

HETEROGENEOUS FENTON CATALYTIC OXIDATION TECHNOLOGY FOR LEACHATE TREATMENT IN GENERAL SOLID WASTE LANDFILLS

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Abstract: To address the challenges posed by the complex water quality, high pollutant concentration, and susceptibility to environmental influences in general solid waste landfill leachate, this study developed a combined treatment process based on heterogeneous Fenton catalytic oxidation. Taking a landfill leachate treatment project as an example, the process route "Denitrification Pretreatment - Heterogeneous Fenton Catalysis - Post-treatment System" was employed. Through the synergistic action of units including mechanical bar screening, coagulation sedimentation, air stripping deammonification, activated carbon adsorption, heterogeneous Fenton oxidation, A/O biological treatment, and advanced filtration/disinfection, efficient pollutant removal was achieved. Practical engineering application demonstrated stable system operation. The effluent quality met the discharge standards specified in Table 2 of the "Standard for Pollution Control on Municipal Solid Waste Landfill" (GB16889-2024), with removal rates for COD, BOD₅, ammonia nitrogen, total nitrogen, and suspended solids reaching 98%, 98.8%, 99.3%, 99.04%, and 98.6% respectively. The TOC degradation rate exceeded 60%. This process offers both environmental and economic benefits, providing a replicable engineering model for the harmless treatment of landfill leachate.

Keywords: Leachate; Heterogeneous Fenton catalysis; Solid waste landfill; Treatment process; Advanced oxidation technology

1 INTRODUCTION

Within China's current solid waste disposal system, incineration and landfilling remain the dominant technological pathways, yet both face significant environmental challenges[1]. Leachate generated during waste landfilling, classified as high-concentration organic wastewater, exhibits complex composition (containing humic substances, heavy metals, inorganic salts, and emerging contaminants like antibiotics and microplastics) and significant fluctuations in quality influenced by factors such as landfill age and climatic conditions[2]. Untreated discharge of this wastewater poses potential threats to ecosystems and human health through groundwater infiltration and soil accumulation[3].

Among typical landfill leachate treatment technologies, recirculation was widely used due to its simplicity and low initial cost. However, long-term operation can lead to salt and recalcitrant organic compound accumulation, causing scaling and fouling in reverse osmosis systems and reduced treatment efficiency[4]. While evaporation enables total volume reduction, the challenge of treating concentrated residues and high energy costs limit its widespread engineering application. Research has examined the effects of temperature and free ammonia on nitrification and nitrite accumulation in landfill leachate[5]. A granular sludge reactor (GSR) achieved efficient nitrogen removal via nitrification/denitrification for treating mature leachate with high ammonia nitrogen content[6], but its effectiveness for other organics was limited. Dynamic membrane bioreactors (DMBR) have also been compared for landfill leachate treatment[7]. In contrast, heterogeneous Fenton catalytic oxidation technology, generating hydroxyl radicals ($\cdot\text{OH}$, redox potential 2.80 V) via H_2O_2 decomposition mediated on the catalyst surface, demonstrates unique advantages in the broad-spectrum degradation of organic pollutants[8]. Compared to traditional homogeneous Fenton systems, this technology overcomes drawbacks such as Fe^{3+} hydrolysis/precipitation, narrow operational pH range, and high sludge production. The recyclability of the supported catalyst further enhances process economics.

Therefore, based on the principles of "reduction, resource recovery, and harmless treatment", and targeting the characteristics of poor biodegradability and high heavy metal content in mature solid waste landfill leachate[9], this study developed a coupled system "Denitrification Pretreatment-Heterogeneous Fenton Catalysis-Advanced Post-treatment". Through the synergistic action of multiple units, efficient pollutant removal was achieved, providing an engineered solution for compliant leachate disposal.

2 WATER QUALITY CHARACTERISTICS OF LANDFILL LEACHATE

Leachate produced from municipal solid waste sanitary landfills is compositionally complex, with water quality and quantity varying greatly due to external factors. It typically contains substantial amounts of organic pollutants (including synthetic compounds from consumer products like cosmetics), inorganic heavy metals, inorganic salts, and emerging contaminants. Inappropriate discharge causes severe environmental pollution and threatens human health.

