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# Feasibility study on enhancing the biodegradability of fresh and old landfill leachate using combined chemical precipitation and Fenton processes

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**Landfill leachate (LL), due to its high concentrations of heavy metals, ammonia nitrogen ($NH_3$-N), and persistent organic compounds, requires effective pretreatment before biological treatment. This study evaluated a three-stage approach—chemical precipitation with lime, ammonia stripping, and Fenton oxidation—for fresh and old leachate from the Aradkooh Waste Processing Complex in Tehran. Lime dosages of 9 g/L for fresh and 18 g/L for old leachate were determined from preliminary experiments.; these values were selected due to their favorable performance in reducing heavy metals and $NH_3$-N. Arsenic showed the highest removal efficiency (93% in fresh leachate, 66% in old), while $NH_3$-N removal reached 93% in both. The Fenton process was optimized using a Box–Behnken design (BBD) and response surface methodology (RSM), with three variables—$H_2O_2$: $Fe^{2+}$ ratio, $H_2O_2$ dosage, and reaction time—and the $BOD_5$/COD ratio as the response. Optimal conditions (A = 2, B = 10, C = 60 min for fresh; A = 2, B = 8.2, C = 75 min for old) increased the $BOD_5$/COD ratio from 0.29 to 0.67 in fresh leachate and from 0.23 to 0.73 in old leachate. Chemical oxygen demand (COD) removal efficiencies in fresh and old leachate were 88.3% and 81.3%, respectively. These findings demonstrate that combining chemical precipitation and Fenton oxidation effectively enhances leachate quality and biodegradability, supporting improved biological treatment performance.**

**Keywords** Fresh leachate, Old leachate, Chemical precipitation, Fenton process, Biodegradability, Response surface methodology

Landfill leachate is a significant environmental pollutant, particularly for contaminating water resources. It originates from the decomposition of waste and the infiltration of rainwater through waste layers[1]. This leachate contains high levels of organic and inorganic compounds, heavy metals, and xenobiotic substances that are notably resistant to degradation and removal.[2,3] Recent research has focused on landfill leachate treatment. Due to microbial activity in the landfill, the concentration of biodegradable organic matter gradually decreases, resulting in a lower biochemical oxygen demand ($BOD_5$) to chemical oxygen demand (COD) ratio. This shift reflects diminished bioremediation potential and limits the effectiveness of biological treatment methods[4,5] .The $BOD_5$/COD ratio is one of the key indicators for characterizing landfill leachate, as it reflects both its biodegradability and its degree of stabilization. This ratio is widely used to determine and classify the age of leachate.[6]. Landfills are generally categorized by age into three groups: young (< 5 years), intermediate (5–10 years), and old (> 10 years)[7]. As the landfill ages, the pH of the leachate tends to increase, while the concentrations of COD, BOD, the $BOD_5$/COD ratio, and heavy metals decrease[8]. Ammonia nitrogen concentration generally rises with landfill age, often continuing to increase during the first decade before gradually declining thereafter. It should be emphasized that the variation in ammonia nitrogen levels can be considerable, frequently

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reaching several hundred milligrams per liter or even higher[9]. Fresh leachates exhibit high biodegradability and can be effectively treated using biological processes. However, over time and with increasing landfill age, non-biodegradable organic compounds gradually accumulate, leading to a reduced $BOD_5$/COD ratio in old leachates[10]. Old leachates are particularly polluted and recalcitrant due to the presence of substantial amounts of resistant compounds such as humic and fulvic acids, which possess complex structures and long molecular chains, making them difficult to degrade[11].

Therefore, the appropriate treatment method for landfill leachate is strongly influenced by its age, and determining the physicochemical characteristics of the leachate prior to treatment is essential for identifying its age and nature[5]. The presence of non-biodegradable organics, ammonia nitrogen ($NH_3$-N), and heavy metals inhibits microbial activity and further reduces biological treatment efficiency[12,13]. To improve performance, leachate toxicity should be reduced first, enabling subsequent biological treatment to operate more effectively[14]. According to recent studies and research developments on landfill leachate treatment technologies, chemical treatment technologies (e.g., advanced oxidation process, chemical precipitation, and coagulation/flocculation), physicochemical treatment technologies (e.g., adsorption, ion exchange, air stripping, and membrane filtration), biological treatment technologies (e.g., aerobic and anaerobic) have been carried out in the world .[3] Among the available approaches, chemical precipitation using lime (CaO) is widely regarded as cost-effective, operationally simple, and effective across a wide temperature range[1]. This method removes metal ions by converting them into insoluble hydroxides, sulfides, or carbonates, which can then be separated by sedimentation, flotation, or filtration[15,16]. Ammonia stripping is extensively used to remove $NH_3$-N from landfill leachate. In this method, the leachate is exposed to countercurrent airflow in a stripping tower, transferring $NH_3$-N from the liquid phase to the gas phase, where it is subsequently absorbed by sulfuric acid ($H_2SO_4$)[17,18]. This method offers a cost-effective alternative to advanced treatments such as reverse osmosis and nanofiltration, making it a promising option for front-end leachate remediation[19]. The Fenton reaction is a widely studied advanced oxidation process that operates under acidic conditions and ambient temperature. In this reaction, hydrogen peroxide ($H_2O_2$) is catalytically decomposed by ferrous ions ($Fe^{2+}$), generating hydroxyl radicals (•OH) that oxidize organic pollutants into water ($H_2O$) and carbon dioxide ($CO_2$).The classical Fenton process involves the following sequence of reactions[20]:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{\cdot} + OH^{-} \tag{1}$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\cdot} + H^{+} \tag{2}$$

$$OH^{\cdot} + H_2O_2 \rightarrow HO_2^{\cdot} + H_2O \tag{3}$$

$$OH^{\cdot} + Fe^{2+} \rightarrow Fe^{3+} + OH^{-} \tag{4}$$

$$Fe^{3+} + HO_2^{\cdot} \rightarrow Fe^{2+} + O_2H^{+} \tag{5}$$

$$Fe^{2+} + HO_2^{\cdot} + H^{+} \rightarrow Fe^{3+}H_2O_2 \tag{6}$$

$$2HO_2^{\cdot} \rightarrow H_2O_2 + O_2 \tag{7}$$

Fenton oxidation offers advantages such as ambient operation conditions, process continuity, and minimal formation of harmful by-products. $H_2O_2$ is readily available, cost-effective, and degrades into non-toxic compounds. Ferrous ions are commonly used as catalysts due to their accessibility and efficiency[21–23]. The study by Hamza Bellouk et al. also confirmed that the sequential application of AOPs after preliminary treatment is a promising alternative to reducing the high organic load of stabilized leachate and that could be largely applied to other types of effluents[24].

Although lime precipitation, ammonia stripping, and Fenton oxidation have each been widely applied in landfill leachate treatment, their combined sequential application has not been systematically evaluated for leachates of different ages originating from the same landfill site. This distinction is important because comparing fresh and old leachate under identical environmental and operational conditions provides a more reliable understanding of how leachate aging influences treatment efficiency. Furthermore, limited studies have optimized this treatment sequence using Box–Behnken design based on response surface methodology (RSM) while simultaneously assessing key performance indicators such as COD removal, $NH_3$-N reduction, biodegradability improvement ($BOD_5$/COD), and toxicity reduction. Therefore, the present study contributes a novel integrated approach that couples chemical precipitation, ammonia stripping, and Fenton oxidation under optimized conditions to enhance the treatability of both fresh and old landfill leachate. This study introduces a novel approach by combining chemical precipitation with the Fenton process to improve the biodegradability of both fresh and old landfill leachate. The sequential application of lime precipitation, ammonia stripping, and Fenton oxidation under optimized BBD conditions enhances the biological treatability of leachate and reduces its pollution load. The treatment sequence begins with lime-induced pH adjustment for heavy metal removal, followed by ammonia stripping to eliminate $NH_3$-N, and concludes with Fenton oxidation to decompose persistent organic pollutants.

## Materials and methods

### Materials

$H_2O_2$ (30% w/w), nitric acid ($HNO_3$, ≥ 90%), hydrochloric acid (HCl, 37%), $Na_2SO_4$ (99%), sodium fluoride (NaF, 99%), sodium sulfate ($Na_2SO_4$, 99%), sodium hydroxide (NaOH, 98%), ferrous sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$), and dry lime were obtained from Sigma-Aldrich and used as received without further purification. COD digestion vials were supplied by Hach (USA).

## Collection of fresh and old leachate samples and initial characterization

Fresh and old leachate samples were collected from the Aradkooh Waste Processing and Disposal Complex, situated 25 km south of Tehran. Covering approximately 1,400 hectares, this facility commenced operations in 1960 and remains the largest waste processing and disposal center in Iran. The Aradkooh controlled landfill site is situated at 35°28′10.45"N, 51°19′40.73"E in Kahrizak district, Tehran Province. According to data from the Tehran Municipality Waste Management Organization, the daily waste input in 1962 reached 5,805 tons, with a per capita waste generation rate of 642.8 g/day. A portion of the solid waste at Aradkooh is processed into energy and compost, while approximately 2,500 tons are landfilled daily[25].

The complex is situated in the southern plains of Tehran and is predominantly composed of alluvial deposits with medium to low permeability, which significantly influence the hydrological behavior of the leachate. The groundwater table in this region is relatively deep, and due to the semi-arid climate of Tehran, annual precipitation is limited. Consequently, most leachate generation results from rainfall infiltration and moisture within the waste. Surface and subsurface drainage systems have been constructed to control leachate flow; however, due to the high volume of incoming waste, leachate accumulation in collection ponds is unavoidable.

The waste disposal site in this complex consists of two main landfill zones: Zone A and Zone B. Zone A, located in the northern part of the complex, represents an old landfill with stabilized conditions, containing waste aged over 10 years. This legacy landfill with an area of 278.8 hectares was operational from 1969 to 1999. Zone A is further divided into two sub-sections: 1) Hosseinabad section (approximately 58.8 hectares) in the northern part of Zone A, which was decommissioned around 1986. 2)Sect. 65 (approximately 220 hectares) in the southern part of Zone A, which received waste from about 1986 to 1999. Zone B, known as the active landfill zone, contains fresh leachate with waste age less than 5 years. This section has been in operation since 1999 with an area of about 137.8 hectares. Notably, the complex lacks a leachate drainage system, resulting in either natural accumulation of leachate in ponds or its migration to the lowest topographic point of the site. Although both zones share similar climatic and hydrological conditions, the differences in waste age and biodegradability lead to significant variations in leachate composition. Accordingly, fresh leachate samples were collected from Zone B (N1 to N6) while old leachate samples were obtained from Zone A (O1 to O7). All sampling was conducted within the same season to minimize environmental variability effects (Fig. 1). Map generated by the authors using Google Earth Pro (version 7.3.6.10441; https://www.google.com/earth/).

Fresh leachate was sampled proportionally from a flowing channel, where 500 mL of leachate was collected every 30 min. Old leachate was sampled proportionally from leachate ponds, with samples taken from two-thirds of the pond depth. A total of 5 L of leachate from each region was collected and transported to the laboratory in separate containers. To preserve the physicochemical integrity of the samples, they were stored at 4 °C in the dark and acidified with $HNO_3$ to reduce the pH below 2, thereby stabilizing dissolved metals[26,27]. Samples were analyzed for pH, COD, biochemical oxygen demand ($BOD_5$), heavy metals, and $NH_3$-N according to Standard Methods[28]. To remove suspended solids, samples were centrifuged at 10,000 rpm for 90 min and subsequently filtered through a 0.45 µm Whatman membrane. Each sample was diluted tenfold to improve measurement accuracy[29]. pH was measured using indicator paper, and COD was determined using Hach ready-to-use vials. All analyses were performed in triplicate ($n = 3$), and results were reported as mean ± standard deviation. Quality assurance was ensured through the use of control samples and repeated analyses. COD and heavy metal concentrations were measured using a DR-5000 spectrophotometer and an inductively coupled plasma spectrometer (Spectro Atcos), both calibrated with standard solutions at their respective wavelengths. Calibration curves were prepared for each parameter, and quality control was maintained throughout the analytical procedures using control samples. The design and specifications of the experiments are listed in Table 1.

## Chemical precipitation with lime and ammonia stripping

In the initial phase, to determine the optimal lime dose, four 1-L containers were prepared using both fresh and old leachate. Dry lime was added at 3, 6, 9,12 and 18 g/L, and the pH of each sample was recorded every 30 min. COD concentrations were then measured, and the percentage reduction in each sample was calculated. The dose that achieved the highest COD removal efficiency was selected as the optimal amount for further use. This optimized dose was applied to 10 L of each leachate type for the main precipitation process. Heavy metals were monitored at their ideal pH levels, which were maintained and recorded every 30 min. A precipitation duration of 2 h was allocated for each pH condition. Final samples were collected from the supernatant for analysis of COD, $BOD_5$, and heavy metals. Following the chemical precipitation process, the sludge was separated, and the clarified supernatant underwent ammonia removal treatment. During this stage, the pH of the solution was increased to 11.5, and the ammonia removal efficiency was evaluated at different time intervals (6, 8, 10, 12, and 14 h) under constant room temperature (approximately 25 °C) and an airflow rate of 2 L/min[30,31]. After determining the optimal exposure time, aeration was initiated using an air pump to strip ammonia gas from the solution. The resulting supernatant was stored at 4 °C in the dark to prevent further chemical reactions and preserve the sample for subsequent analyses.

