

# Eco-Friendly Optimization of Landfill Leachate Treatment via Agricultural Waste-Derived Coagulants and Advanced Oxidation

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## ABSTRACT

Landfill Leachate (LL) presents a significant environmental concern, particularly in rapidly developing nations such as Oman, due to its high concentrations of persistent pollutants including ammonia (NH<sub>3</sub>), color-causing compounds, and organic matter. These contaminants are often resistant to removal by conventional treatment methods. This study aimed to develop an effective and eco-friendly treatment strategy for stabilized LL by integrating two processes: Persulfate Advanced Oxidation Processes (P-AOP) and Coagulation-Flocculation (C-F). The specific objectives were to: i) extract natural coagulants from date pits using the Soxhlet method, ii) enhance pollutant removal through the combined P-AOP and C-F approach, and iii) optimize the process using Response Surface Methodology (RSM). The hybrid treatment method achieved high removal efficiencies: 96% for color, 60% for NH<sub>3</sub>, and 74% for Chemical Oxygen Demand (COD). Additionally, a 12.433×10<sup>3</sup>% increase in Total Suspended Solids (TSS) was observed, attributed to floc formation, which signifies effective coagulation. These findings confirm the potential of the integrated approach and highlight the feasibility of using date pits as a sustainable alternative to chemical coagulants.

*Keywords-landfill leachate; catechin tannins; coagulation-flocculation; persulfate advanced oxidation; optimization*

## I. INTRODUCTION

Sanitary landfilling remains the most prevalent method for managing urban solid waste worldwide. While it provides an organized and practical means of waste disposal, it also generates Landfill Leachate (LL), a hazardous liquid byproduct rich in complex and refractory contaminants. The composition

of LL is highly variable, influenced by landfill age, waste composition, and biochemical processes, and often includes harmful substances such as heavy metals, ammonia (NH<sub>3</sub>), and organic pollutants [1]. In regions like Oman, where urbanization and population growth continue to escalate, the increasing volume of waste has placed a growing burden on

landfills, amplifying the risk of environmental contamination from untreated or poorly treated leachate.

Current LL treatment methods frequently rely on chemical-intensive technologies that are not only expensive but also pose risks of secondary pollution. These systems often require imported reagents and advanced infrastructure, both of which are limited in Oman [2]. Furthermore, new emerging pollutants such as pharmaceutical residues and microplastics present additional treatment challenges, as conventional methods are often ineffective against them. Despite technological advancements, notable research gaps persist, particularly in the synergistic application of Advanced Oxidation Processes (AOPs) with natural coagulants. Limited studies have explored the combined use of persulfate-based AOPs and bio-derived coagulants, such as catechin tannins extracted from Omani date pits, a readily available agricultural byproduct [2].

This study addresses the challenge of LL management by integrating Persulfate Advanced Oxidation Processes (P-AOP) with Coagulation-Flocculation (C-F) using natural catechin tannins from date pits. The objective is to remove critical pollutants, including Chemical Oxygen Demand (COD), color, Total Suspended Solids (TSS), and  $\text{NH}_3$ , from stabilized LL. This approach offers a low-cost, eco-friendly, and scalable solution tailored to Oman's environmental and resource constraints. By promoting the use of local agricultural waste, this research aligns with Oman Vision 2040 and advances multiple United Nations Sustainable Development Goals (SDGs), including: Goal 6 (clean water and sanitation), Goal 9 (industry, innovation, and infrastructure), and Goal 12 (responsible consumption and production). Overall, the project offers a practical and sustainable solution for LL treatment in Oman [3, 4].

## II. MATERIALS AND METHODS

The initial phase of this research focused on the collection and analysis of four 1-liter bottles of raw LL samples from the Barka Engineered Landfill in Oman. Sampling was conducted under the supervision of landfill engineers to ensure safety and accuracy. Personal Protective Equipment (PPE), insulated cool boxes, and sterilized polypropylene bottles were used for safe handling and storage [5]. Samples were then transported to the Waste to Energy Laboratory at the National University of Science and Technology for analysis. Key parameters, including COD, TSS,  $\text{NH}_3$ , and color, were assessed using internationally recognized protocols (USEPA and APHA), establishing baseline contamination levels [6].