Leachate pollutants can be categorized into four groups: inorganic macro-pollutants, non-biodegradable organics, dissolved organic matter, and heavy metals. Key discharge indicators include Chemical Oxygen Demand (COD), color (CN), Ammonia Nitrogen ($\text{NH}_3\text{-N}$), Total Nitrogen (TN), and Total Phosphorus (TP)[10]. Organic pollutants often consist largely of hard-to-degrade humic substances like humic and fulvic acids.

Landfill age is a major factor influencing leachate composition. Researchers typically classify leachate based on landfill age: less than 5 years (young), 5-10 years (intermediate), and over 10 years (mature/old). Notably, as landfill age increases, COD levels gradually decrease, accompanied by increasing humification, leading to progressively worse biodegradability[11]. Changes in other water quality characteristics are shown in Table 1.

Table 1 Variation of Landfill Leachate Water Quality Over Time

Characteristic	Young	Intermediate	Mature
Filling time (year)	<5	5-10	>10
pH	<6.5	6.5-7.5	>7.5
COD (mg/L)	>10000	4000-10000	<4000
BOD ₅ /COD	0.5-1.0	0.1-0.5	<0.1
Ammonia Nitrogen	<400	-	>400
Heavy Metals	Low - Medium	Low	Low
Biodegradability	Good	Moderate	Poor

3 LEACHATE WATER QUALITY INDICATORS

The target water body for this study is mature leachate from a general solid waste landfill site. Determination of its water quality parameters is based on 36 consecutive months of monitoring data from this landfill and the stringent requirements of the "Standard for Pollution Control on Municipal Solid Waste Landfill" (GB16889-2024). Due to a landfill age exceeding 10 years, the mature leachate exhibits characteristics of high ammonia nitrogen (3000-3500 mg/L), low biodegradability ($\text{BOD}_5/\text{COD} < 0.1$), and humic substance enrichment. Compared to young leachate, although its COD concentration is reduced below 4000 mg/L, the molecular structure of organic matter is more complex, and the ionic strength of heavy metals and inorganic salts is higher.

During water quality detection, a spatio-temporal dynamic analysis method was employed: samples were collected from different landfill areas (e.g., center, periphery) and during typical seasons (rainy season, dry season), covering 23 conventional indicators including COD, BOD₅, ammonia nitrogen, total nitrogen, suspended solids, and trace heavy metals. The data showed COD concentration fluctuations up to 33.3% (4500-6000 mg/L). Ammonia nitrogen concentration exhibited seasonal fluctuations influenced by the waste degradation stage, consistent with the literature conclusion that "mature leachate quality is significantly regulated by landfill layer microbial activity". Specific design water quality indicators are shown in the table 2 below:

Table 2 Influent and Effluent Water Quality of Leachate

Parameter	Influent Quality	Effluent Standard
COD/($\text{mg}\cdot\text{L}^{-1}$)	4500-6000	100
BOD ₅ /($\text{mg}\cdot\text{L}^{-1}$)	2000-3000	30
Ammonia Nitrogen/($\text{mg}\cdot\text{L}^{-1}$)	3000-3500	25
Total Nitrogen/($\text{mg}\cdot\text{L}^{-1}$)	3200-4000	40
Suspended Solids/($\text{mg}\cdot\text{L}^{-1}$)	1000-2000	30
Manganese/($\mu\text{g}\cdot\text{L}^{-1}$)	2160-3000	1500
Total Bacteria/($\text{CFU}\cdot\text{mL}^{-1}$)	1000-2000	1000

4 TREATMENT PROCESS FLOW DESIGN

The landfill leachate treatment process is illustrated in Figure 1: Leachate passes through a 5 mm mechanical bar screen to intercept debris before entering an equalization tank (HRT=24 h, mixing/homogenization). It is then pumped to a coagulation sedimentation tank where Polymeric Aluminum Ferric Chloride (PAFC) (2.0 g/L) and Polyacrylamide (PAM) (12 mg/L) are dosed to remove suspended solids. The pretreated water phase enters an air stripping deammonification tower (pH=11, gas-to-liquid ratio 5000:1) for ammonia removal, followed by deep impurity removal in an activated carbon fiber adsorption column (contact time 2 h). The purified water phase is pumped into the heterogeneous Fenton reactor (loaded iron-based catalyst, pH 3-5, H_2O_2 dosage 1.2 times theoretical value, HRT=2-3 h) for catalytic oxidation degradation of organics. The effluent is dosed with lime milk for neutralization to pH 7-8 to precipitate metal ions. The neutralized water phase enters an A/O biological tank (anaerobic 4 h / aerobic 8 h) for nitrogen and phosphorus removal, followed by chemical precipitation dosing Ferric Sulfate (30 mg/L) for enhanced phosphorus removal. The settled effluent sequentially passes through a quartz sand filter (particle size 0.5-1.2 mm) → activated carbon filter to adsorb residual pollutants, and finally undergoes chlorine dioxide disinfection (5-10 mg/L, contact time 30-60 min). The Fenton catalyst can be recycled. If effluent testing exceeds standards (COD >100 mg/L or $\text{NH}_3\text{-N}$ >25 mg/L), the flow is diverted back to the biological tank or Fenton unit for enhanced treatment based on the parameter.