## Fenton process

Design-Expert software (v13) was used to design and optimize the experimental setup. The process optimization employed the Box–Behnken design and analysis of variance (ANOVA) within the RSM framework to identify the most effective operating conditions. Based on the experimental matrix, the following steps were carried out using varying reaction times, $H_2O_2$ doses, and $Fe^{2+}$ concentrations:

- 500 mL of pretreated leachate from the chemical precipitation stage (both fresh and old) was separated.
- The pH of each sample was adjusted to 3 using 98% $H_2SO_4$

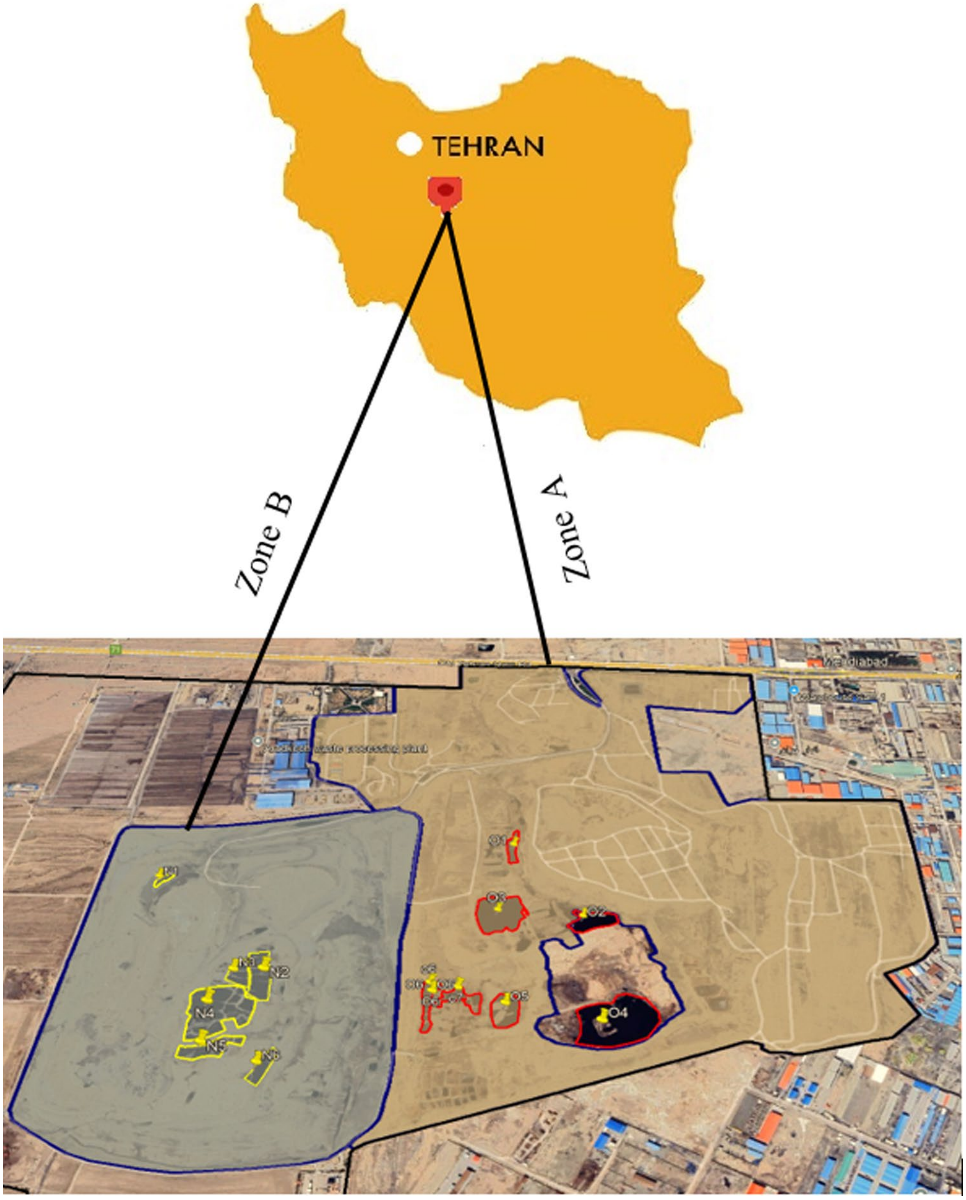


**Fig. 1**. Area planning of Aradkooh waste landfill.

| Stage | Process | Leachate type | Main variables | Experimental conditions | Measured parameters |
|---|---|---|---|---|---|
| 1 | Chemical precipitation with lime | Fresh & old | Lime dose, pH,time | Lime dose:3,6,9,12,18 g/l<br>Volume:5L;<br>pH recorded every 30 min;<br>contact time :2 h | $BOD_5$,COD,$BOD_5$/COD,<br>Heavy metals |
| 2 | Ammonia stripping | Fresh & old | Aeration time | pH adjusted to 11.5;diferent durations tested; Aeration at optimal time; Supernatant stored at $4^0$ c | $NH_3$-N |
| 3 | Fenton process | Fresh & old | $H_2O_2$,$Fe^{2+}$,reaction time | 500 ml pretreated leachate; pH adjusted to 3; $H_2O_2$ and $FeSO_4$-$7H_2O$ add per BBD; Final pH adjusted to 8.5 | $BOD_5$,COD,$BOD_5$/COD |

**Table 1**. Description of stages, variables, and measurement indicators in leachate treatment via chemical precipitation, ammonia stripping, and fenton.

- Required volumes of 30% $H_2O_2$ and $FeSO_4 \cdot 7H_2O$ were prepared according to the experimental design.
- Samples were transferred to Falcon tubes, followed by sequential addition of $FeSO_4 \cdot 7H_2O$ and $H_2O_2$. The reaction proceeded for the designated time interval.
- After the reaction, the pH was increased to 8.5 using NaOH, allowing sufficient time for $Fe(OH)_3$ floc formation and settling
- Supernatants were then separated, and COD and $BOD_5$ were measured.

## Statistical analyses

Statistical analysis was performed using Excel v16 and Design-Expert v13. To examine the interaction between input variables and system responses, ANOVA was employed. The quality of the model fit was evaluated using the coefficient of determination ($R^2$) and adjusted $R^2$, while Fisher's F-test was applied to determine the significance of the model. A *P*-value threshold of 0.05 was used to determine statistical significance. Three-dimensional (3D) surface plots and contour plots were created to visualize parameter interactions at three levels. The optimal operating region was identified through an overlay plot and analysis of its key factors. Model reliability was confirmed by comparing experimental results with predicted values derived from regression equations.

## Results and discussion

### Characteristics of fresh and old leachate before and after chemical precipitation and ammonia stripping

Table 2 presents the physicochemical characteristics of untreated fresh and old leachate before and after treatment with lime-induced chemical precipitation and ammonia stripping. The percentage change for each parameter is also reported. The $BOD_5$/COD ratio in fresh leachate was 0.29, which exceeded that of old leachate (0.23). As landfill age increased, leachate pH rose while COD, $BOD_5$, $BOD_5$/COD ratio, and heavy metal concentrations declined. This trend aligns with the findings of Dhamsaniya et al.[8], indicating a reduction in readily biodegradable organic compounds over time, leaving more recalcitrant or non-degradable fractions. Heavy metal analysis revealed that iron was the dominant metal in both leachate types, corroborating the observations of Hosseini Beinabaj et al. In samples from the active landfill, iron concentrations ranged from 22.94 to 17.01 mg/L. Conversely, in the old landfill, manganese was predominant, with a peak concentration of 15.71 mg/L[32]. Ammonia ($NH_3$-N) concentrations in both leachates decreased by approximately 93% after the stripping process. Furthermore, the $BOD_5$/COD ratio increased by 20% in fresh leachate and 26% in old leachate. These findings are consistent with Bellouk et al. (2025), who reported that aeration pretreatment achieved 54% COD, 61% color, and 55% Abs254 removal in young landfill leachate. This similarity highlights the importance of applying an initial pretreatment step—whether aeration or lime precipitation—to reduce organic load and enhance the efficiency of subsequent advanced oxidation processes[33].

Figure 2 illustrates the reduction of heavy metal concentrations following chemical precipitation. The results confirm the effectiveness of lime treatment in removing heavy metals from both leachate types, with consistently higher removal efficiencies observed in fresh leachate. This discrepancy may stem from the lower pH and greater abundance of free metal ions in fresh leachate, facilitating conversion into insoluble forms. In contrast, old leachate is likely to contain more stable organometallic complexes that resist precipitation. Metals such as lead and cadmium exhibited substantial reductions, underscoring the value of lime as a mitigating agent for hazardous metals. Arsenic displayed the highest removal efficiency in both leachate types, while mercury remained largely unaffected. Chromium removal may be attributed to the reduction of $Cr^{6+}$ to $Cr^{3+}$, followed by precipitation. These findings affirm that lime-based chemical precipitation is a viable pretreatment strategy for reducing leachate toxicity and improving environmental safety. Moreover, the results underscore the importance

| | **Fresh.Leachate(Less than 5 years)** | | | **Old.Leachate(More than 10 years)** | | |
|---|---|---|---|---|---|---|
| **Parameters** | **Raw. Leachate** | **After.chemical precipitation** | **(Removal%)** | **Raw. Leachate** | **After.chemical precipitation** | **(Removal%)** |
| pH | 7.5 | 11 | - | 8 | 11 | - |
| $BOD_5$ (mg/l) | 6500 | 3500 | 46 | 525 | 290 | 44 |
| COD (mg/l) | 22,000 | 10,000 | 54 | 2200 | 1000 | 54 |
| $BOD_5$/COD | 0.29 | 0.35 | – | 0.23 | 0.29 | - |
| Al(ppb) | 676 | 530 | 21.5 | 721 | 346 | 52 |
| As(ppb) | 15 | 1.05 | 93 | 15 | 5.1 | 66 |
| Cd(ppb) | 3.5 | 2.1 | 40 | 3.5 | 2.73 | 22 |
| Cr(ppb) | 1000 | 900 | 10 | 1200 | 960 | 20 |
| Cu(ppb) | 50 | 43 | 14 | 37 | 32 | 13.5 |
| Fe(ppb) | 3900 | 3003 | 23 | 3400 | 3332 | 2 |
| Hg(ppb) | 1 | 1 | 0 | 1 | 1 | 0 |
| Mn(ppb) | 418 | 112.8 | 73 | 94 | 84.6 | 10 |
| Pb(ppb) | 36 | 15.8 | 56 | 36 | 10.8 | 70 |
| Zn(ppb) | 250 | 200 | 20 | 250 | 137.5 | 45 |

**Table 2**. Characteristics of fresh and old Aradkooh leachate before and after chemical precipitation with lime and ammonia stripping.

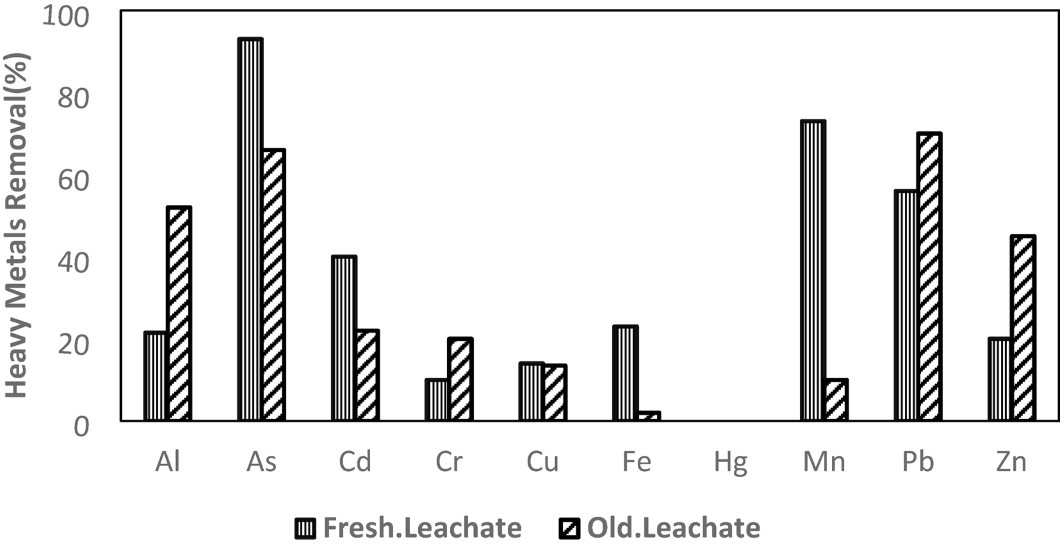


**Fig. 2**. Graph of heavy metal reduction in fresh and old leachate after chemical precipitation with lime.

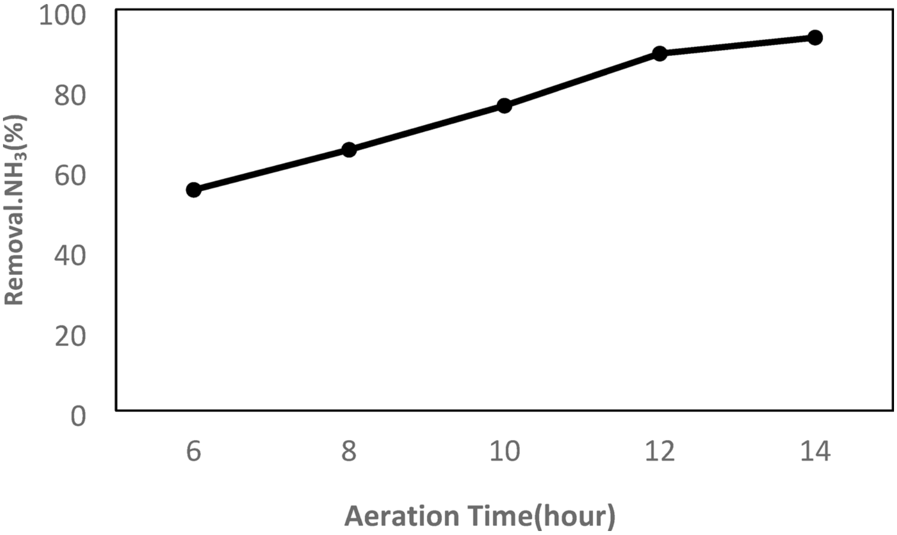


**Fig. 3**. Ammonia reduction curve per unit time using the ammonia stripping method.

of considering leachate age when designing optimal treatment systems. In the study by Abdel-Shafy[34], CaO was used to extract and reduce heavy metals, achieving removal efficiencies of 93% for manganese and 100% for copper and nickel, results that closely align with those of the present study. Similarly, Ramalho et al. reported the highest metal removal for iron, with other metals showing 71–98% removal. Their study highlighted the influence of CaO dosage and stirring time on organic/inorganic load removal and sludge sedimentation. Increasing lime concentration (from 27.6 to 33.3 g/L) elevated sludge volume without significant gains in COD and $NH_3$-N removal. Thus, 27.6 g/L was identified as optimal. Stirring at 300 rpm for 40 min delivered the best results using 160 mL of a 200 g/L CaO solution per liter of LL[1].

Figure 3 depicts the time-dependent reduction in ammonia via stripping. The horizontal axis represents time (hours), and the vertical axis shows the percentage of ammonia removed. Between 6 and 14 h, a consistent rise in removal efficiency was observed. At hour 6, the removal rate reached approximately 55%, indicating the initiation of mass transfer from the liquid to the gas phase. Efficiency increased continuously, peaking at 93% by 14 h. This upward trend underscores the importance of contact time in improving process performance. The pronounced increase between hours 12 and 14 suggests near-saturation, where most ammonia is transferred and removed. These findings emphasize the need to allocate sufficient residence time when designing stripping units. The ammonia stripping technique proved effective for $NH_3$-N reduction and can serve as a reliable pretreatment stage in nitrogen load mitigation. Ferraz et al. (2013) reported an 88% ammonia removal rate from 100 L of leachate via aeration, reinforcing the consistency and validity of the current study's findings[30]. In parallel with the results of the current study, Bellouk, H., et al. demonstrated effective treatment of young landfill leachate from Fez City using aeration. Their study achieved a reduction of $NH_4^+$ from 298 to 137 mg/L, $BOD_5$ from 30,000 to 1000 mg/L and COD from 12,080 to 5,586 mg/L, along with a significant decrease in heavy metal concentrations[33].