The second phase focused on extracting catechin tannins from Omani date pits, specifically the Fardh and Khalas varieties. The pits were thoroughly cleaned, dried, and milled to a particle size of 1 mm. Tannin extraction was carried out using the Soxhlet method with 50% ethanol at 80 °C for a minimum of 19.5 hours. The extract was then dried into crystals, ground, and stored. The suitability of the tannins as natural coagulants was confirmed through Fourier Transform Infrared Spectroscopy (FTIR) and Ferric chloride tests [7].

In the third phase, stabilized leachate was treated using a C-F process with the extracted tannins. Variables including tannin dosage (70-110 mg/L), pH (5-8), reaction time (60-180

minutes), and agitation speed were optimized to enhance treatment efficiency. Coagulation was conducted under rapid mixing to ensure uniform distribution, followed by flocculation at 60 RPM to facilitate floc formation. The resulting suspensions were then subjected to a sedimentation period of 60 minutes.

The fourth phase involved treatment via the P-AOP. Sodium persulfate was activated with zinc sulfate heptahydrate in a 1:6 molar ratio at pH 11. The oxidation reaction was carried out under controlled conditions with agitation at 200 RPM for 140 minutes to degrade persistent organic contaminants. Treatment efficiency was evaluated using spectrophotometry and specialized kits to measure COD,  $\text{NH}_3$  concentration, color intensity, and TSS before and after treatment [8]. To further refine the treatment processes, the study applied Design Expert software for Response Surface Methodology (RSM) for 18 experimental runs, which facilitated the identification of optimal operational conditions for the experimental setup.

## III. RESULTS AND DISCUSSION

### A. FTIR Results for the Extracted Catechin Tannin

The FTIR spectra of the extracted tannins exhibited functional group signals consistent with those of high purity catechin, confirming the presence of these tannins. Both spectra showed a broad O-H stretching band near  $\sim 3300 \text{ cm}^{-1}$ , characteristic of hydroxyl groups and indicative of hydrogen bonding. This aligns with the major absorption peak at  $3317.90 \text{ cm}^{-1}$  observed in the high-purity catechin spectrum [9], as shown in Figure 1. A C=C stretching band around  $\sim 1600 \text{ cm}^{-1}$  was also present in both spectra, associated with aromatic rings typical of catechin tannins. Additionally, a C-H bending peak near  $\sim 1400 \text{ cm}^{-1}$  suggested the presence of aliphatic chains. While the extracted tannins demonstrated comparable spectral features, minor differences in peak intensity and position were noted, potentially due to variations in the extraction method or source material (Omani date pits) [10, 11], as shown in Figure 2.

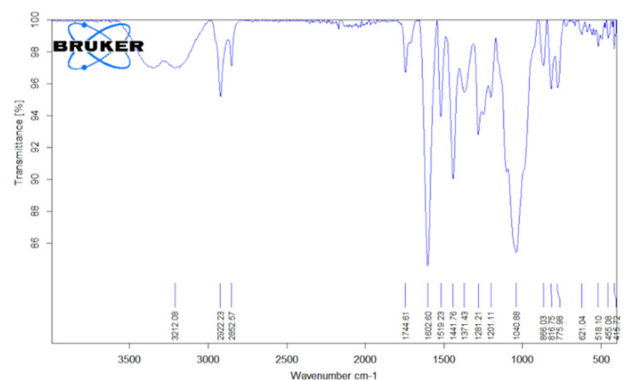


Fig. 1. FTIR spectrum of Fardh catechin tannin.