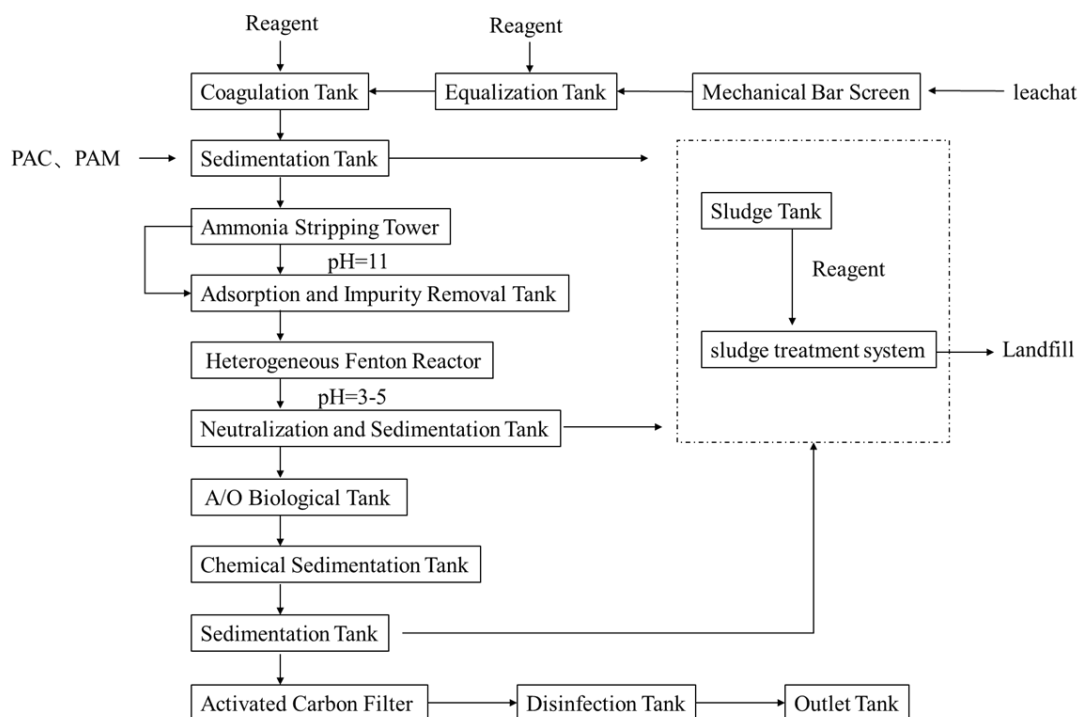


Figure 1 Process Flow Diagram

5 TREATMENT TECHNOLOGY SCHEME DESIGN

5.1 Pretreatment System

5.1.1 Bar screen

Leachate first passes through a bar screen. A mechanical bar screen is used to intercept larger suspended and floating solids (e.g., plastics, wood blocks, fibers) in the leachate, preventing these impurities from entering subsequent units and causing clogging or damage. The bar spacing is set at 5 mm, effectively intercepting larger particles and ensuring smooth operation of subsequent processes.

5.1.2 Equalization tank

Screened leachate enters the equalization tank. Its primary function is to balance water quality and quantity, as leachate generation and composition fluctuate significantly due to rainfall, waste filling rates, etc. The effective tank volume is 1000 m³, with a hydraulic retention time (HRT) of 24 hours. Mixing equipment ensures thorough homogenization, preventing stratification and providing stable influent conditions for downstream treatment units.