## Results of the fenton process and the effects of key parameters ($H_2O_2$: $Fe^{2+}$, $H_2O_2$, Time)

To evaluate the Fenton process, an experimental framework was developed using Design-Expert software (v13), as outlined in Table 3. The design aimed to optimize the process performance in enhancing the $BOD_5$/COD ratio of LL and incorporated a structured set of experimental conditions to assess the influence of key operational parameters. The statistical framework employed the BBD, incorporating independent variables, coded levels, number of runs, and the targeted response variable. Three independent variables were considered: the $H_2O_2$: $Fe^{2+}$ molar ratio, which significantly influences •OH radical generation; the $H_2O_2$ dosage as the oxidant; and the reaction time, which governs the extent of oxidative conversion. The selected response variable was the $BOD_5$/COD ratio, serving as a performance indicator for the Fenton process. Based on the collected experimental data, a multivariate regression model was fitted, and corresponding response surface, contour, and utility plots were generated. Table 2 served as the foundational input for subsequent statistical analysis and parameter optimization.

The design enabled identification of optimal values for each parameter under conditions that maximized the $BOD_5$/COD ratio. As highly reactive oxidants, •OH radicals play a crucial role in degrading organic pollutants in LL. These species can target C–H and C=C bonds and react with functional groups such as phenols, amines, and aromatics, breaking down complex molecular structures into simpler or inorganic forms. The primary mechanism involves electrophilic attack by •OH on reactive centers of organic compounds. However, when $H_2O_2$ is present in excess, undesirable side reactions may occur—such as with •OH itself—leading to reduced treatment efficiency. One such reaction is: $\bullet OH + H_2O_2 \rightarrow HO_2\bullet + H_2O$.

These secondary reactions may yield more stable, less degradable byproducts. In some cases, partially oxidized intermediates may exhibit greater resistance than the original compounds. Therefore, maintaining an optimal $H_2O_2$: $Fe^{2+}$ ratio, oxidant dosage, and contact time is essential to maximize treatment efficacy and suppress side reactions. The results of this study align with those of Bellouk et al. (2025), who demonstrated that optimal AOP performance occurs at acidic pH (≈3) and is strongly dependent on oxidant dosage. Similar to their findings, the present study confirms that the $H_2O_2$: $Fe^{2+}$ ratio and oxidant concentration are the most influential parameters governing the improvement of the $BOD_5$/COD ratio[33].

According to Table 3. The experimental design included three independent variables (A, B, and C) and seven response variables. The response variables were defined as follows, with Response 4 (R4) considered the primary response variable used for all major analyses and graphical evaluations:

*R1: $BOD_5$* (mg/L) The biochemical oxygen demand measured in each experimental run after applying the specified treatment conditions.

*R2: COD* (mg/L) The chemical oxygen demand measured in each run.

*R3: $BOD_5$/COD ratio* The biodegradability index calculated for each run as the ratio of $BOD_5$ (R1) to COD (R2).

*R4: Percentage increase in the $BOD_5$/COD ratio relative to raw leachate* This response represents the improvement in biodegradability after the Fenton process compared to the raw leachate. It was calculated using Eq. (8):

$$\mathrm{R4} = \frac{\left(\frac{\mathrm{BOD_5}}{\mathrm{COD}}\right)\mathrm{Raw} - \left(\frac{\mathrm{BOD_5}}{\mathrm{COD}}\right)\mathrm{After\ Fenton}}{\left(\frac{\mathrm{BOD_5}}{\mathrm{COD}}\right)Raw} \times 100 \tag{8}$$

| File version | 13.0.5.0 | Design model | Quadratic | Both exchanges | |
|---|---|---|---|---|---|
| **Study type** | **Response surface** | **Subtype** | **Randomized** | **Runs:26.00** | |
| **Factor** | **Units** | **Type** | **Minimum** | **Maximum** | **Std. Dev** |
| A: $H_2O_2$:$Fe^{2+}$ | ratio | Numeric | 2.00 | 6.00 | 1.65 |
| B: $H_2O_2$ | g/l | Numeric | 1.00 | 10.00 | 3.61 |
| C: Time | min | Numeric | 60.00 | 90.00 | 12.75 |
| D: Leachate | – | Categoric | – | – | 2.00 |
| Response | Name | Units | Minimum | Maximum | Std. Dev |
| R1 | $BOD_5$ | mg/l | 65 | 3200 | 1093.60 |
| R2 | COD | mg/l | 100 | 7619 | 2068.46 |
| R3<br>R4 | (($BOD_5$/COD))<br>$BOD_5$/COD | -<br>%increase/Raw | 0.37<br>59 | 0.87<br>230 | 0.1497<br>52.55 |
| R5 | ($BOD_5$/COD) | %increase/after.p | 6 | 200 | 43.91 |
| R6 | $BOD_5$.Removal | % | 13 | 90 | 27.85 |
| R7 | COD.Removal | % | 58 | 93.5 | 11.06 |

**Table 3.** Specification for design expert software used for fenton experiments.

*R5: Percentage increase in the $BOD_5$/COD ratio relative to the value after chemical precipitation* This response indicates the enhancement in biodegradability achieved by the Fenton process compared to the leachate condition after lime precipitation.

*R6: $BOD_5$ removal efficiency (%)* The percentage reduction in $BOD_5$ in each run after the Fenton process, calculated relative to its initial concentration in the raw leachate.

*R7: COD removal efficiency (%)* The percentage reduction in COD in each run after the Fenton process, calculated relative to its initial concentration in the raw leachate.

Table 4 reports the regression coefficients associated with the $BOD_5$/COD response variable. The RSM was used to model the interactions between three variables (A: $H_2O_2$: $Fe^{2+}$, B: $H_2O_2$ dose, C: reaction time) and the response variable. The use of BBD enabled the construction of empirical models and predictive equations. To evaluate model validity, ANOVA was performed. Among the three main variables A, B, and C, only variable C was not statistically significant at the 95% confidence level. Nevertheless, the applied models were overall evaluated as statistically significant at the 95% confidence level. Four critical metrics were applied to assess model quality:

1. *Prob. > F*: to determine model significance
2. *Lack of Fit test*: to evaluate model adequacy
3. *Adequate Precision*: to assess signal-to-noise ratio
4. *$R^2$*: to determine how well the predicted and actual data align

The model was accepted as valid based on the following criteria: Prob. > F < 0.05, Lack of Fit > 0.05, Adequate Precision ≥ 4, and $R^2 \geq 0.8$. In this study, the RSM model achieved an $R^2$ of 0.9919, indicating strong agreement between the predicted and observed data. Further evaluation using P-values confirmed that all variables significantly influenced the $BOD_5$/COD ratio. The adjusted $R^2$ (98.30%) supported the robustness of the quadratic model. Additionally, a low coefficient of variation (CV = 5.00) indicated high experimental accuracy and reproducibility. Regression analysis revealed that the $H_2O_2$ dose had the most pronounced effect on the $BOD_5$/COD ratio, confirming the process's sensitivity to oxidant concentration. The model also showed that optimal treatment conditions differed for fresh and old leachate, likely due to differences in chemical composition and reactivity. Overall, the application of BBD as a statistical tool enabled rigorous optimization of Fenton conditions and provided a quantitative basis for evaluating combined treatment efficiency. Equation (9) represents the optimized $BOD_5$/COD ratio for fresh LL, while Eq. (10) corresponds to the old LL.

$$
\begin{aligned}
(\mathrm{BOD_5/COD}) = &+100.47645 - 25.37335\,(\mathrm{A}) + 1.97453\,(\mathrm{B}) + 1.58624\,(\mathrm{C}) \\
&+ 0.472831\,(\mathrm{A}*\mathrm{B}) + 0.152608\,(\mathrm{A}*\mathrm{C}) - 0.004002\,(\mathrm{B}*\mathrm{C}) \\
&- 0.122028\,(\mathrm{A}*\mathrm{A}) - 0.190251\,(\mathrm{B}*\mathrm{B}) - 0.012424\,(\mathrm{C}*\mathrm{C})
\end{aligned}
\tag{9}
$$

$$
\begin{aligned}
(\mathrm{BOD_5/COD}) = &+196.42815 - 25.65755\,(\mathrm{A}) + 3.61273\,(\mathrm{B}) + 1.43360\,(\mathrm{C}) \\
&+ 0.472831\,(\mathrm{A}*\mathrm{B}) + 0.152608\,(\mathrm{A}*\mathrm{C}) - 0.004002\,(\mathrm{B}*\mathrm{C}) \\
&- 0.122028\,(\mathrm{A}*\mathrm{A}) - 0.190251\,(\mathrm{B}*\mathrm{B}) - 0.012424\,(\mathrm{C}*\mathrm{C})
\end{aligned}
\tag{10}
$$

| Source | Sum of squares | df | Mean square | F-value | *p*-value |
|---|---|---|---|---|---|
| Model | 68,483.20 | 13 | 5267.94 | 112.44 | < 0.0001<br>significant |
| A:$H_2O_2$:$Fe^{2+}$ | 8213.08 | 1 | 8213.08 | 175.30 | < 0.0001 |
| B:$H_2O_2$ | 1272.27 | 1 | 1272.27 | 27.16 | 0.0002 |
| C:Time | 174.91 | 1 | 174.91 | 3.73 | 0.0773 |
| D:Leachate | 44,841.44 | 1 | 44,841.44 | 957.11 | < 0.0001 |
| AB | 156.22 | 1 | 156.22 | 3.33 | 0.0928 |
| AC | 204.59 | 1 | 204.59 | 4.37 | 0.0586 |
| AD | 0.9787 | 1 | 0.9787 | 0.0209 | 0.8875 |
| BC | 0.7613 | 1 | 0.7613 | 0.0163 | 0.9007 |
| BD | 181.31 | 1 | 181.31 | 3.87 | 0.0727 |
| CD | 17.83 | 1 | 17.83 | 0.3806 | 0.5488 |
| $A^2$ | 1.23 | 1 | 1.23 | 0.0263 | 0.8739 |
| $B^2$ | 67.73 | 1 | 67.73 | 1.45 | 0.2524 |
| $C^2$ | 26.36 | 1 | 26.36 | 0.5626 | 0.4677 |
| Lack of Fit | 528.80 | 7 | 75.54 | 0.6012 | 0.7875<br>Not significant |
| Pure Error | 33.41 | 5 | 6.68 | Adjusted $R^2$ | 0.9830 |
| Std. Dev | 6.84 | $R^2$ | 0.9919 | Predicted $R^2$ | 0.9640 |
| Mean | 136.84 | C.V | 5.00 | Adeq Precision | 33.9806 |

**Table 4.** ANOVA table to examine the response variable $BOD_5$/COD.

Figure 4 presents a set of diagnostic plots used to evaluate the robustness of the multivariate regression model developed through RSM for treatment process optimization. These diagnostics confirm that the model satisfies the essential statistical assumptions. The residuals follow a normal distribution, the errors are randomly dispersed, and the predicted values show strong agreement with the experimental data. Moreover, the Box–Cox analysis indicates that no substantial data transformation is required, further supporting the validity of the model without additional adjustments. Collectively, these results verify the suitability of the regression model for optimizing the treatment process.

Specifically, Fig. 4A confirms the normality of residuals, as the points closely follow the diagonal reference line. Figure 4B displays a random and uniform scatter of residuals around zero, indicating homoscedasticity and the absence of variance-related bias. Figure 4C shows that residuals fluctuate randomly across the run order, demonstrating that no time-dependent or sequence-related patterns influence the model. Figure 4D illustrates strong agreement between predicted and actual values, confirming the high predictive accuracy of the model. Figure 4E indicates that residuals are consistently distributed across experimental blocks, suggesting negligible block effects. Finally, Fig. 4F shows that the optimal lambda value is close to 1, confirming that no data transformation is necessary and that the model performs adequately in its original form.

Figure 5 illustrates the model's sensitivity to variations in independent variables, identifying which parameter most significantly influences the $BOD_5$/COD response. The horizontal axis shows incremental variations around the center point of the experimental design, while the vertical axis displays changes in the predicted $BOD_5$/COD value. The gradient of each curve indicates the relative influence of each factor. The $H_2O_2$: $Fe^{2+}$ ratio exhibited the steepest slope, revealing the model's high sensitivity to this parameter. Variations in this ratio had a pronounced impact on Fenton process efficiency, as it controls •OH radical generation. Accurate adjustment of this ratio was thus critical to maximizing the $BOD_5$/COD response. The curve for $H_2O_2$ concentration also showed a substantial slope, although less steep. While increasing the $H_2O_2$ dosage improved the process up to a point, excessively high concentrations led to diminishing returns or adverse effects, such as radical scavenging or side-product formation. This behavior confirms the existence of an optimal $H_2O_2$ concentration. The curve associated with reaction time was relatively flat, indicating a smaller effect on the response than the other variables. Although adequate time is required to complete oxidation reactions, extending reaction time beyond a threshold did not significantly enhance process efficiency. Overall, Fig. 5 demonstrates that the $H_2O_2$: $Fe^{2+}$ ratio was the most influential variable in improving the $BOD_5$/COD ratio, followed by $H_2O_2$ concentration and reaction time. This insight is critical for scaling the Fenton process in industrial applications and provides a reliable foundation for fine-tuning operating parameters. The study by Imane El Mrabet et al. demonstrated that the Fenton-like process was successfully applied for the pretreatment of raw landfill leachate highly loaded with organic matter. The efficiency of this process is closely affected by the initial pH of leachate and the dosages of $H_2O_2$ and $Fe^{3+}$.Therefore, the optimization of these parameters should be considered in order to achieve maximum removal of organic pollutants[35].