These results confirm that the extraction process successfully preserved the key functional groups of catechin tannins. However, the observed spectral deviations indicate

potential for refining the extraction technique to improve product purity and consistency. Enhancing extraction parameters may yield higher-quality tannins for future applications [12, 13].

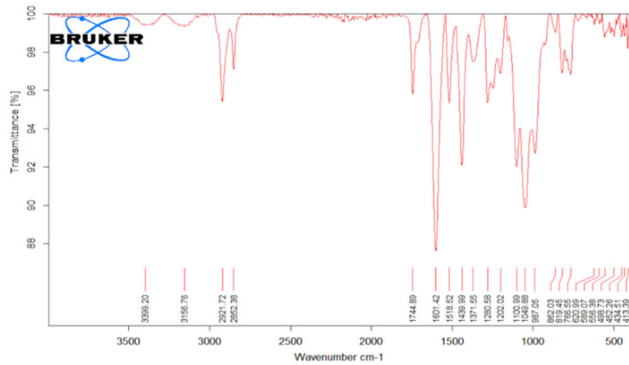


Fig. 2. FTIR spectrum of Khalas catechin tannin.

**B. Color Removal Results**

Figure 3 presents the 3D RSM illustrating the effect of tannin dosage and time on color removal efficiency (measured in Pt-Co units) at a constant pH of 8. The corresponding predictive models are expressed in terms of coded factors (1) and actual factors (2).

$$\text{Color} = 94.64 + 0.48 \cdot B - 0.8 \cdot C + 0.7425 \cdot C^2 \quad (1)$$

$$\text{Color} = 97.76750 + 0.2400 \cdot \text{pH} + 0.062833 \cdot \text{Time} + 0.000206 \cdot \text{Time}^2 \quad (2)$$

As shown in Figure 3, the coded model (1) indicates that pH has a positive coefficient, implying slightly higher color removal at lower pH values. This observation is consistent with the optimal performance of polyphenolic tannins under mildly acidic to neutral conditions. Time follows a quadratic

relationship, where color removal improves up to an optimal reaction period, beyond which additional contact time provides negligible enhancement. The response surface further demonstrates that the lowest color concentration is predicted at approximately 70 mg/L tannin dosage and 60-90 min reaction time. These results confirm that neither excessive coagulant dosage nor prolonged reaction time significantly improves performance, highlighting the importance of optimizing both factors.

**C. COD Removal Results**

Figure 4 presents the RSM plot illustrating COD removal efficiency as a function of tannin dosage and reaction time. The response surface reveals that both pH and tannin dosage significantly affect COD removal, with pH exhibiting the strongest negative influence, as indicated by the steep slope in the plot. The regression equations highlight key interaction effects, particularly between tannin dosage and pH, and between pH and time. The presence of quadratic terms indicates nonlinear behavior, suggesting that both insufficient and excessive dosing can reduce efficiency. Overall, the model effectively identifies optimal operating conditions, underscoring the need for precise control of pH, dosage, and reaction time to maximize COD removal efficiency.

Final equation in terms of coded factors:

$$\text{COD} = 68.8 - 1.83 \cdot A - 8.24 \cdot B - 0.68 \cdot C - 1.35 \cdot AB + 1.28 \cdot AC - 0.575 \cdot BC + 2.4 \cdot A^2 + 3.63 \cdot B^2 - 2.87 \cdot C^2 \quad (3)$$

Final equation in terms of actual factors:

$$\text{COD} = 164.39268 - 1.13346 \cdot \text{Tannin Dosage} - 11.40393 \cdot \text{pH} + 0.112982 \cdot \text{Time} - 0.033750 \cdot \text{Tannin Dosage} \cdot \text{pH} + 0.001062 \cdot \text{Tannin Dosage} \cdot \text{Time} - 0.004792 \cdot \text{pH} \cdot \text{Time} + 0.006205 \cdot \text{Tannin Dosage}^2 + 0.908036 \cdot \text{pH}^2 - 0.000797 \cdot \text{Time}^2 \quad (4)$$

