate precision (AP) ratios (10.66), comparing experimental with predicted values, were above 4 for TOC removal, indicating the model's effectiveness in navigating the design space. The coefficient of variation (CV) was 7.84% for TOC removal, which is below 10%, underscoring the model's reliability and precision.

The ANOVA for the quadratic model (Table S1 in Appendix) shows a significant overall effect on the response variable, with an *F*-value of 5.30 and a *p*-value of 0.0018, indicating the model's statistical significance. The lack of fit test, with an *F*-value of 2.16 and a *p*-value of 0.2389, indicates that the lack of fit is not significant, suggesting the quadratic model adequately fits the data. Further, Factors *A* (O_3 flow rate) and *B* (UV exposure) have significant effects on the response, with *F*-values of 20.31 and 19.32 and *p*-values of 0.0005 and 0.0006, respectively, indicating substantial impacts from changes in O_3 and UV levels. Interaction terms like *AB* have lower *F*-values and non-significant *p*-values, indicating minimal impact. Whereas quadratic terms A^2, B^2, C^2, and D^2 show significant effects, suggesting that the relationship between these factors and the response variable is not strictly linear.

Table 2. Fit summary statistics of different models in ANOVA analysis

Source	Std. Dev.	R^2	Sequential *p*-value	Lack of Fit *p*-value	Adjusted R^2	Predicted R^2	Remark
Linear	3.12	0.4741	0.0030	0.0925	0.3865	0.1894	
2FI	3.43	0.5249	0.9177	0.0621	0.2609	0.5159	
Quadratic	2.25	0.8412	0.0026	0.2389	0.6825	0.1898	Suggested
Cubic	1.47	0.9710	0.0785	0.7365	0.8469	0.3697	

3.2.2 *Optimization of operating parameters*

The RSM was utilised to formulate the final quadratic models in terms of operating parameters for TOC removals to predict the optimum operating conditions (Eq. (2)). Where the positive coefficient represents the synergistic response, and the negative coefficient signifies the antagonistic effect during the TOC removal. In this regard, the ozonation, UV exposer, AC dose and combination of O_3/UV, O_3/H_2O_2, and AC/H_2O_2 have been found to impact the TOC removal positively.

$$\begin{aligned}\text{TOC Removal } &= 40.33 + 0.10A + 0.69B + 1.95C - 3.63D + 1.21A^2 - 0.0022B^2 - 0.05C^2 \\ &+ 0.20D^2 + 0.03AB - 0.11AC + 0.19AD - 0.009BC - 0.0059BD + 0.00078CD\end{aligned} \quad (2)$$

The optimal TOC removal (65.95%) was predicted by this model (Eq. (2)) at an O_3 flow rate of 3.17 L/min, UV

exposure of 62.04 min, *AC* dose of 10.10 mg/L, and H_2O_2 dosing of 12.98 mM. The high removal of TOC with the integration of O_3/UV/H_2O_2 and *AC* represents a robust AOP that exploits the synergistic interactions to effectively degrade a wide spectrum of aqueous pollutants.[17,19] In this system, UV irradiation facilitates the photolytic decomposition of ozone and hydrogen peroxide, generating highly reactive hydroxyl radicals (•OH) and other reactive oxygen species (ROS), which are non-selective and capable of initiating chain reactions for the oxidation and mineralisation of organic pollutants.[19] Further, catalytic ozonation enhances this mechanism by employing catalysts, such as *AC*, to accelerate ozone decomposition and sustain a higher yield of •OH.[17] This combined process offers multiple advantages, including enhanced oxidative potential due to the intensified generation of reactive oxygen species, accelerated reaction kinetics through catalytic intervention, and broader applicability in treating recalcitrant pollutants, including persistent organic compounds, dyes, pharmaceuticals, and endocrine disruptors.[1,4,19,28,29] Additionally, the process facilitates near-complete mineralisation of organic contaminants into benign end-products such as carbon dioxide and water, thereby minimising the generation of toxic by-products.