5.1.3 Coagulation sedimentation

Leachate from the equalization tank enters the coagulation sedimentation tank. During coagulation, Polymeric Aluminum Ferric Chloride (PAFC) and Polyacrylamide (PAM) are dosed. PAFC acts as a coagulant; its hydrolyzed polynuclear hydroxyl complexes destabilize colloidal particles through adsorption, bridging, and charge neutralization. PAM acts as a flocculant, promoting aggregation of destabilized particles into larger flocs for easier sedimentation and separation.

Coagulant dosing experiments investigated the removal efficiency of COD and TN. At a constant PAM dose of 20 mg/L, COD and TN removal rates increased with PAFC dosage, reaching maxima at 2.5 g/L PAFC (67.4% COD removal, 54.2% TN removal). At a constant PAFC dose of 2.00 g/L, COD and TN removal showed no clear relationship with PAM dose, though a PAM dose of 24 mg/L yielded good results (62.2% COD, 50.0% TN removal). Results are shown in Table 3. Considering cost-effectiveness, optimal doses were determined as PAFC 2.50 g/L and PAM 20 mg/L. At these doses, COD and NH₃-N removal rates reached 61.5% and 47.9%, respectively, indicating effective treatment.

Table 3 Optimal Coagulant Dosage

Exp. No.	PAFC/ (g·L ⁻¹)	PAM/ (mg·L ⁻¹)	COD Removal /%	TN Removal /%
1	1.5	20	47.9	46.7
2	1.75	20	53.9	47.9
3	2.00	20	59.8	49.2
4	2.25	20	65.0	50.0
5	2.50	20	67.4	54.2
6	2.00	12	61.5	47.9
7	2.00	16	62.2	48.3
8	2.00	20	61.1	46.7
9	2.00	24	62.2	50.0

10	2.00	28	62.8	47.9
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A tube settler is used, increasing the settling area and efficiency, effectively removing suspended solids, some heavy metals, and organics. However, the COD concentration in the coagulation effluent remains relatively high, requiring further treatment.

5.2 Heterogeneous Fenton Catalytic Oxidation

5.2.1 Reaction principle

Pretreated leachate enters the heterogeneous Fenton reactor. Within the reactor, the heterogeneous Fenton catalyst reacts with hydrogen peroxide (H_2O_2). The catalyst is an iron-based material supported on activated carbon. The reaction principle involves: On the catalyst surface, H_2O_2 decomposes under the catalysis of iron oxides to generate highly oxidizing hydroxyl radicals ($\cdot\text{OH}$, $E^\circ = 2.80 \text{ V}$). These radicals non-selectively oxidize and decompose organic pollutants in the leachate, breaking down macromolecules into smaller compounds or even mineralizing them to CO_2 and H_2O . Concurrently, iron ions on the catalyst surface undergo redox cycling (Fe^{3+} reduced to Fe^{2+} , Fe^{2+} reacting with H_2O_2 to regenerate $\cdot\text{OH}$), sustaining the reaction. Being supported, the catalyst minimizes loss and allows reuse, enhancing stability and economics.

5.2.2 Reaction condition control

Strict control ensures optimal performance. Reaction pH is maintained between 3-5, where catalyst activity and $\cdot\text{OH}$ generation efficiency are high. Online pH monitors provide real-time feedback for automatic sulfuric acid or sodium hydroxide dosing. Temperature is controlled at 30-40°C using a heating/cooling system. H_2O_2 dosage is set at 1.2 times the theoretical requirement based on influent COD, ensuring sufficient oxidant. Hydraulic Retention Time (HRT) is 2-3 hours, allowing sufficient contact time between pollutants and $\cdot\text{OH}$.

5.2.3 Reaction equipment

The heterogeneous Fenton reactor is a Continuous Stirred Tank Reactor (CSTR) made of corrosion-resistant stainless steel. An internal agitator (100-150 rpm) ensures thorough mixing of leachate, catalyst, and H_2O_2 , enhancing reaction efficiency. A bottom distribution system ensures uniform influent entry, preventing short-circuiting. A vent at the top collects and treats minor amounts of harmful gases generated during the reaction.

5.3 Post-treatment

5.3.1 Neutralization and precipitation

Effluent from the Fenton reactor enters the neutralization/precipitation tank. Due to its acidic nature, lime milk is dosed first to adjust pH to 7-8, precipitating metal ions (e.g., iron, heavy metals) as hydroxides. Lime dosage is automatically controlled based on real-time pH and metal ion concentration monitoring. Precipitation and separation further reduce metal ion content in the effluent.