Design-Expert® Software  
Factor Coding: Actual

Colour (Pt-Co)

● Design points above predicted value

○ Design points below predicted value

93 97

X1 = C: Time

X2 = A: Tannin Dosage

Actual Factor

B: pH = 8

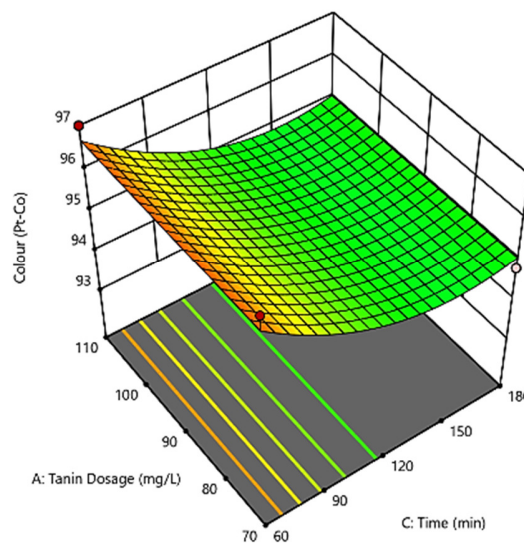


Fig. 3. RSM plot depicting the color removal efficiency with respect to time and dosage.

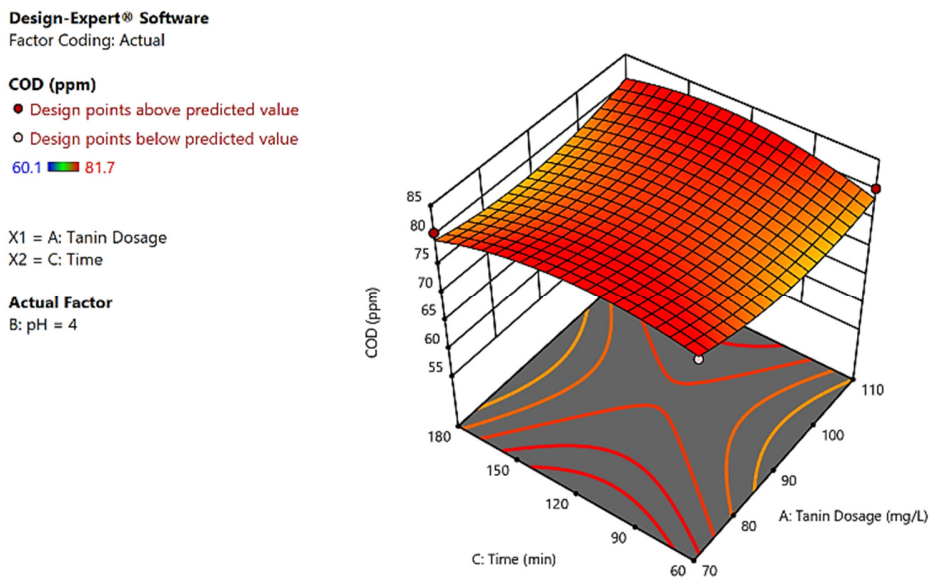


Fig. 4. RSM plot depicting the COD removal efficiency with respect to time and dosage.

**D. Ammonia Removal Results**

Figure 5 presents the RSM plot illustrating NH<sub>3</sub> removal efficiency as a function of tannin dosage and reaction time. The plot and corresponding equations indicate that NH<sub>3</sub> removal efficiency improves slightly with increased treatment time and tannin dosage but declines significantly with increasing pH. Among the three factors, pH has the strongest negative effect, as reflected by its relatively large regression coefficient. The linear nature of the model suggests minimal interaction or nonlinear effects within the studied range. These findings emphasize the importance of maintaining a lower pH while optimizing both dosage and reaction time to achieve maximum NH<sub>3</sub> removal [14, 15].