Further, experiments conducted under these optimal conditions demonstrated TOC removal of 64.31 ± 3.25%, with an error percentage below 10%, which is deemed to be acceptable for parameter-involving experiments. In addition, to evaluate the model's prediction capability, predicted and experimental TOC removal values were plotted (Figure 2). Figure 2a represents the residual distribution in the model and compares predicted versus actual TOC. Residuals following a normal distribution scatter around the reference line, while inconsistent residual distribution indicates inefficiency. The results exhibited strong agreement between projected and observed outcomes, with residuals within the ± 3 mg/L range, which demonstrate good agreement with experimental data. Whereas, Figure 2b depicts externally studentised residuals versus experimental run order, checking for lurking variables. A random scatter suggests no time-related variables affecting the results, with randomisation and blocking safeguarding the analysis from trends. The trend from all the runs remains within the red lines, confirming the model's assumptions. Most green points are near the zero point of the externally studentised residuals, validating the TOC removal models (Eq. (2)) for this investigation.[30]

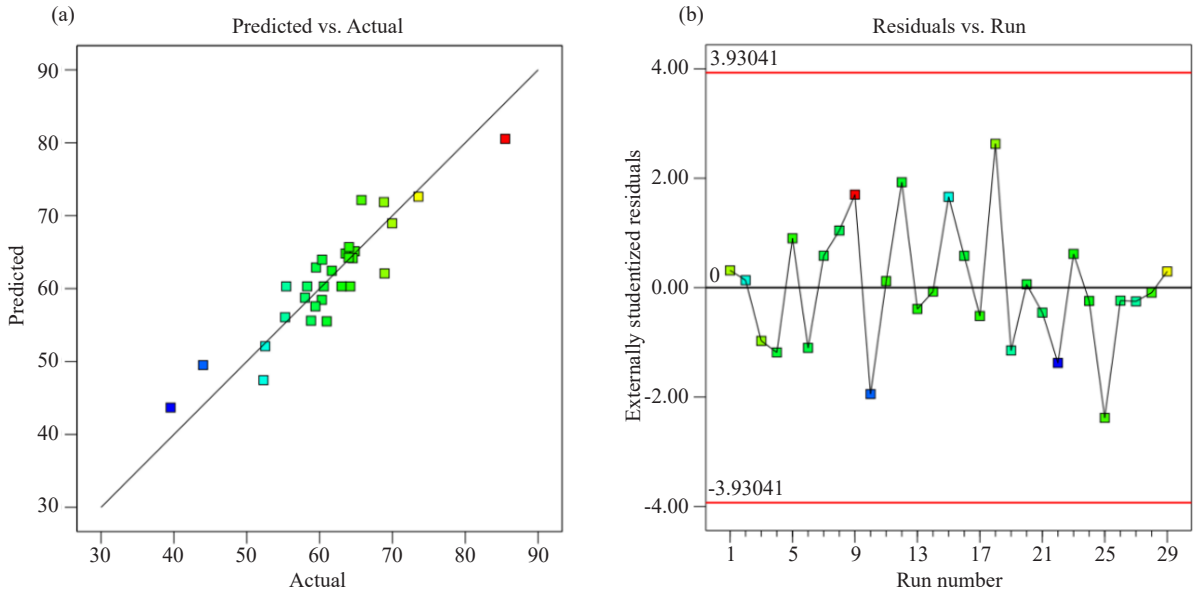

Figure 2. (a) Correlation between actual and predicted values based on RSM approach; and (b) correlation between externally studentised residuals and Run number from the quadratic model. (Green points represents the good agreement between actual and predicted values, while, blue indicates intermediate agreement, yellow signify the moderate agreement, and red points imply the poor agreement)