5.3.2 Filtration

The neutralized effluent enters the filtration unit, combining sand filtration and activated carbon filtration. The sand filter uses quartz sand (0.5-1.2 mm) to remove residual fine suspended solids and colloidal matter, reducing turbidity. The granular activated carbon (GAC) filter utilizes its highly porous structure and large surface area to adsorb residual organics, color, odor, and trace heavy metals, polishing the effluent quality.

5.3.3 Disinfection

The filtered effluent undergoes disinfection using chlorine dioxide (ClO_2). ClO_2 is a strong oxidant effective at killing bacteria, viruses, and pathogens[12]. Dosage is 5-10 mg/L, generated on-site. A contact time of 30-60 minutes ensures effective disinfection, preventing microbial hazards upon discharge.

6 OPERATION AND PERFORMANCE ANALYSIS

(1) The physical pretreatment technology in this project, addressing the suspended solids issue in leachate, developed a physical process. By screening oil-absorbing media and optimizing filtration conditions, the levels of SS, oil content, and turbidity in the water phase were reduced. This configuration ensured high filtration efficiency and excellent water quality.

(2) The advanced oxidation technology for the pretreated water phase developed heterogeneous Fenton catalysis. Experimental conditions including H_2O_2 ratio, reaction pH, flow rate, and temperature were optimized. Utilizing the highly oxidizing hydroxyl radicals generated in-situ as the primary oxidant, recalcitrant organic pollutants in the wastewater were oxidized and degraded, even mineralized to CO_2 , H_2O , and small carboxylic acids, while simultaneously reducing ammonia and total nitrogen, achieving the goal of harmless treatment.

(3) Post-treatment technology was developed to complement the advanced oxidation unit, targeting residual TOC, ammonia nitrogen, and total nitrogen in the effluent. Adsorption was employed to separate harmful substances, utilizing the well-developed pore structure, vast surface area, and various functional groups of the adsorbent to remove diverse organic pollutants and metal ions from the leachate. In this case study, effluent concentrations of COD, BOD, $\text{NH}_3\text{-N}$, and SS met discharge standard limits. Figure 2 shows the leachate treatment performance.

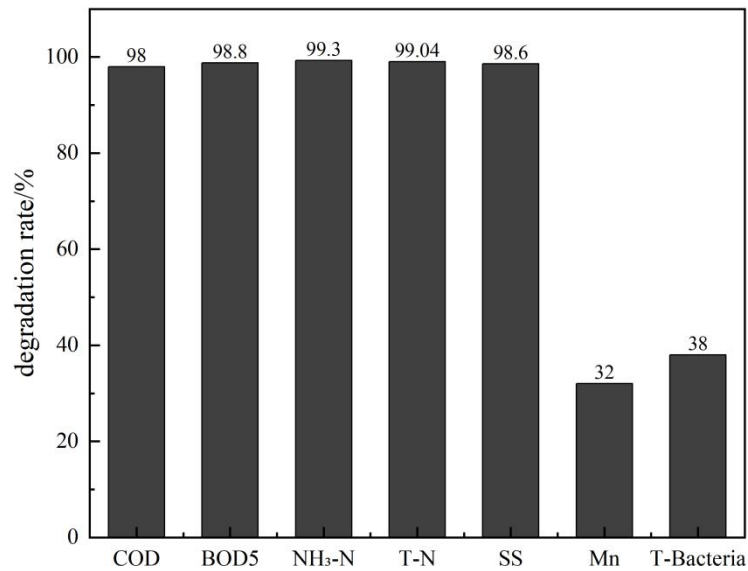


Figure 2 Leachate Treatment Performance

(4) Data collected during stable operation of the equipment showed TOC removal exceeding 60%, reaching a maximum of 75%. All indicators met design requirements, and treatment costs were reduced by 17.5%. Figures 3, 4, and 5 illustrate H₂O₂ decomposition and TOC removal performance.