Final equation in terms of coded factors:

$$NH_3 = 97.51 + 0.41 \cdot A - 1.87 \cdot B + 0.48 \cdot C \quad (5)$$

Final equation in terms of actual factors:

$$NH_3 = 100.31611 + 0.0205 \cdot \text{Tannin Dosage} - 0.935 \cdot \text{pH} + 0.008 \cdot \text{Time} \quad (6)$$

**E. TSS Increase Results**

Figure 6 presents the RSM plot illustrating the increase in TSS as a function of tannin dosage and reaction time.

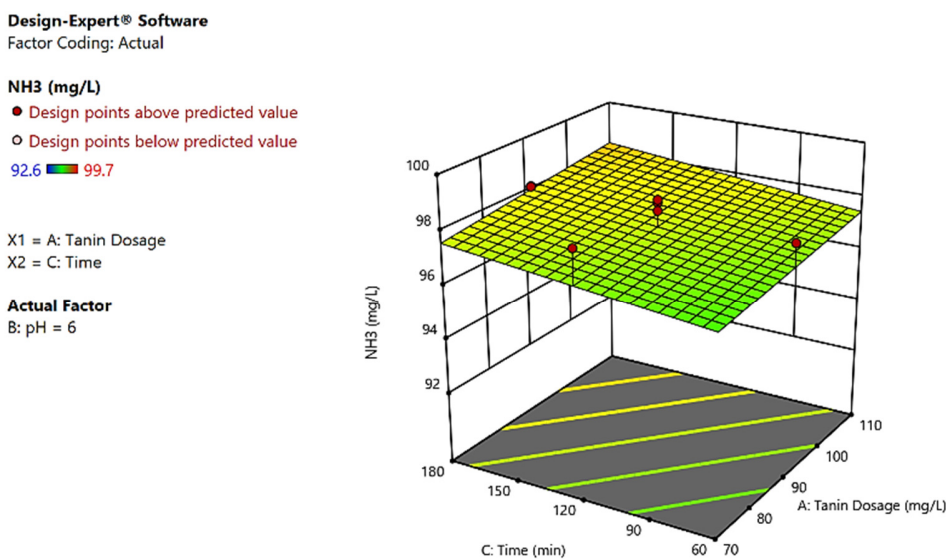


Fig. 5. RSM plot depicting the ammonia removal efficiency with respect to time and dosage

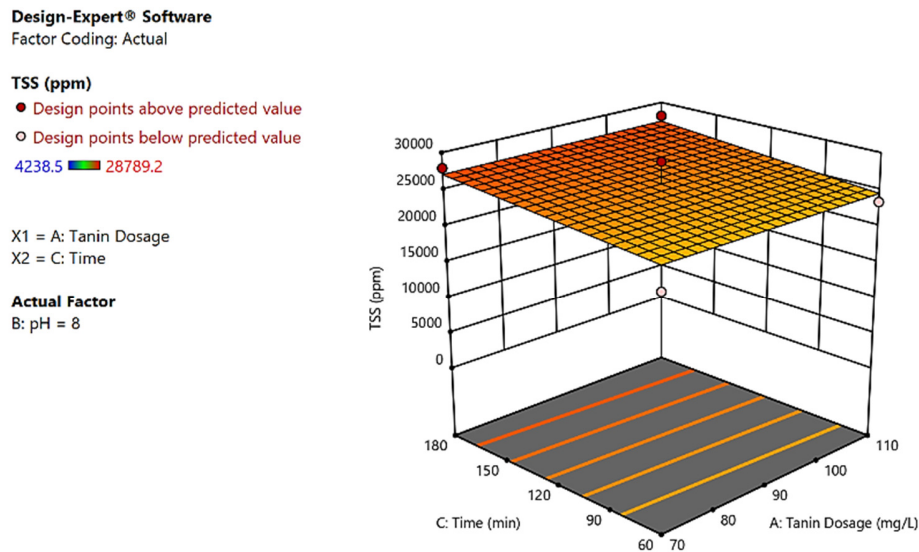


Fig. 6. RSM plot depicting the TSS increase with respect to time and dosage.