3.2.3 *Impact of operating parameters on treatment efficiency*

To further examine the interaction effects of operating parameters on TOC removal through the integrated ozonation process, a 3D surface and corresponding contour graphs were plotted using Eq. (2), as shown in Figure 3. The

cumulative effect of UV exposure time and O_3 flow rate at constant *AC* and H_2O_2 dose on TOC removal is presented in Figure 3a. The combined effect of UV and O_3 achieved 50% degradation within 28 min of UV exposure at 1 L/min of ozonation rate, increasing to 70% with 5 L/min of O_3 for 55 min of UV exposure. These results align with previous findings; for instance, Sharma et al. reported 60% of TOC removal with 90 min of UV and O_3 exposure.[22]

Furthermore, Figure 3a also indicates that TOC removal efficiency can be maintained through complementary adjustments of O_3 and UV parameters, indicating a compensatory relationship. Short-term UV exposure with high O_3 flow rates rapidly produces •OH through ozone photolysis, enhancing oxidative degradation.[31] Conversely, long-term UV exposure with slow O_3 flow, sustains O_3 depletion and secondary product formation, which decompose through photolysis, enhancing treatment efficiency.[31]

Figure 3b demonstrates the impact of catalytic ozonation (O_3 and *AC*) on the removal of TOC. The figure shows that boosting the flow rate of O_3 from 1 L/min to 5 L/min, while maintaining a constant *AC* dose of 1 mg/L, resulted in an increase in TOC removal from 50% to 70% during a reaction period of 55 min. Whereas, at a low O_3 flow rate of 1 L/min, the maximum removal rate increased from 30% at 1 mg/L of AC dose to 55% with a dosage of 20 mg/L of AC. When the O_3 supply is at its maximum level of 5 L/min, an excessive amount of AC damages the removal of TOC, suggesting the leaching of compounds from the *AC*. These findings are in accordance with the previous investigations that exceeding a specific *AC* quantity can inhibit TOC removal by reducing pollutant and O_3 concentration per unit area, thus diminishing catalytic efficiency.[32]

The peroxone method, which involves the addition of H_2O_2 to ozonation, demonstrates enhanced removal of TOC when the O_3 flow rate is increased, particularly at the lowest H_2O_2 dosage (Figure 3c), resulting in 80% of TOC removal. Further, when the O_3 flow rate is low, increasing the H_2O_2 dosage has minimal effect on the elimination of TOC, emphasising the significance of O_3. In addition, it was noted that when the O_3 flow rate is increased, there is a phenomenon known as scavenging, where H_2O_2 competes with contaminants for O_3. This competition leads to a reduction in the efficiency of TOC removal. Prior instances of comparable scavenging processes have been documented.[33] For instance, Lin et al. found that a concentration of 5 mM H_2O_2 yielded greater effectiveness compared to 40 mM when used in conjunction with a consistent provision of O_3,[34] therefore confirming the present discoveries.