Figure 6 illustrates the individual effects of each independent variable on the $BOD_5$/COD response, with variable values plotted along the horizontal axis and corresponding response values on the vertical axis. Each curve represents the change in response associated with varying one parameter, while the remaining variables are held constant at their central levels. The curve for the $H_2O_2$: $Fe^{2+}$ ratio displays a pronounced slope, confirming that this parameter is the most influential factor in the Fenton process. At lower values, insufficient •OH generation leads to limited oxidation performance. As the ratio increases, process efficiency improves markedly. However, at excessively high ratios, a decline in performance is observed, likely due to radical overconsumption or the generation of stable side-products that reduce oxidizing potential. The $H_2O_2$ concentration curve also shows an upward trend, though with a gentler gradient. Increasing oxidant dosage enhances the process up to a threshold, beyond which diminishing returns or adverse effects emerge, possibly due to saturation or unproductive radical reactions. The reaction time curve shows a gradual increase in the $BOD_5$/COD response with increasing reaction time. Short durations are insufficient for complete oxidation, while longer times allow more extensive pollutant degradation. However, beyond a certain point, the curve flattens, indicating that extended reaction times yield negligible additional benefits. These results reaffirm that the $H_2O_2$: $Fe^{2+}$ ratio is the most critical variable in optimizing the Fenton process, followed by $H_2O_2$ concentration and reaction time. This insight is vital for refining operating conditions and scaling up leachate treatment systems for industrial applications.

The Fenton process operates most efficiently at acidic pH, particularly below 3. In this study, the Fenton reaction was conducted consistently at pH = 3, a value corroborated by the findings of Dhamsaniya et al.[8], reinforcing the validity of this pH as an optimal operational parameter. Similarly, Jegadeesan et al. reported that pH = 3 yields the best results for organic pollutant degradation, in full agreement with the current experimental setup[36]. Da Costa et al. (2018) further explored a range of pH values (1.5, 3, and 5) and concluded that pH = 3 was optimal for maximizing both pollutant removal and the biodegradability of LL[37]. These findings collectively affirm the importance of strict pH control in enhancing the efficiency of the Fenton reaction. At elevated pH, $H_2O_2$ exhibits a lower dissociation coefficient, leading to lower hydroxyl radical (•OH) generation. Additionally, iron ions are less stable under alkaline conditions, further diminishing the system's oxidative capacity. Increasing the $H_2O_2$ concentration relative to $Fe^{2+}$ can initially enhance process performance; however, at excessively high dosages, process efficiency declines. This reduction is likely caused by secondary reactions in which excess $H_2O_2$ consumes hydroxyl radicals (e.g., $\bullet OH + H_2O_2 \rightarrow HO_2\bullet + H_2O$), thereby lowering the concentration of effective oxidants available for organic matter degradation. Reaction time also significantly influences the Fenton process. Efficiency improved with increasing duration, with the maximum performance observed at 75 min. This is consistent with findings by Kajitvichyanukul and Suntronvipart, who identified the optimal reaction time within the 60–90-min range[38]. Time is a key parameter that directly affects both performance and cost-efficiency in the application of this process. El Mrabet et al. evaluated the effects of pH, $Fe^{2+}$ concentration, and $H_2O_2$ dosage and reported optimal values of pH = 2.8, $Fe^{2+}$ = 1621 mg/L, and $H_2O_2$ = 2500 mg/L, resulting in COD removal

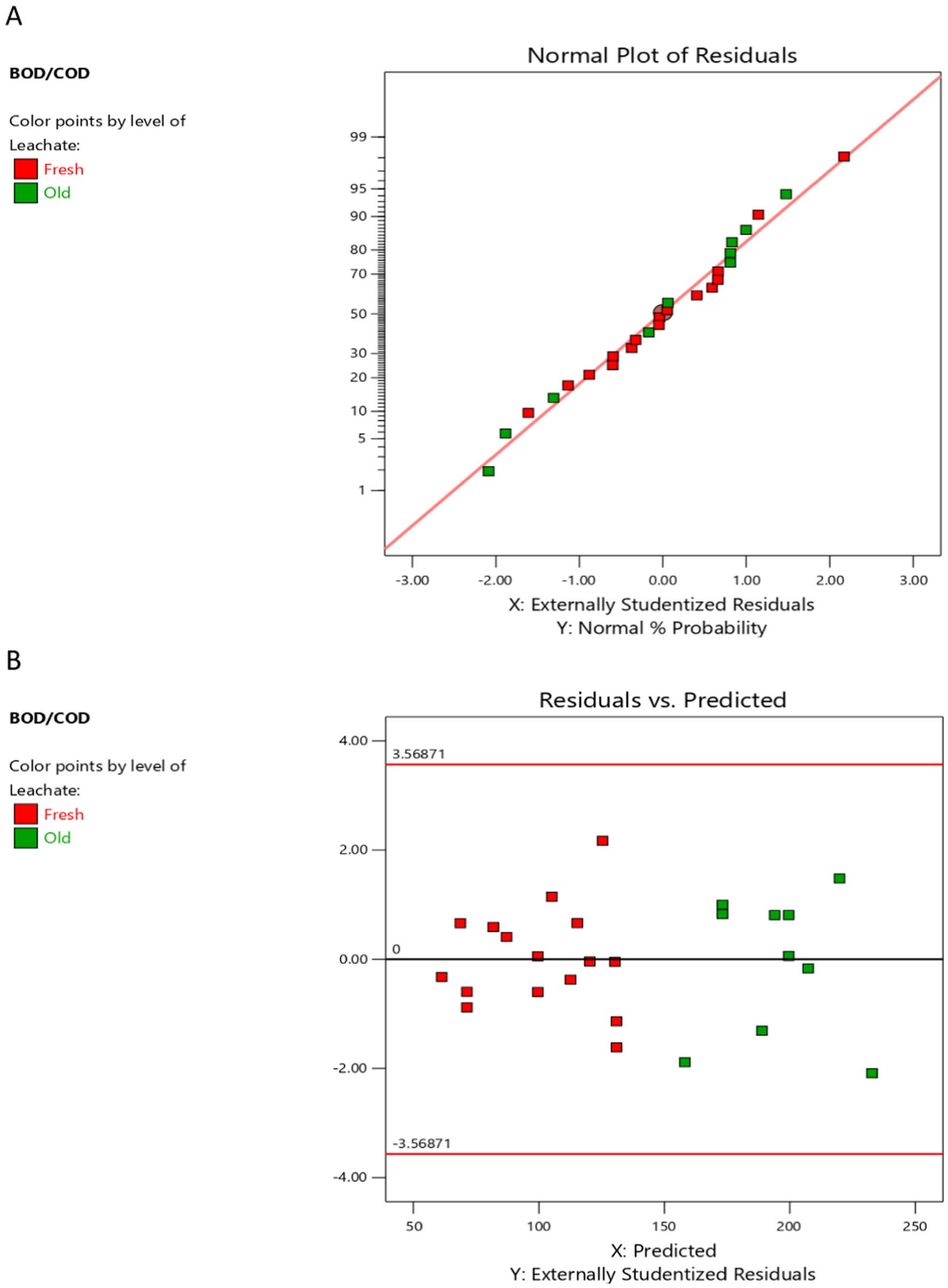


**Fig. 4**. Diagnostics chart ((**A**) normal plot of residuals, (**B**) Residuals vs. Predicted, (**C**) Residuals vs. Run, (**D**) Predicted vs. Actual, (**E**) Residuals vs. Block, (**F**) Box–Cox plot for power transforms).