The regression equations indicate that all three factors contribute positively to TSS levels, with pH having the most pronounced effect [16]. The sharp increase in TSS with rising pH and extended treatment time suggests that, although these conditions may enhance contaminant removal, they can also promote the formation of excessive suspended solids. This underscores the importance of balancing operational parameters to prevent undesirable side effects such as turbidity or sludge accumulation, which may compromise the quality of the treated effluent.

Final Equation in Terms of Coded Factors:

$$TSS = 15800.95 + 76.92 \cdot A + 10003.84 \cdot B + 1342.14 \cdot C \tag{7}$$

Final Equation in Terms of Actual Factors:

$$TSS = -17240.99 + 3.846 \cdot \text{Tannin Dosage} + 5001.92 \cdot \text{pH} + 22.369 \cdot \text{Time} \tag{8}$$

F. Discussion

The study demonstrated the effectiveness of combining tannin-based C-F with the P-AOP in treating stabilized LL. Significant removal efficiencies were achieved, including a 74% reduction in COD, a 60% reduction in NH<sub>3</sub>, and a 96% reduction in color. Additionally, TSS increased by 12.433×10<sup>3</sup>%, reflecting the efficacy of the C-F process in forming flocs that aid contaminant removal [17, 18], as shown in Table I.

TABLE I. COD, NH<sub>3</sub>, AND COLOR INITIAL AND FINAL CONCENTRATIONS

	Initial	Final	% Reduction
COD (mg/L)	1280	332.8	74
NH <sub>3</sub> (mg/L)	4170	1668	60
Color (Pt-Co)	33600	1344	96
TSS (mg/L)	260	32585.8	12433

Optimization of the treatment process identified optimal operating conditions at a tannin dosage of 70 mg/L, pH 5.8, and a reaction time of 60 minutes. A key innovation of this study was the use of catechin tannins extracted from Omani date pits as a natural, sustainable coagulant. This approach offered an eco-friendly alternative to conventional chemical coagulants by utilizing agricultural waste and minimizing dependence on synthetic chemicals. Integrating natural tannins with advanced oxidation not only enhanced contaminant removal but also aligned with sustainability objectives. In summary, the study validated this hybrid approach as an effective and sustainable method for managing complex stabilized leachate, offering a novel and efficient waste treatment solution [19, 20].

IV. CONCLUSION

The study effectively addressed the complex challenges associated with stabilized Landfill Leachate (LL) treatment through a structured, multi-phase experimental approach. In the initial phase, leachate characterization revealed elevated pollutant concentrations, emphasizing the necessity for advanced hybrid treatment technologies. The extraction of catechin tannins from Omani date pits demonstrated that the Fardh variety consistently yielded higher tannin content compared to Khalas. Subsequent characterization via Fourier Transform Infrared (FTIR) spectroscopy and Ferric chloride assays confirmed the purity and coagulant potential of the extracted tannins, reinforcing their role as a sustainable and eco-friendly alternative to conventional chemical coagulants. This strategy aligns with circular economy principles and advances the United Nations Sustainable Development Goals (SDGs) by promoting innovative, resource-efficient waste valorization practices.

The integration of Coagulation-Flocculation (C-F) with the Persulfate Advanced Oxidation Process (P-AOP) achieved substantial reductions in Chemical Oxygen Demand (COD) of 74%, ammonia (NH<sub>3</sub>) of 60%, and color of 96%, and an

increase in the Total Suspended Solids (TSS) of  $12.433 \times 10^3\%$ , thereby validating the overall efficacy of the proposed hybrid treatment system.

The successful use of naturally sourced tannins enhances the environmental compatibility of the treatment process while reducing chemical dependency. For future research, integrating complementary biological treatment stages to improve nitrogen removal, optimizing process parameters, and conducting pilot-scale studies are recommended to ensure reliable performance under operational conditions.

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