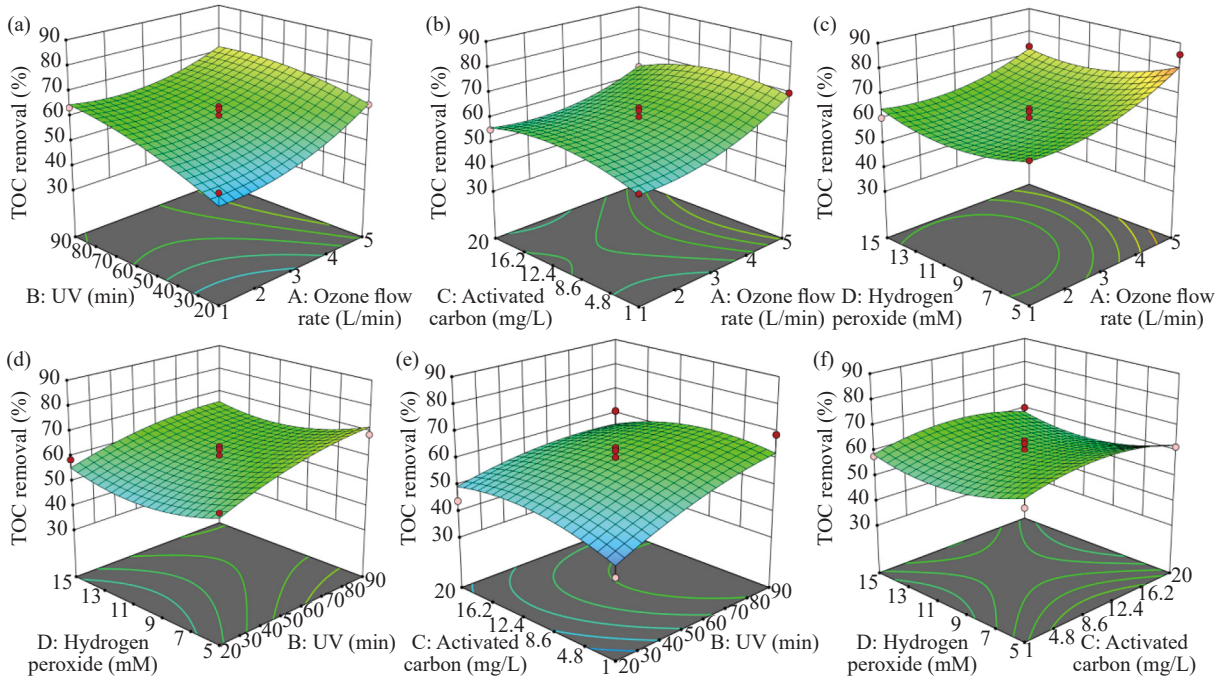

Figure 3. A 3-D dimensional response surface and contour plots for parameters affecting TOC removal from secondary treated effluent: (a) effect of UV exposure (min) and O_3 flow rate (L/min), (b) effect of activated carbon dose (mg/L) and O_3 flow rate (L/min), (c) effect of hydrogen peroxide dose (mM) and O_3 flow rate (L/min), (d) effect of hydrogen peroxide dose (mM) and UV exposure (min), (e) effect of activated carbon dose (mg/L) and UV exposure (min), (f) effect of hydrogen peroxide dose (mM) and activated carbon dose (mg/L)

Similarly, high H_2O_2 dosage inhibited TOC removal in conjunction with UV treatment, reducing TOC removal from 72% to 65% as the H_2O_2 dose increased from 5 mM to 15 mM (Figure 3d). Excessive H_2O_2 competes with pollutants for UV light absorption, hindering •OH radical generation and highlighting the need for optimal H_2O_2 dosing.[35] Figure 3e shows the effect of adsorption with UV exposure, indicating that increasing AC initially improves TOC removal with high UV treatment; however, after reaching an optimal dose, TOC removal decreases due to hindered UV penetration.[36] This trend aligns with previous studies, confirming the findings.[37] Maximum TOC removal was observed with an 8.6 mg/L AC dose and 90 min of UV exposure. The finding with the combined use of H_2O_2 and AC indicates that when the AC dose is increased while keeping the H_2O_2 concentration constant, the elimination of TOC increases until it reaches an ideal point and then remains constant (Figure 3f). Zao and his colleagues have also reported similar findings, highlighting the significant influence of the AC/H_2O_2 ratio.[38] It is crucial to avoid overdosing on both H_2O_2 and AC in order to maximise the availability of •OH radicals. This ensures efficient oxidation of target compounds and minimises scavenging effects in the solutions.