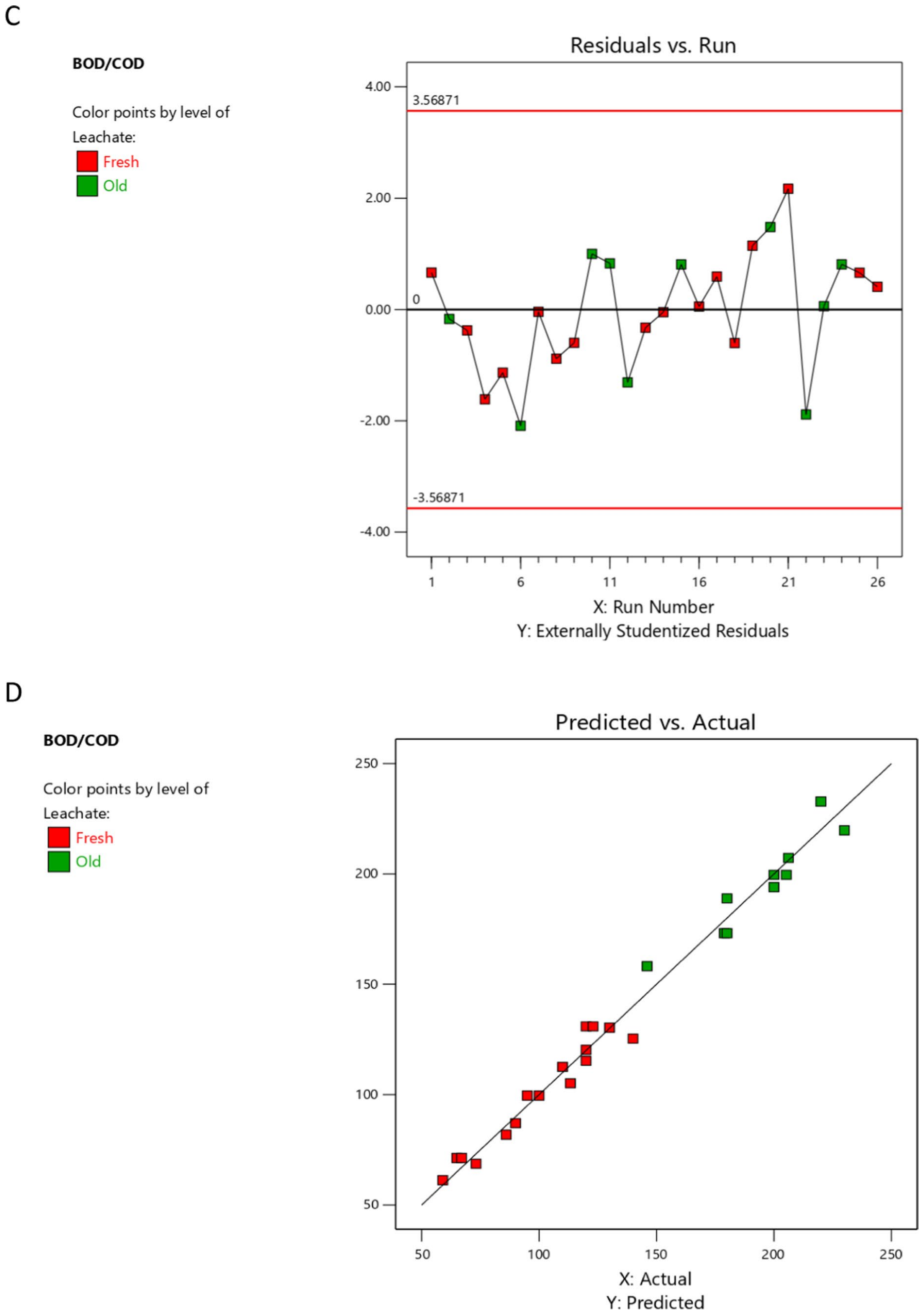


**Fig. 4.** (continued)

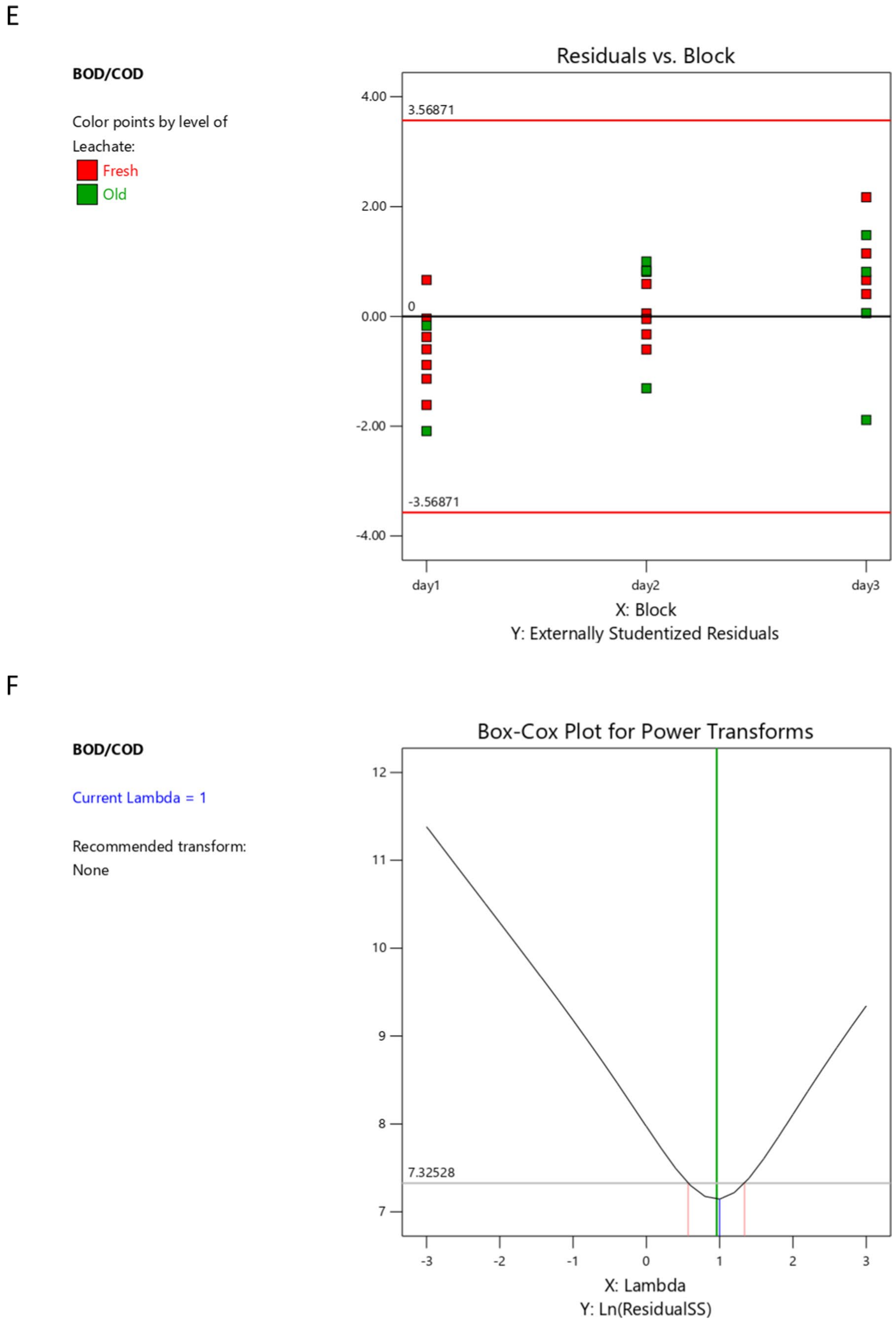


**Fig. 4.** (continued)

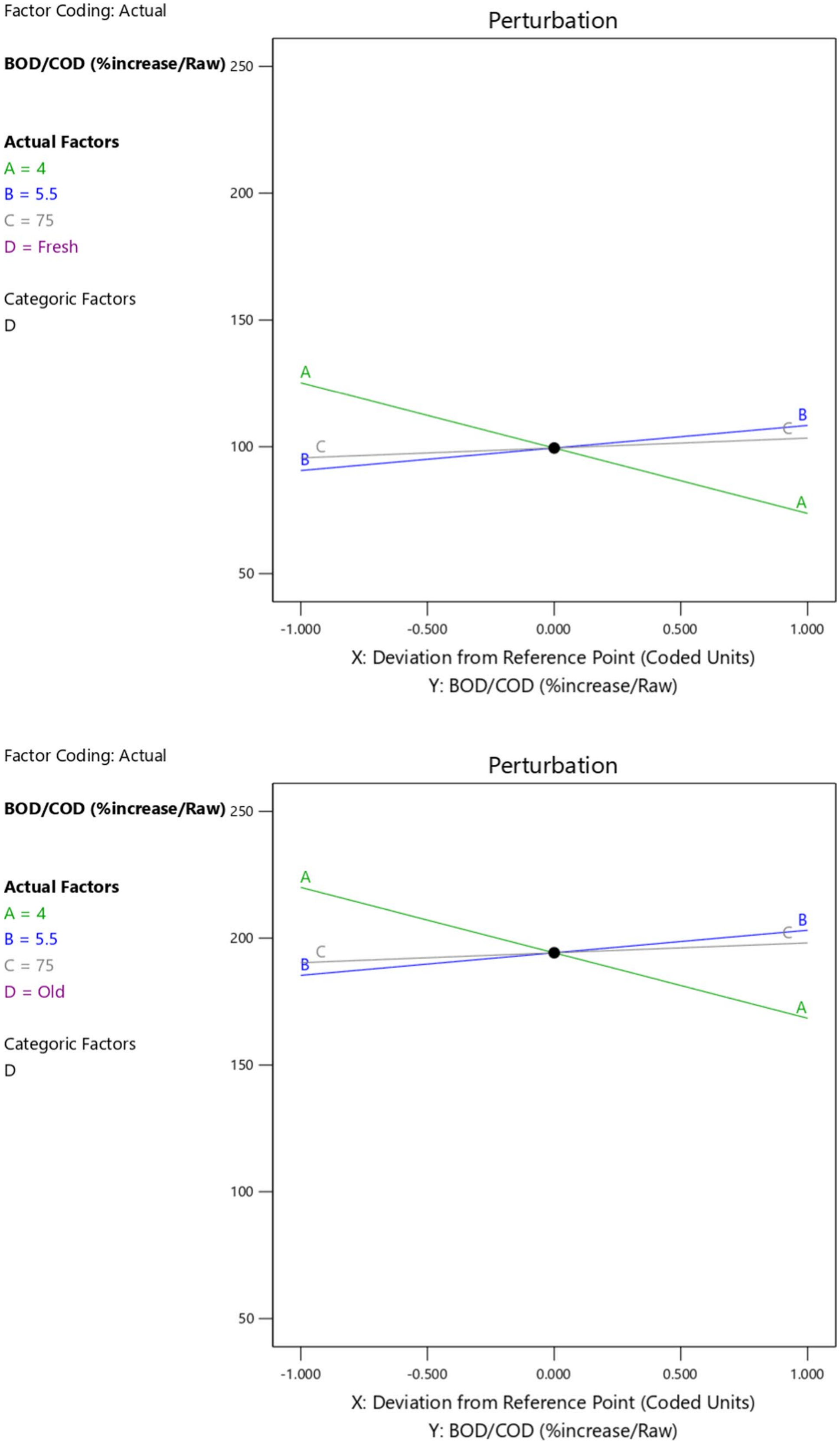


**Fig. 5**. Perturbation chart (**A** $H_2O_2$:$Fe^{2+}$, **B** $H_2O_2$, **C** Time).

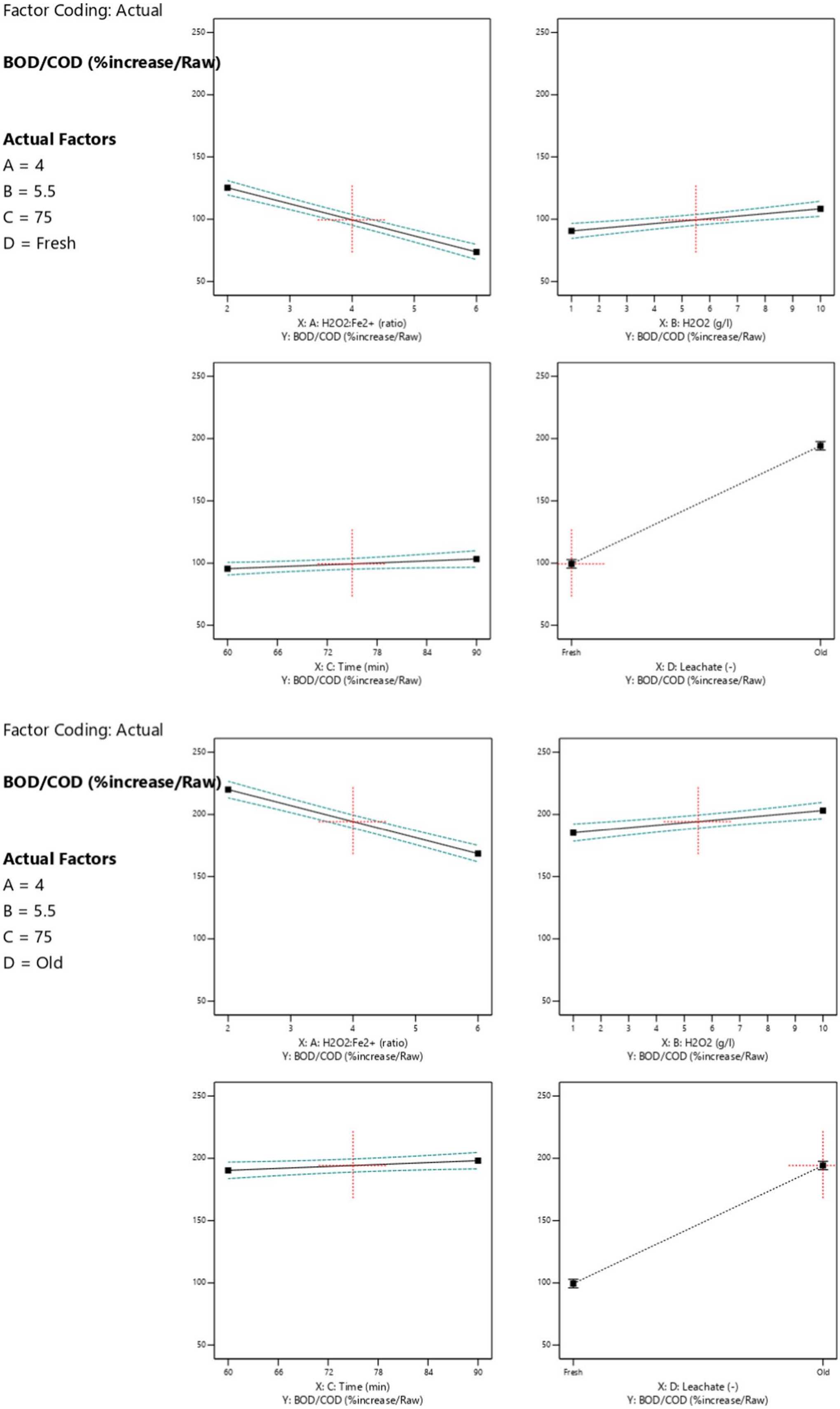


**Fig. 6**. Individual effect trends of variables on response.

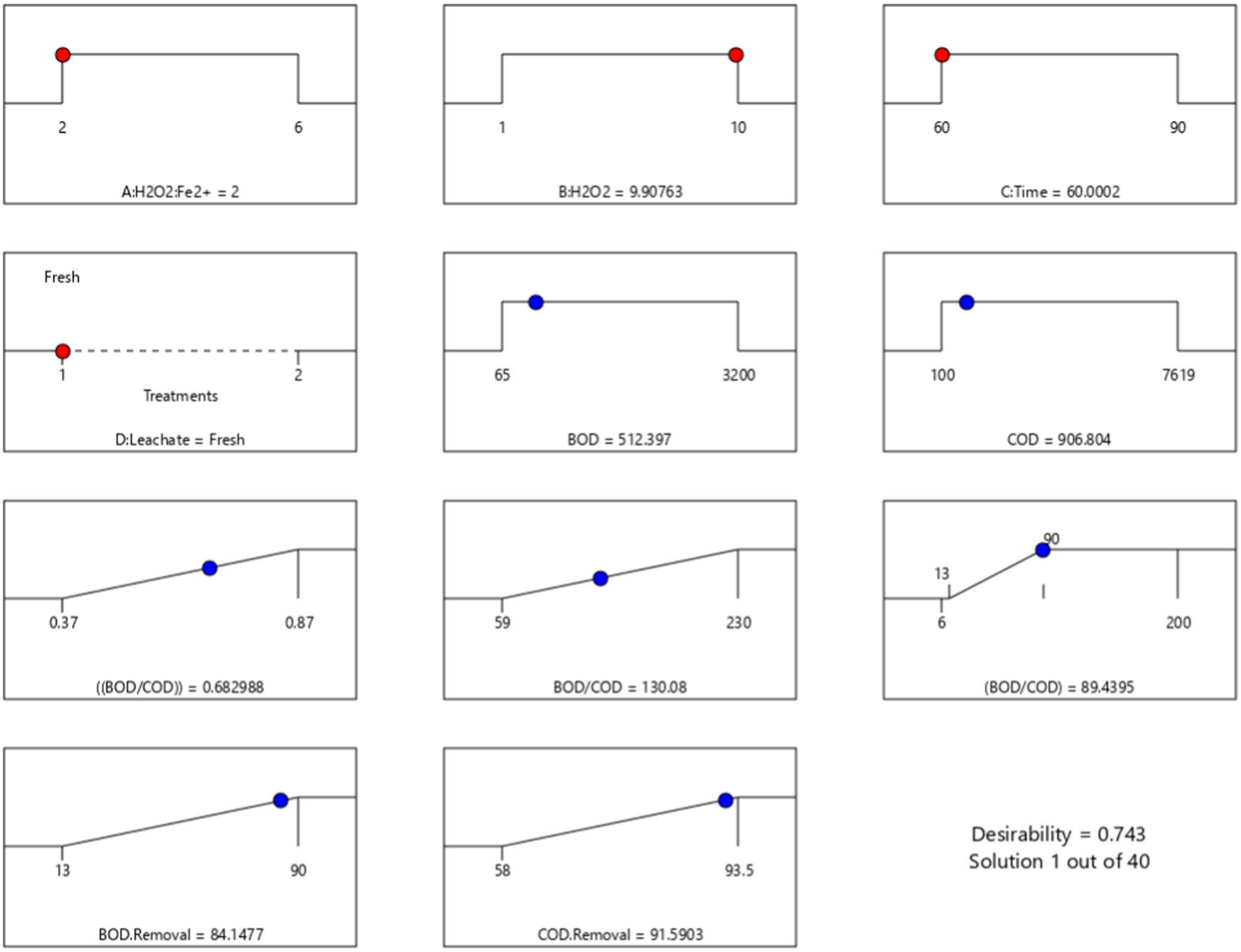


**Fig. 7**. Desirability Ramp plot for optimized variables.

efficiency of 85%[39], which aligns closely with the outcomes of the present study. Likewise, the findings by de Sousa et al. demonstrated that the Fenton process increased the $BOD_5$/COD ratio to 0.77, indicating a significant enhancement in the biological treatability of LL[40]. To determine optimal conditions for maximizing the $BOD_5$/COD ratio, independent variables were explored across predefined ranges. The optimization objective was to maximize this ratio while maintaining efficient process performance. Figure 7, derived using RSM, illustrates the influence of the independent variables on the overall desirability score. This plot is instrumental in the process optimization stage, as it delineates the ideal operational ranges that yield the most favorable treatment outcomes. Based on RSM optimization, the ideal parameter values were as follows: Fresh LL: A = 2, B = 10, C = 60, Old LL: A = 2, B = 8.2, C = 75. These values represent the optimal $H_2O_2$: $Fe^{2+}$ ratio, $H_2O_2$ concentration (g/L), and reaction time (minutes), respectively. Further validation is provided by the study of Maslahati Roudi et al., who reported optimal Fenton conditions under the constraints of pH = 3, $Fe^{2+}$ = 781.25 mg/L, $H_2O_2$: $Fe^{2+}$ ratio = 2, and reaction time of 28.04 min. Under these settings, a COD removal efficiency of 97.83% was achieved[31]. The $H_2O_2$:$Fe^{2+}$ ratio applied in their study is consistent with that used in the present investigation, reaffirming its effectiveness in enhancing the oxidation efficiency of the Fenton process[20]. In accordance with the findings of the current research, a study conducted by Roger I. Méndez-Novelo et al. employed a three-stage Fenton process under optimized conditions (contact time, pH, and ratios of [COD]/[$H_2O_2$] and [$Fe^{2+}$]/[H2O2]) for treating leachate from the Mérida sanitary landfill in Mexico. The objective was to enhance the biodegradability index, yielding the following results: In Stage 1, 71.26% COD removal was achieved; Stage 2 showed increased COD removal to 91.74%; and Stage 3 attained 95.12% COD removal. Additionally, the biodegradability index improved from 0.06 to 0.48, indicating the leachate's greater potential for subsequent biological treatment[41].