3.2.4 *Cube plot and kinetic analysis*

The cube plot in Figure 4a illustrates the interplay among O_3 flow rate, UV, *AC*, and H_2O_2 dose on TOC removal efficiency. The axis of the cube denotes all the experimental variable factors from low to high, and the coordinates points stand for the outcome result for TOC removal (%). The lowest removal of TOC (37.46%) was observed at low ranges of UV, O_3 flow rate, and *AC* dose, while the highest removal (72.95%) was achieved at high O_3 flow rate, maximum UV exposure, and low *AC* dose (Figure 4a). It reveals nuanced relationships when lower O_3 flow rates coupled with increased *AC* dosage exhibit synergistic effects, enhancing TOC removal, while higher O_3 flow rates diminish the impact of activated carbon, suggesting a dominance of O_3 oxidation. The interplay between O_3 flow rate and H_2O_2 dosage for TOC removal is intricate; at diminished O_3 flow rates, augmenting the H_2O_2 dosage can significantly improve TOC removal efficiency. This enhancement occurs because the available O_3 is insufficient for the optimal utilisation of H_2O_2, thereby enabling greater •OH generation, which serves as the principal oxidising agent in these processes. However, at elevated O_3 flow rates, the efficacy of increasing the H_2O_2 dosage may diminish or even exhibit an adverse effect. This phenomenon arises from the propensity of surplus O_3 to interact directly with organic substrates, potentially diverting reaction pathways and diminishing •OH formation, thereby reducing the overall efficiency of TOC removal.

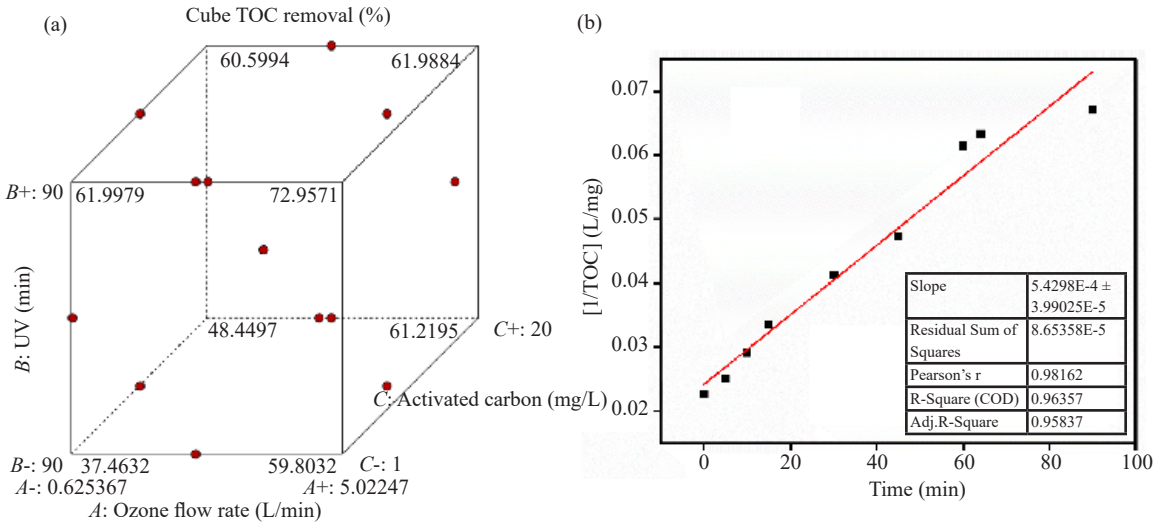

Figure 4. (a) Cube Plot obtained from the RSM optimisation; and (b) Kinetic plot of integrated ozonation process at the optimised condition

Similarly, the interaction between activated carbon dose and H_2O_2 dose highlights their complementary roles in TOC removal, albeit with diminishing returns as H_2O_2 concentration rises. To explore the kinetics of TOC removal via the O_3/UV/*AC*/H_2O_2-based integrated ozonation process, an experiment was conducted under optimal conditions (Figure 4b). Sampling over time enabled analysis of the TOC parameter, and results indicated an excellent fit with the second-order kinetic model, as depicted in Figure 4b, with a regression coefficient of 0.96 and a rate constant of 0.00053 (L/mg·min).

3.3 *Economic and environmental analysis*

Performing an economic analysis for wastewater treatment technologies is crucial for determining the most effective and financially feasible options for removing TOC present in the secondary treated wastewater. This investigation evaluates four distinct methodologies: ultraviolet (UV) radiation, ozonation (O_3) treatment, adsorption, and an integrated ozonation process. The economic analysis was performed per unit of TOC (mg/L) removal from the secondary treated effluent. This economic analysis comprises chemicals and energy costs for daily operations. The capital and fixed cost of the operation has not been considered in the analysis as the previous investigation have found that the long-term life cycle and different procurement procedures differ for the different make of instruments.

Table 3. Overall cost analysis for the applied methodologies for the TOC removal

Methodology	Component	Energy (W)	Cost (₹)	Energy requirement at optimum conditions (kWh)	Chemical cost at optimum conditions (₹)	Operational cost ($/(mg/L) of TOC)
UV	UV lamp	8	700	1.016	NA	0.016
	Magnetic stirrer	500	5,000		NA	
Ozonation	Oxygen concentrator	450	35,000	0.65	NA	0.004
	Ozone generator	200	27,000		NA	
Adsorption	Magnetic stirrer	500	5,000	1	NA	0.003
	Activated carbon	NA	1.11/g of AC	NA	0.022	
Integrated process	UV lamp	8	700	0.6721	NA	0.002
	Oxygen concentrator	450	35,000			
	Ozone generator	200	27,000			
	Activated carbon	NA	1.11/g of AC	NA	0.011	
	Hydrogen peroxide	NA	198	NA	3.96	

The energy consumption and its associated cost were estimated based on the electrical energy consumption in kilowatt-hours (kWh) and the cost of electricity in India (7 rupees/kWh) as presented in Table 3. Further, the chemical requirement was taken as per the optimised values and the market price for the same in terms of cost calculations (Table 3). As per the calculation, the UV process has been found the most costlier in operation with 0.016 $/(mg/L) of TOC removal with the lowest being the integrated ozonation process with 0.002 $/(mg/L) of TOC removal. The operating cost of the simple ozonation process was found to be 0.004 $/(mg/L) of TOC; the difference between the integrated process and simple ozonation was found to be due to the effectiveness of the process achieving high TOC removal in less time, thus compensating for the chemical cost.

Further, the endpoint impact assessment revealed the lowest environmental footprint associated with the integrated TOC removal approach and the maximum by the UV treatment (Table 4), with the highest risk on human health from exposure to chemical and pollutant substances emitted throughout the procedure's life cycle. The midpoint

normalization results also corroborated this observation with the highest risk of human carcinogenic toxicity due to pollutant emittance from the energy consumption during the UV procedure (Figure S2 in Appendix). The midpoint characterization results imply electricity consumption to be the major cause of human carcinogenic toxicity. In this regard, the continuous ozonation in the process causes turbulence in the reactor and limits the application of the artificial stirrer, thus reducing the electricity consumption. Further, the high TOC removal capacity in less time compared to the simple ozonation process also provides an edge to the integrated process. Thus, the integrated ozonation process is more feasible for the TOC removal from secondary treated effluent.

Table 4. Single point score of different TOC removal approaches obtained for endpoint impacts of ReCiPe 2016 (H)

Damage category	Unit	UV treatment (TOC removal)	Ozonation (TOC removal)	Integrated (TOC removal)	Adsorption (TOC removal)
Total	Pt	12.25514	2.440316	1.285202	1.886343
Human health	Pt	11.79105	2.347904	1.236512	1.814909
Ecosystems	Pt	0.372495	0.074173	0.03907	0.057336
Resources	Pt	0.091592	0.018238	0.009619	0.014099