In the contour map (Fig. 8) for fresh *leachate*, zones represented by warmer colors and denser lines correspond to conditions yielding the highest increase in the $BOD_5$/COD ratio. Fresh *leachate*, being more chemically reactive, responds more effectively within specific ranges of $H_2O_2$: $Fe^{2+}$ ratio and $H_2O_2$ dose. The curved contour lines illustrate the interaction between these variables; simultaneous increases in both can enhance or reduce process efficiency depending on the region of the curve. In contrast, the contour map for old *leachate* shows more localized optimal zones, reflecting its lower reactivity and the need for more precise control of

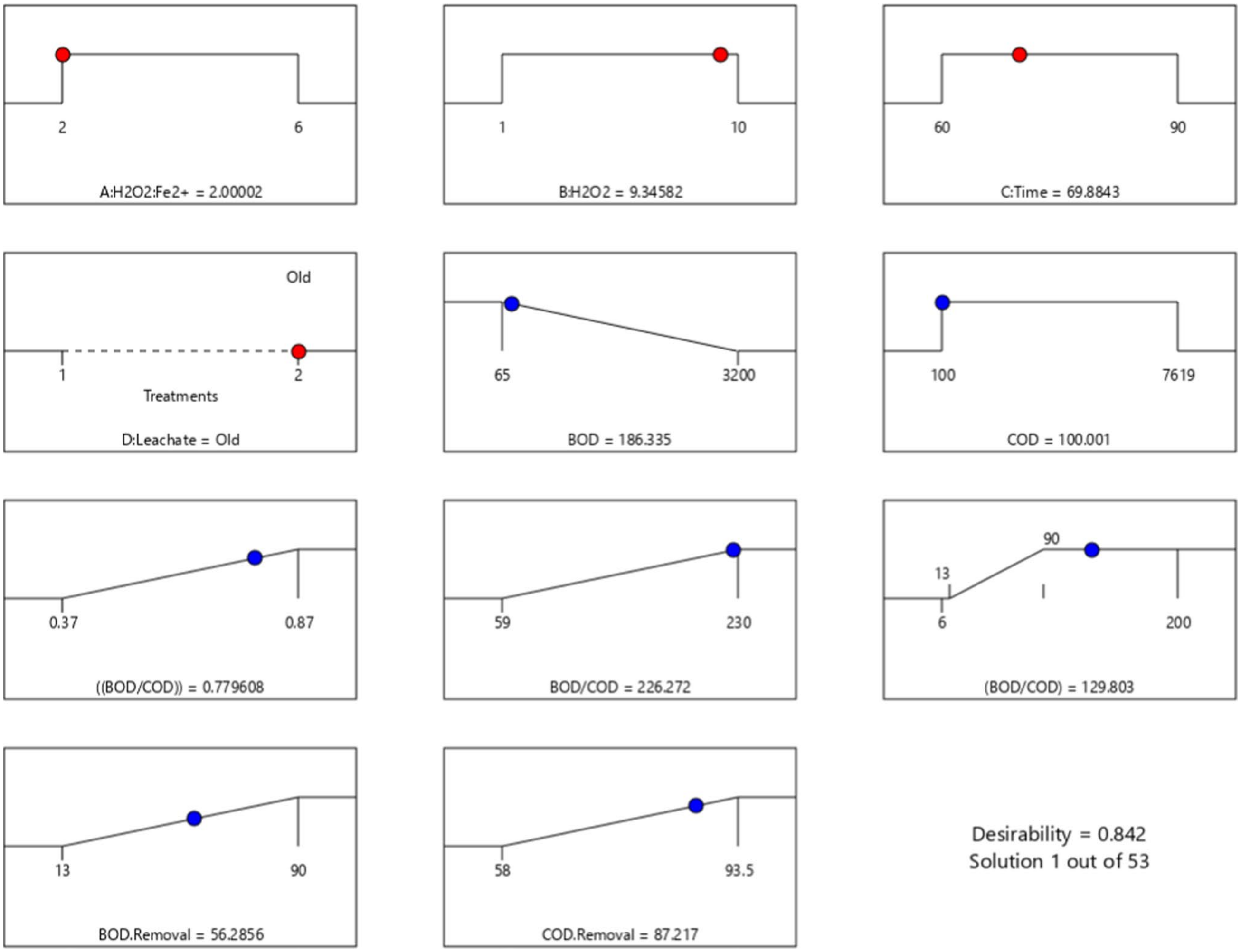


**Fig. 7.** (continued)

operational parameters. The reduced responsiveness is attributed to the presence of more stable and recalcitrant organic constituents. As demonstrated by the present study, a novel advanced oxidation process (AOP) using ultrasound-Photo-Fenton (US-P-FP) was employed by Bellouk, H., et al. for treating stabilized landfill leachate from the city of Fez, Morocco. Operational factors ($Fe^{2+}$ dosage, pH, $H_2O_2$ dosage, ultrasonic treatment (US), and UV-A radiation) were optimized using a two-level factorial design. The findings revealed the highest landfill leachate COD removal of 93% under optimal operational conditions: $[Fe^{2+}] = 446$ mg/L, $[H_2O_2] = 250$ mg/L, and pH = 3, in the simultaneous presence of both US and UV-A irradiation[42].

Figure 9 presents 3D surface plots developed within the RSM framework to depict the optimal treatment conditions for fresh and old leachate. These plots illustrate the combined effect of two independent variables on the $BOD_5$/COD response. The 3D surface of fresh leachate shows steeper gradients and sharper peaks, suggesting higher chemical reactivity and greater sensitivity to changes in input variables. Elevated areas represent parameter combinations that maximize the $BOD_5$/COD ratio. Conversely, the 3D surface for old leachate is flatter with less pronounced peaks, indicating reduced reactivity and a narrower operational window for optimal outcomes. This behavior results from the complex and stable nature of organic pollutants present in old leachate, which require more stringent oxidative conditions for effective degradation. In a comparative analysis, Maslahati Roudi et al. reported a COD removal efficiency of 97.8% under optimized Fenton conditions[20]. In the current study, COD removal efficiencies were 88.33% for fresh *leachate* and 81.28% for old leachate, confirming the consistent and robust performance of the Fenton process across different matrices, albeit with slightly lower yields.

Table 5 summarizes the outcomes of the integrated chemical precipitation and Fenton processes under optimal operational conditions. All values are reported as mean ± standard deviation. For fresh *leachate*, optimal parameters were A = 2, B = 10, C = 60, while for old leachate, the values were A = 2, B = 8.2, C = 75. Under these conditions, the $BOD_5$/COD ratio increased by 135.42 ± 25% in fresh leachate and 215.00 ± 20% in old leachate. Initial COD measurements indicated that fresh leachate had a higher organic load and lower biodegradability in its raw state than old leachate. While chemical precipitation alone produced notable COD reduction, its effectiveness was less than that of the Fenton process, particularly in treating old leachate containing more resistant organic compounds. The combined approach of chemical precipitation followed by Fenton oxidation