4. Conclusion

This investigation showed that the O_3/UV/*AC*/H_2O_2-based integrated ozonation process is highly effective in treating secondary treated effluent for TOC removal to minimise the presence of emerging contaminants in the final treated effluent. To simulate and improve the process, the statistical technique of RSM was employed, and the regression analysis demonstrated that the data conformed well to a second-order polynomial model. The quadratic model predicts that under optimal conditions, TOC removal efficiency can reach up to 66%. Further, the investigation shows that the dosage of UV and O_3 do play a major role in the degradation process of TOC and have a symbiotic relationship with each other. Excessive use of H_2O_2 has a detrimental effect due to its quenching effect. In addition, the dosage of *AC* is crucial since an excessive amount might result in agglomeration, leaching, and obstruction of UV radiation. The kinetic investigation also demonstrated that the data exhibited a strong match with a second-order kinetic model, as evidenced by a regression coefficient of 0.96 and a rate constant of 0.0005 (L/mg·min). The economic analysis reveals that the integrated ozonation process, with an operating cost of 0.002 $/(mg/L) of TOC, is more cost-effective than other methods. Further, its incorporation into wastewater treatment for TOC removal, along with its potential to lower energy consumption and reduce environmental impact, as demonstrated by LCA, establishes it as a promising technology for sustainable and efficient wastewater management.

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Conflict of interest

The authors declare that they have no conflict of interest.

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Appendix

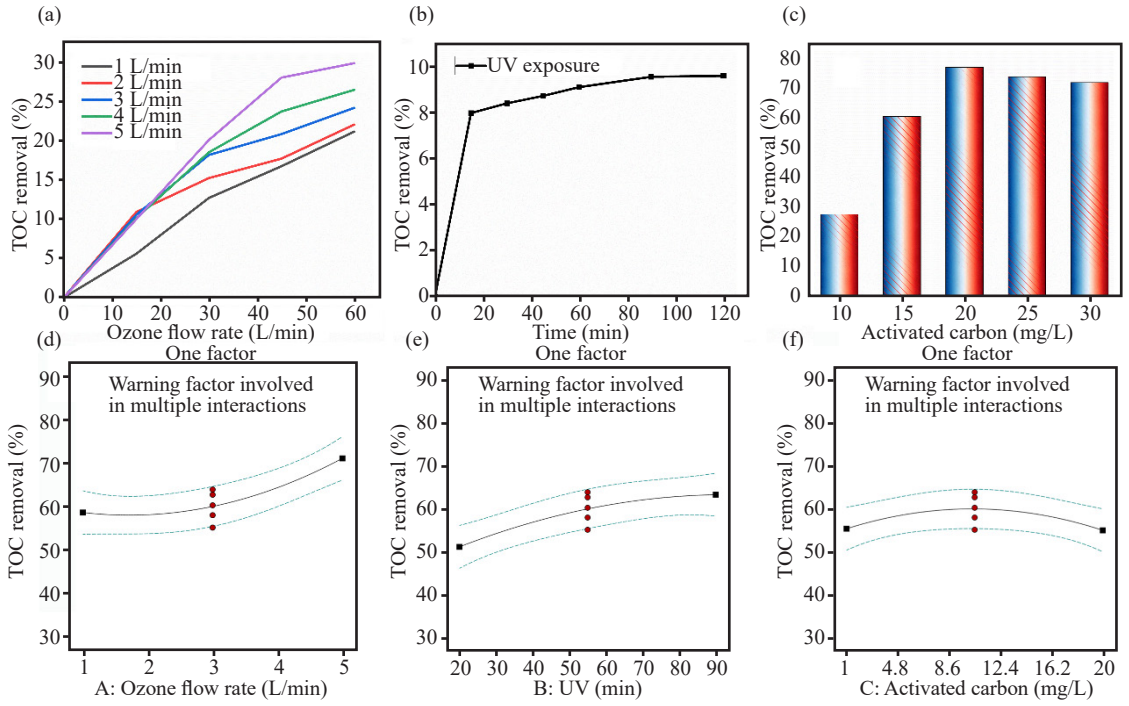

Figure S1. Single-step treatment of the different technologies for TOC removal from secondary treated effluent: (a) and (d) effect of ozonation flow rate (mg/L) and ANOVA one-way analysis of variance for the ozonation flow rate, respectively; (b) and (e) effect of UV exposure time (min) and ANOVA one-way analysis of variance for the UV exposure time (min), respectively; (c) and (f) effect of activated carbon dose (mg/L) and ANOVA one-way analysis of variance for the activated carbon dose (mg/L), respectively