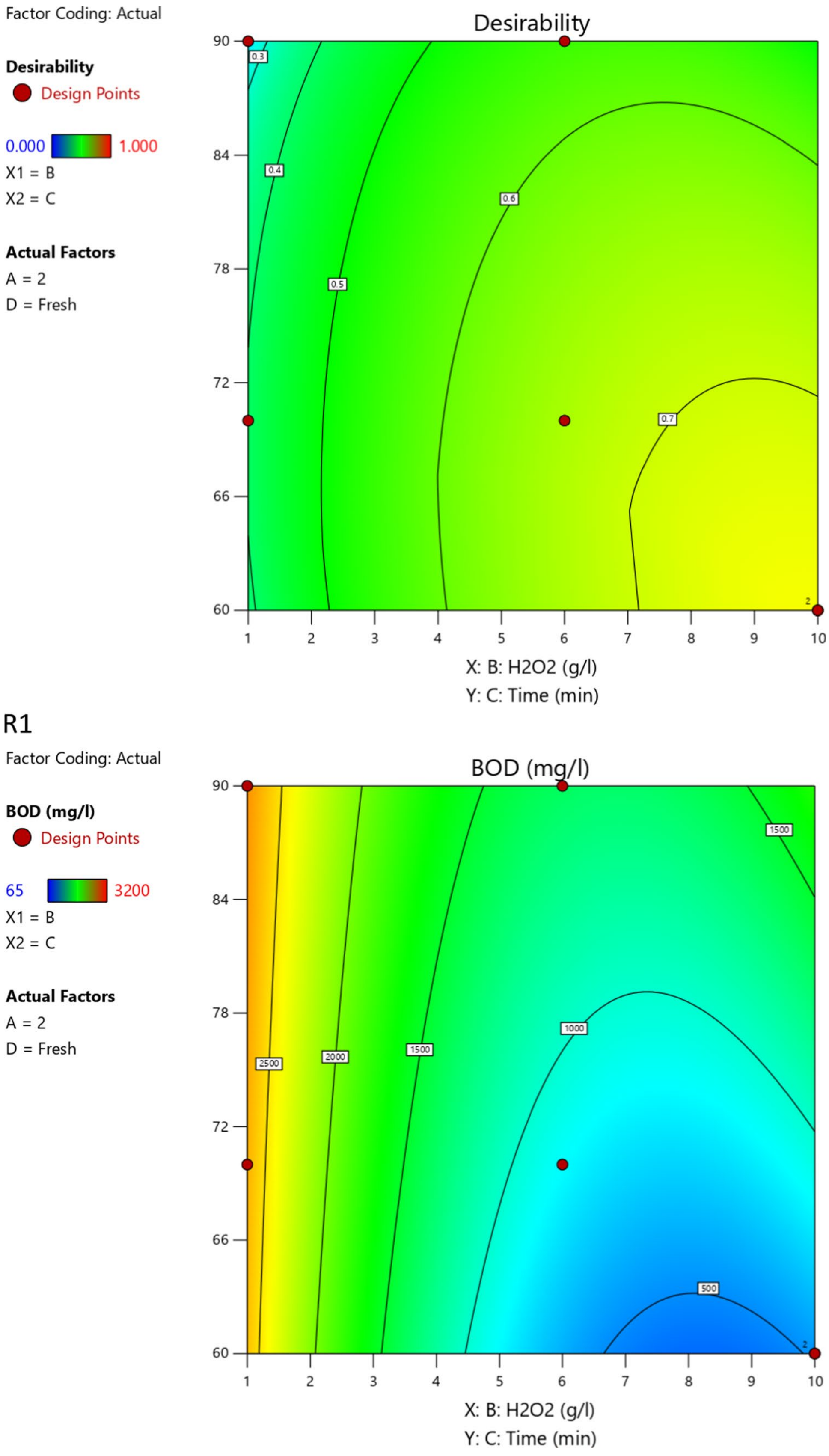


**Fig. 8**. Contour plots of optimal conditions for fresh and old leachate.

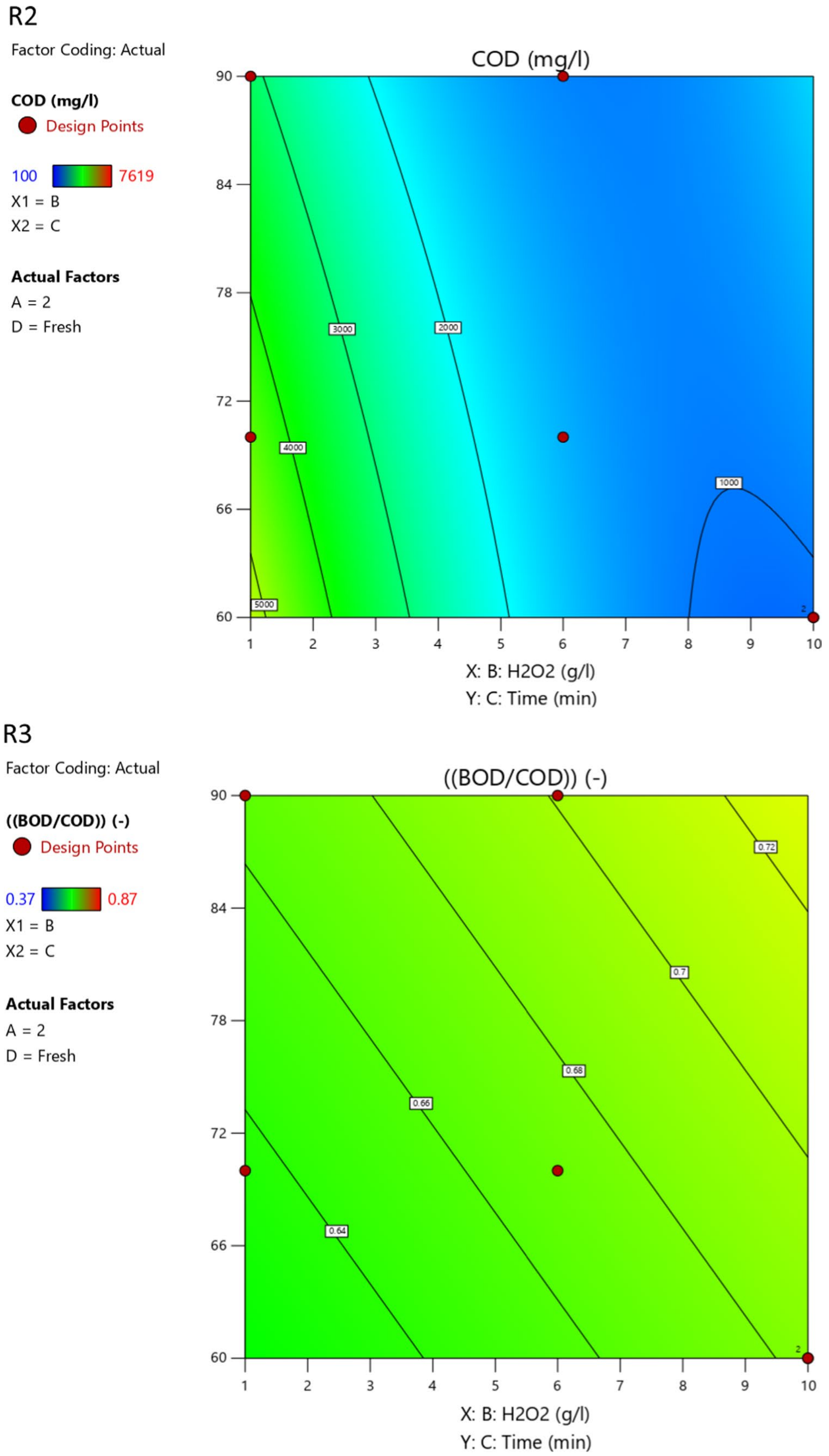


**Fig. 8.** (continued)

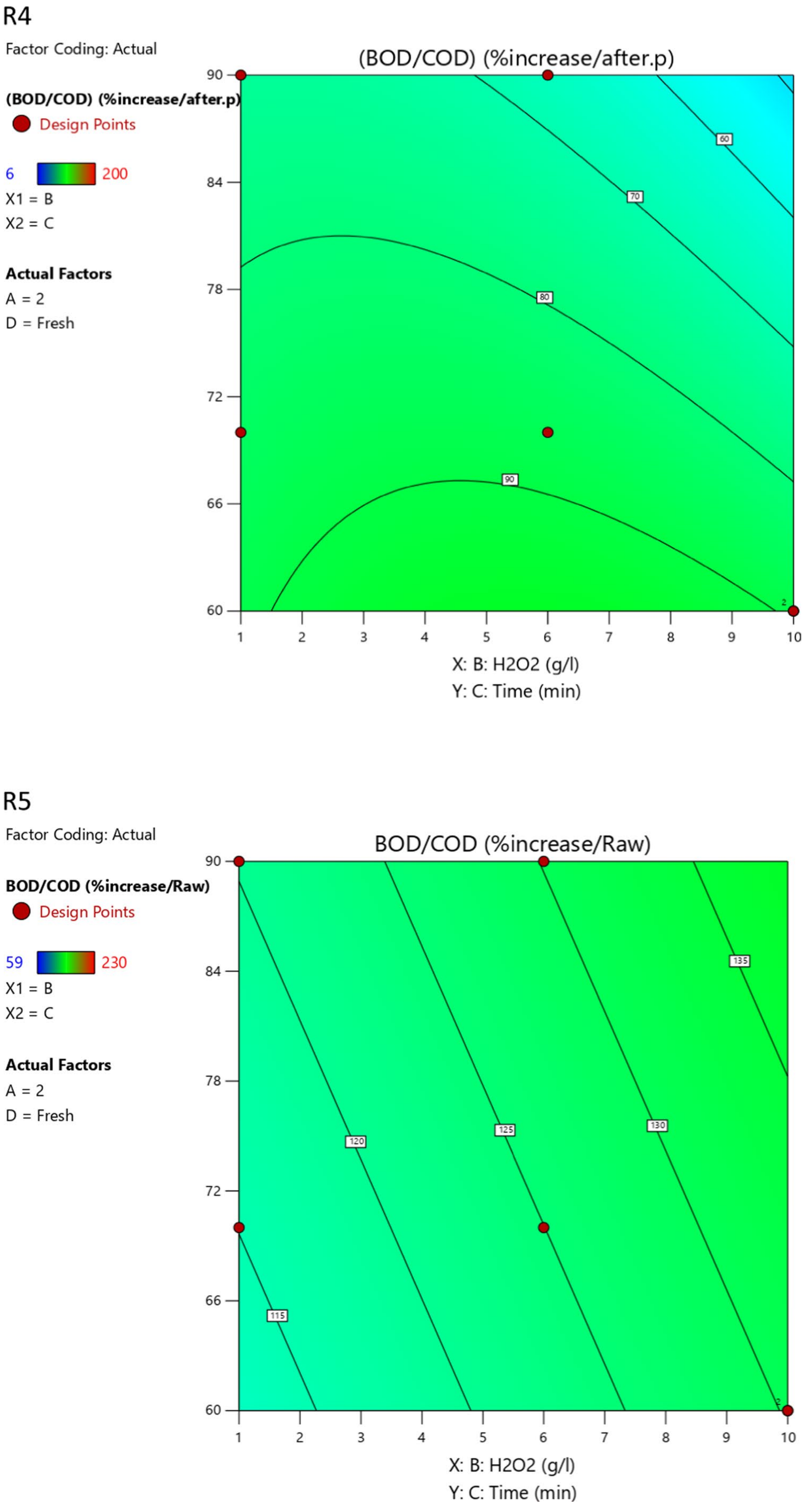
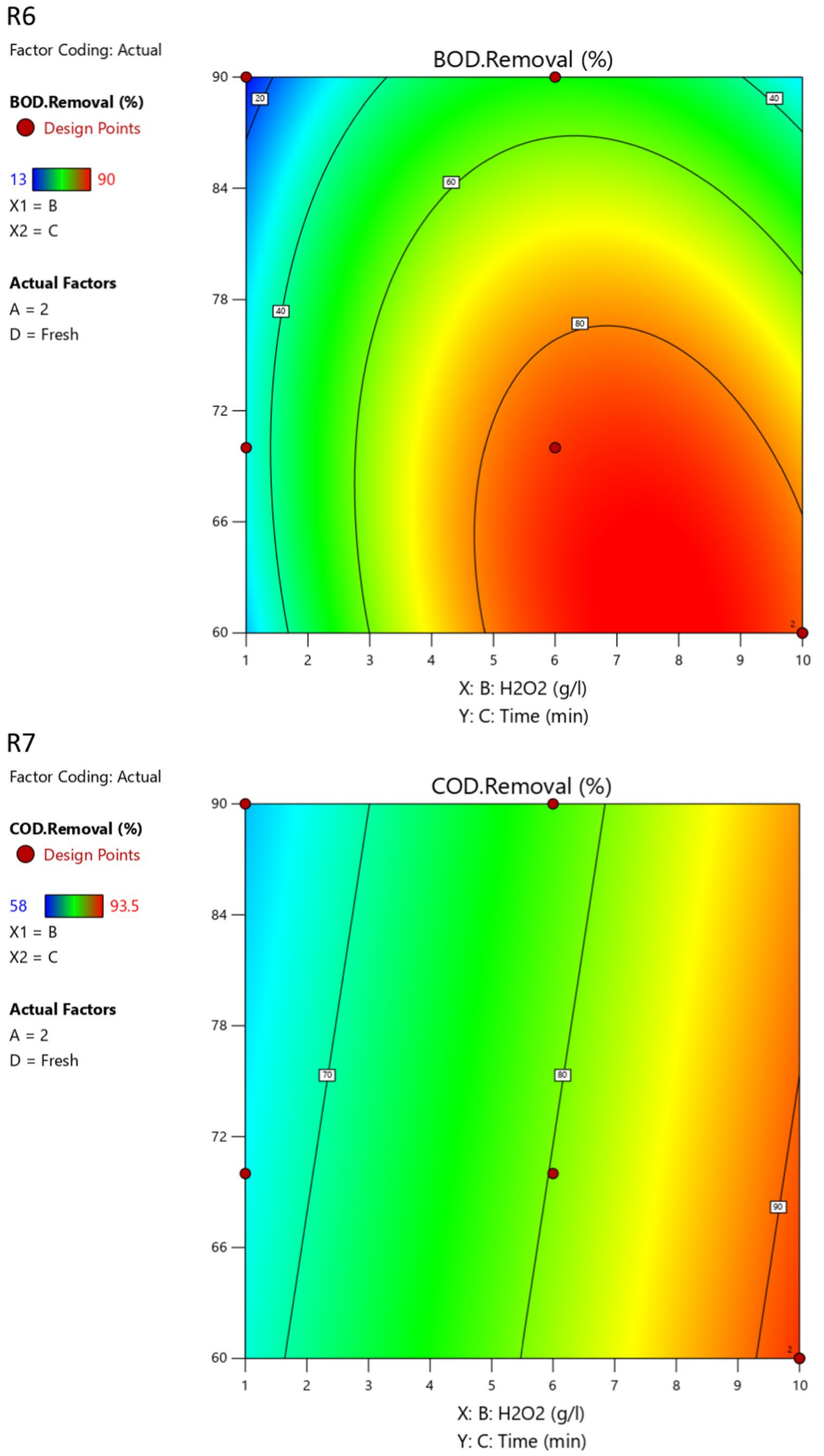


**Fig. 8.** (continued)



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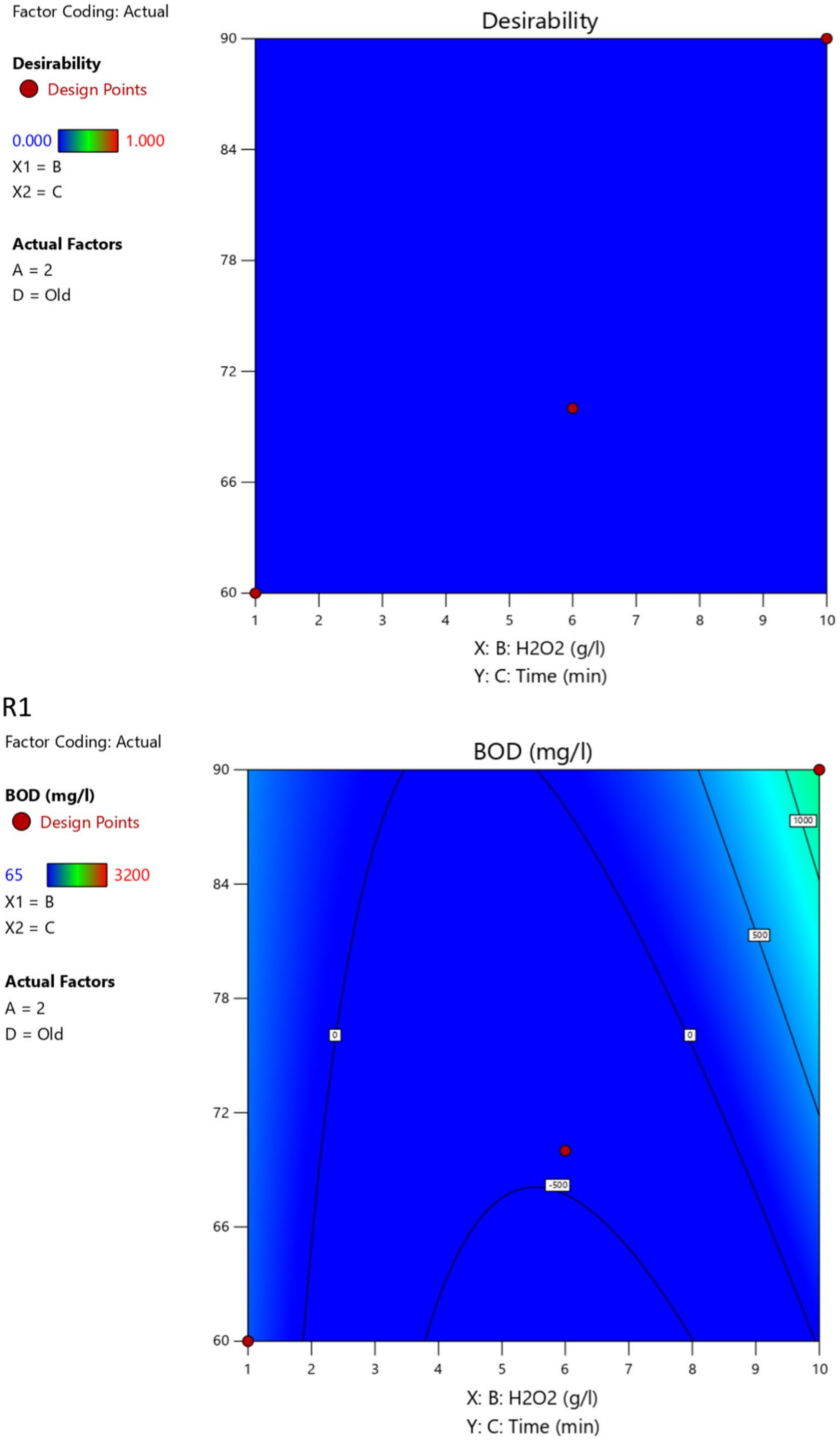
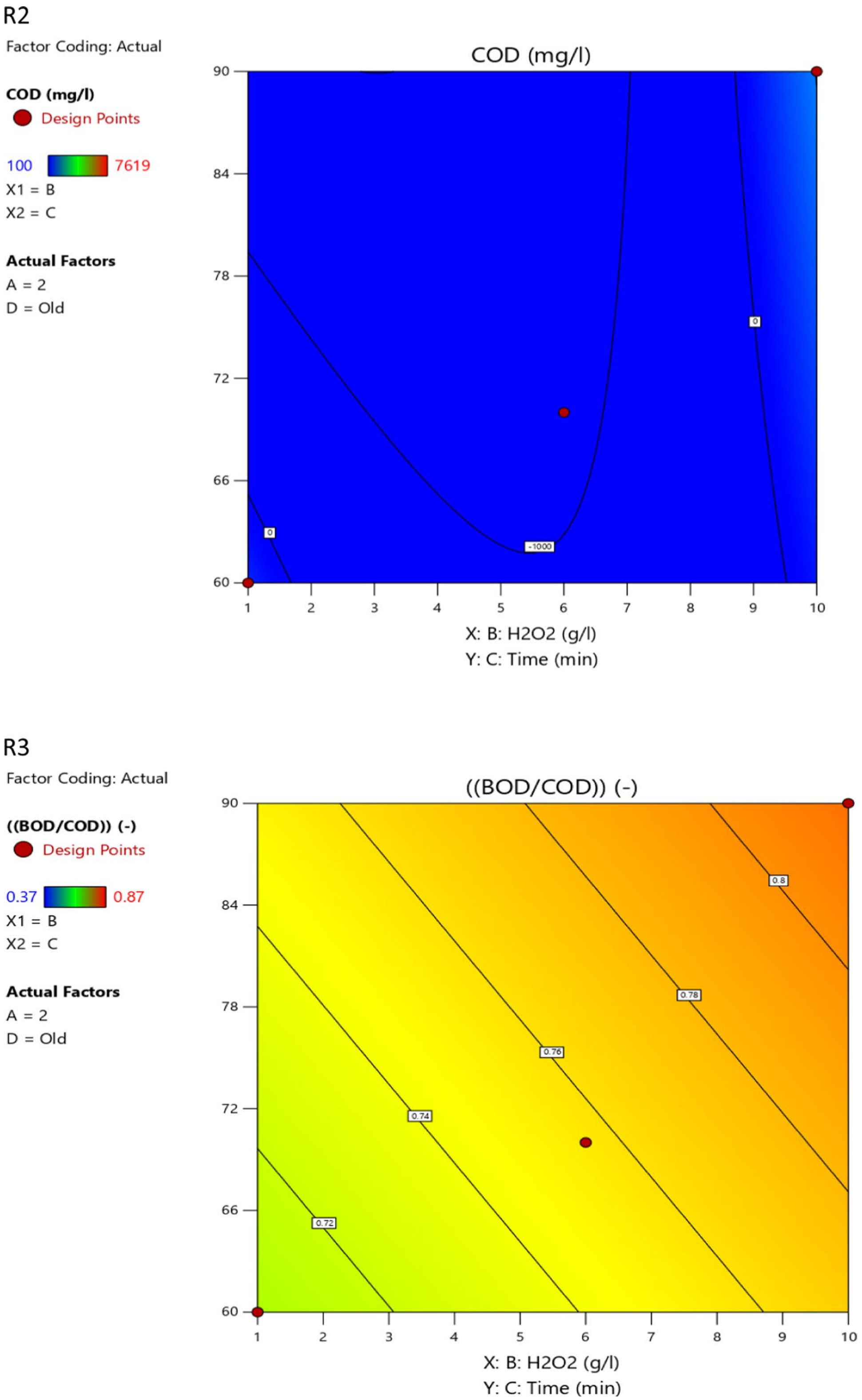


**Fig. 8.** (continued)

yielded the most significant COD reduction across both leachate types, demonstrating a synergistic effect that enhances the removal of persistent organic pollutants.