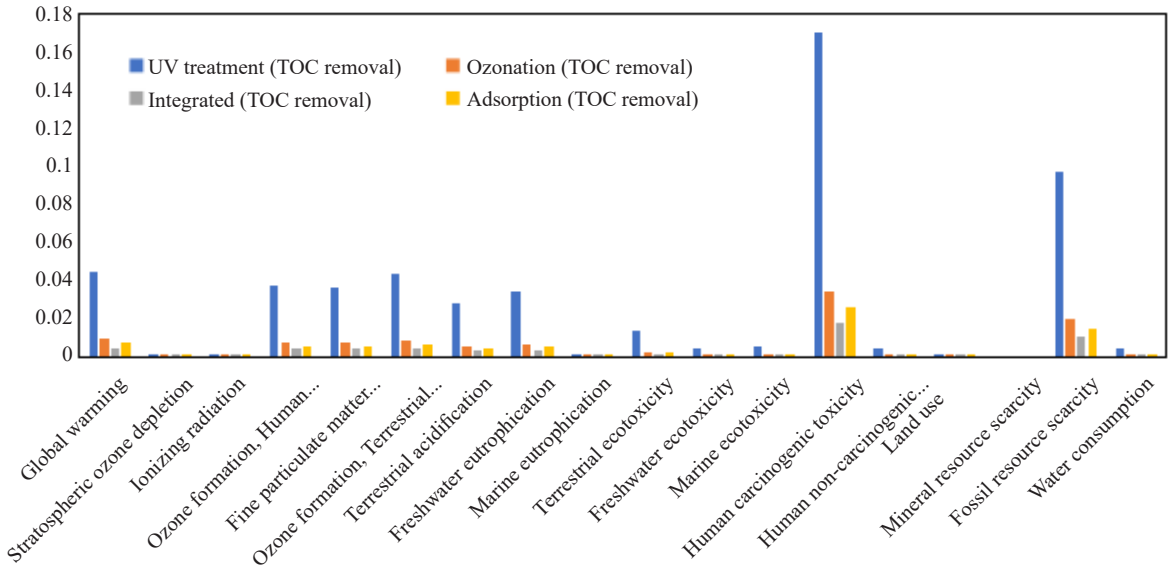

Figure S2. Comparative midpoint normalization result of different TOC removal approaches

Table S1. Regression coefficients and P-values for the quadratic model for TOC removal using integrated Ozonation process

Source	Sum of squares	df	Mean square	*F*-value	*p*-value	
Model	374.42	14	26.74	5.30	0.0018	Significant
A-O_3	102.53	1	102.53	20.31	0.0005	
B-UV	97.53	1	97.53	19.32	0.0006	
C-Adsorption	0.0019	1	0.0019	0.0182	0.0894	
D-H_2O_2	10.86	1	10.86	2.15	0.1645	
AB	5.86	1	5.86	1.16	0.2996	
AC	4.14	1	4.14	0.8205	0.3804	
AD	3.25	1	3.25	0.6444	0.4355	
BC	8.38	1	8.38	1.66	0.2184	
BD	0.9604	1	0.9604	0.1903	0.6693	
CD	0.0012	1	0.0012	0.0002	0.9878	
A^2	33.51	1	33.51	6.64	0.0220	
B^2	10.97	1	10.97	2.17	0.1625	
C^2	33.00	1	33.00	6.54	0.0228	
D^2	37.69	1	37.69	7.47	0.0162	
Residual	70.66	14	5.05			
Lack of fit	59.60	10	5.96	2.16	0.2389	Not significant
Pure error	11.06	4	2.77			
Cor total	445.08	28				