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These results underscore the efficacy of integrating chemical precipitation and the Fenton process as a robust pretreatment strategy for leachate, providing significant improvements in pollutant removal and biodegradability enhancement prior to biological treatment stages.

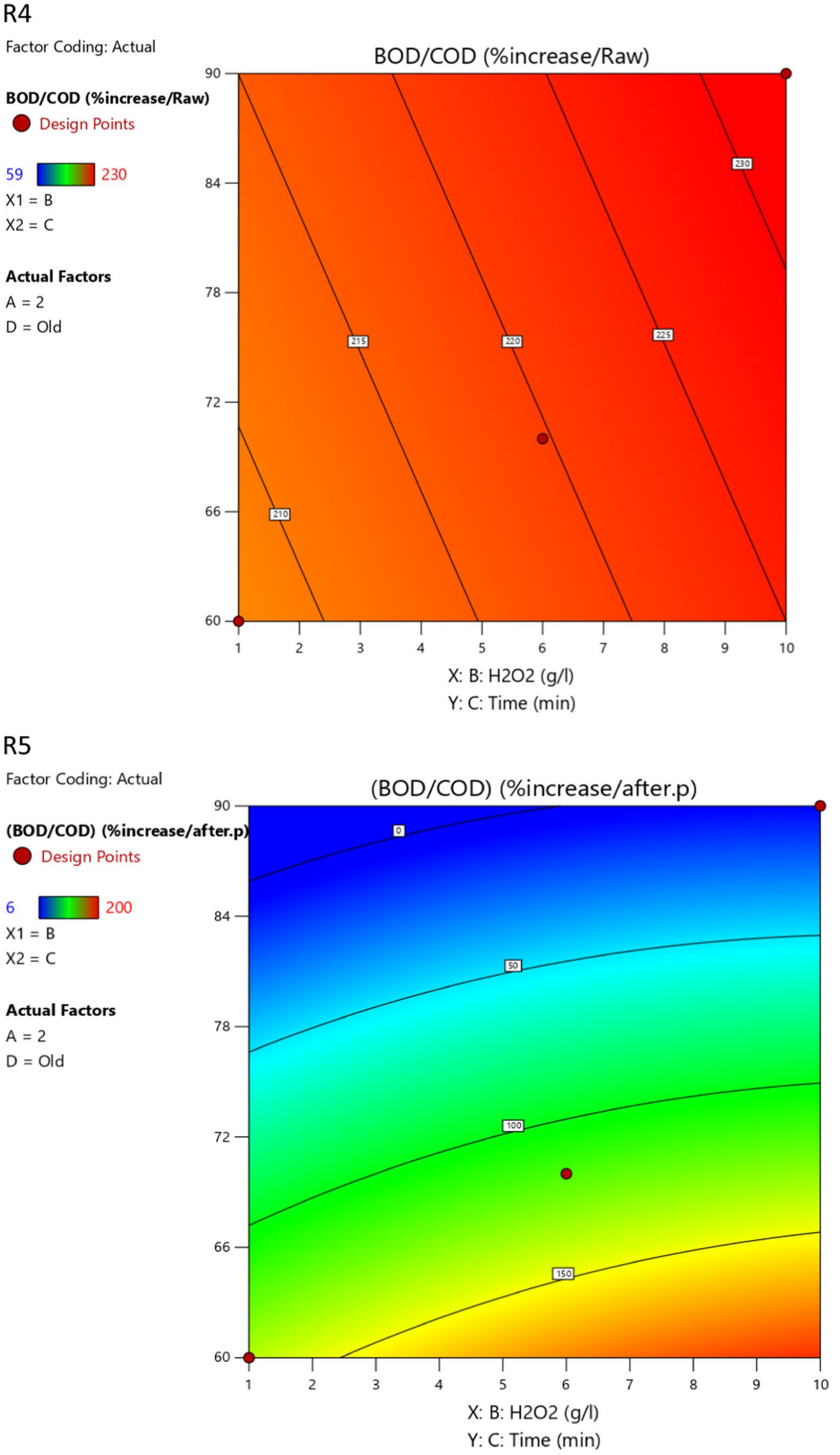

**Fig. 8.** (continued)

## Conclusion

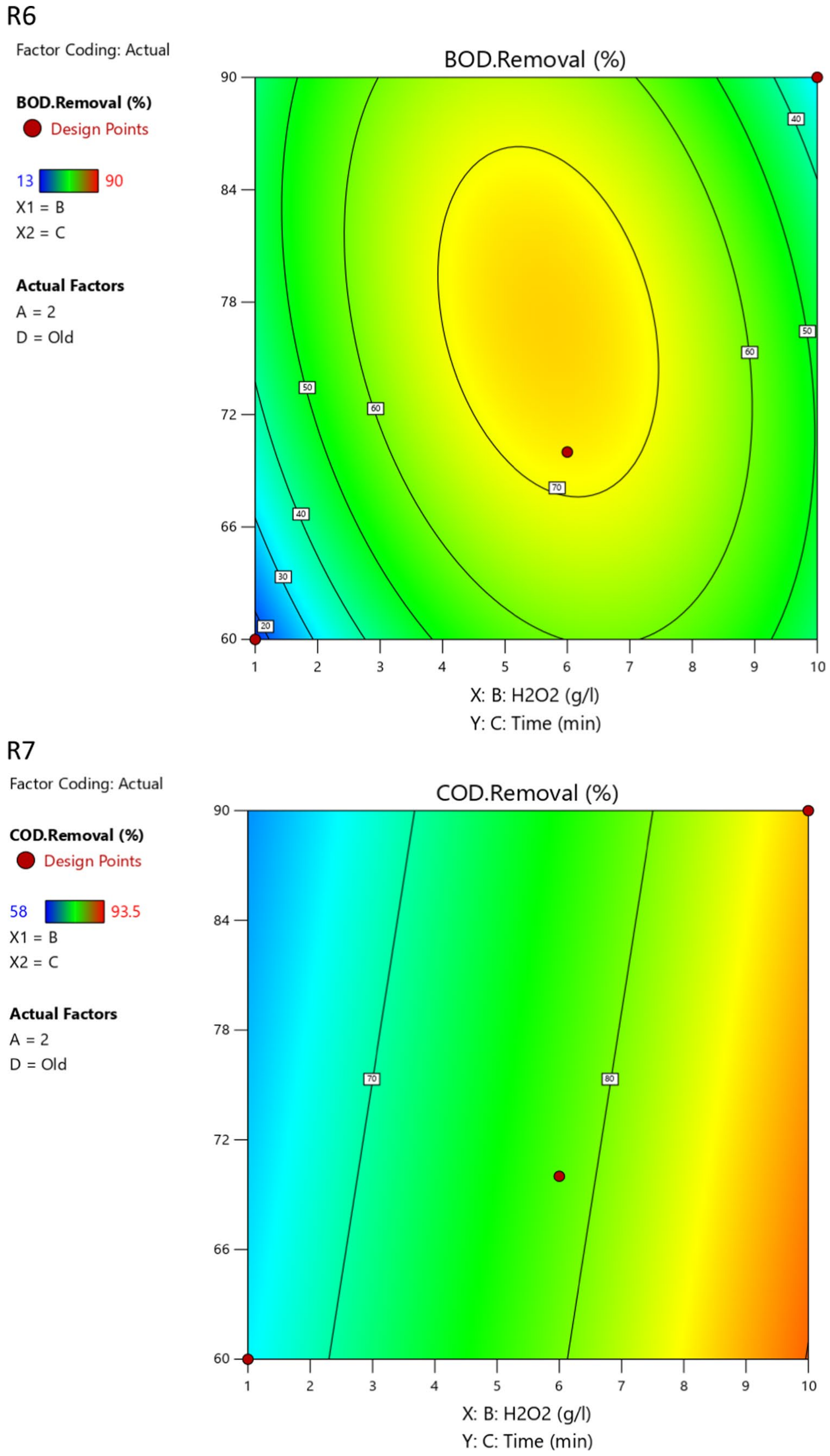

**Fig. 8.** (continued)

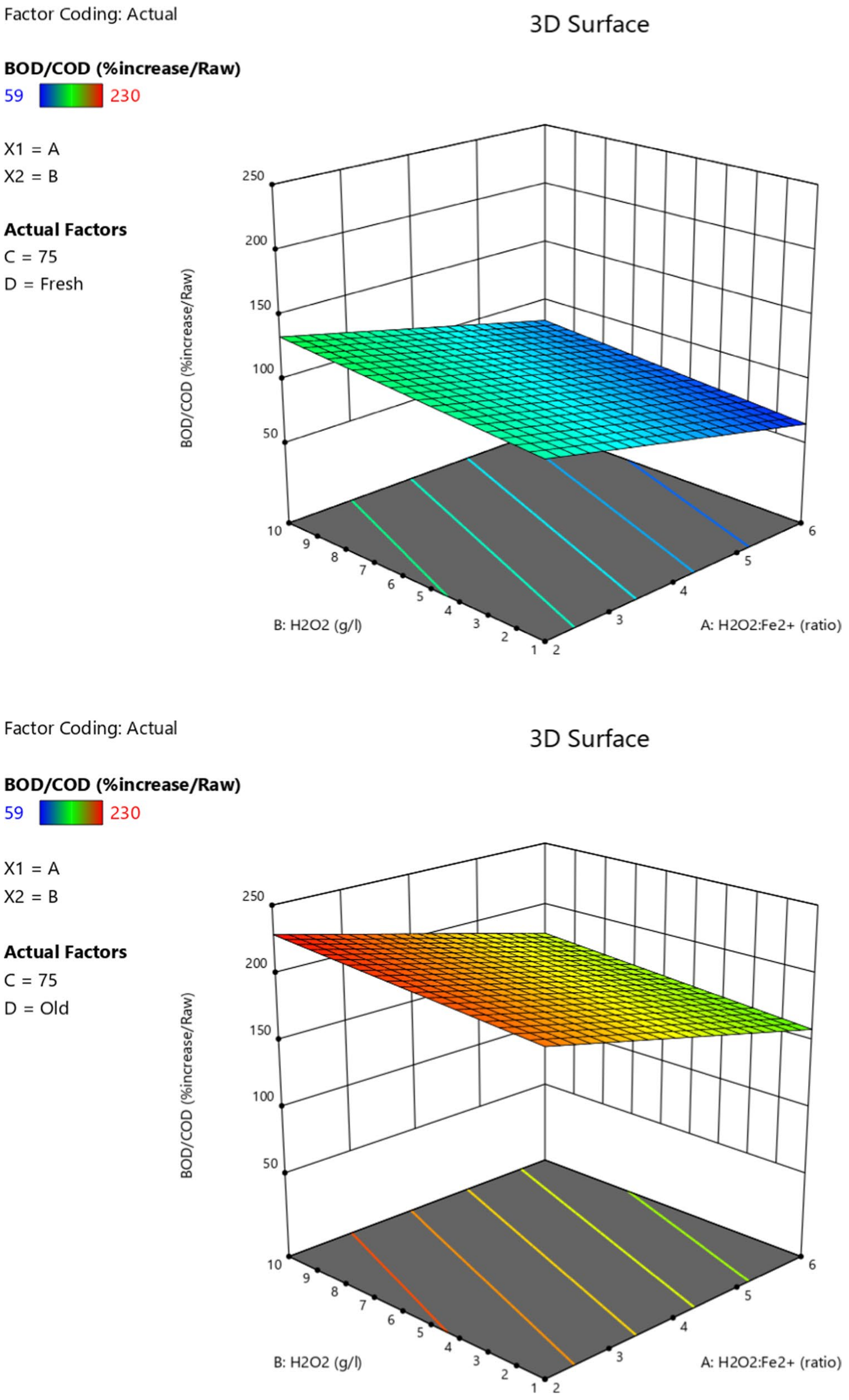

**Fig. 9**. 3D surface plots of optimal conditions for fresh and old leachate.

This study evaluated strategies for enhancing the biodegradability of fresh and old landfill leachate (measured by the $BOD_5$/COD ratio) using a combined pretreatment approach involving chemical precipitation with CaO and Fenton oxidation. The results demonstrated that integrating these two methods can effectively improve the biodegradability of leachates. Chemical precipitation with CaO significantly reduced heavy metal concentrations,

| Parameter | Raw.leachate | After.Chemical precipitation | After.fenton | %increase/after.chemical precipitation + fenton | %increase/ after.fenton |
|---|---|---|---|---|---|
| ($BOD_5$/COD) Fresh leachate | 0.29 | 0.35 | 0.67 ± 0.1 | 135.42 ± 25 | 90.00 ± 15 |
| ($BOD_5$/COD) Old leachate | 0.23 | 0.29 | 0.73 ± 0.09 | 215.00 ± 20 | 96.07 ± 10 |

**Table 5**. Overall result of chemical precipitation and Fenton in fresh and old leachate.

while the combined treatment approach led to relative improvements in the $BOD_5$/COD ratio of 135.42 ± 25% for fresh leachate and 215.00 ± 20% for old leachate, indicating a substantial enhancement in biodegradability. Under optimal Fenton oxidation conditions (A = 2, B = 10, C = 60 for fresh leachate and A = 2, B = 8.2, C = 75 for old leachate), the $BOD_5$/COD ratio increased by 90 ± 15% and 96.07 ± 10%, respectively. Although both methods exhibited high efficiency in improving biodegradability, potential challenges such as the use of chemicals (e.g., $FeSO_4$ and $H_2O_2$), sludge production, and energy consumption require careful consideration. Despite promising laboratory-scale results, practical implementation of this combined approach necessitates further research, including pilot-scale studies to assess reagent consumption, sludge generation, operational costs, and environmental aspects, as well as optimization of reagent dosages, investigation of alternative catalysts, and long-term performance evaluation under real operational conditions.

## Data availability

All collected data generated and analyzed in this study are included in the supplementary materials; additional dataset details or further materials are available from the first author upon reasonable request.

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## Author contributions

Tayebeh Rasolevandi: Writing – original draft, Investigation, Conceptualization. Kazem Naddafi: Methodology, Investigation, curation, Visualization. Supervision. Mohammad Sadegh Hassanvand: Resources, Formal analysis, Conceptualization. Mahdi Hadi: Software, Formal analysis, Data curation. Mahmood Alimohammadi: Visualization, Resources, Formal analysis. Kamyar Yaghmaeian : Writing – review & editing, Validation, Supervision.

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## Declarations

## Competing interests

The authors declare no competing interests.

## Additional information

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