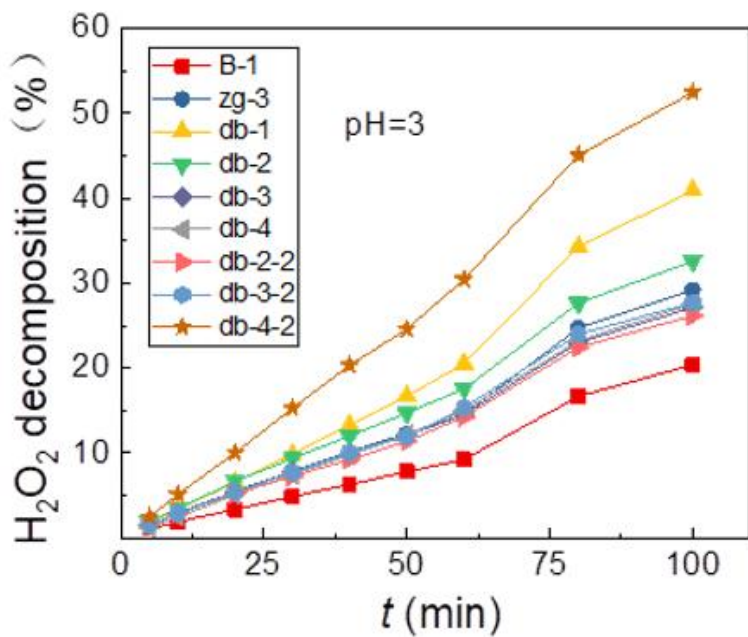


Figure 3 H₂O₂ Decomposition Rate

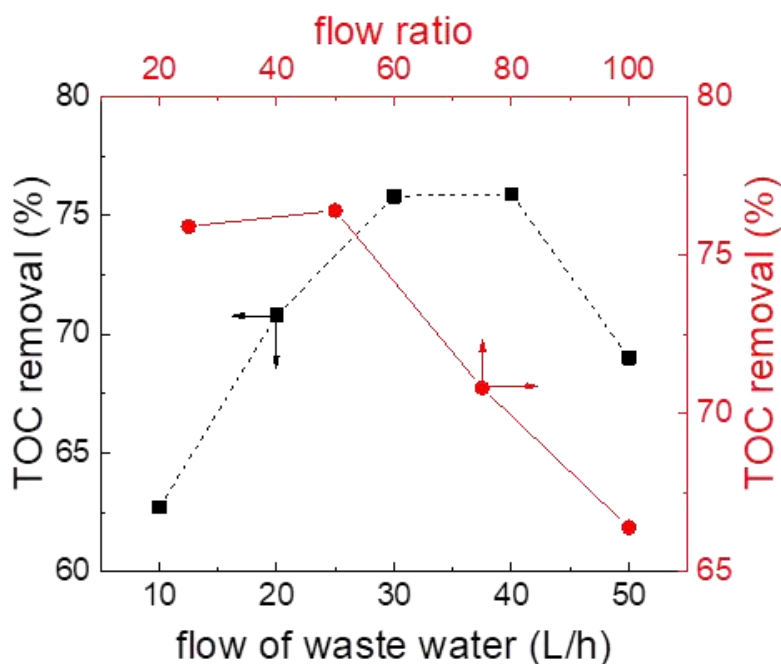


Figure 4 TOC Removal Performance

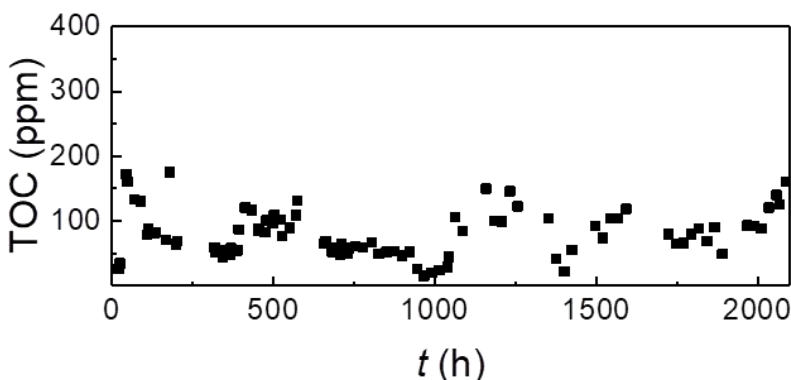


Figure 5 TOC Removal Performance

7 CONCLUSION

This study focused on the characteristics of mature leachate from general solid waste landfills and constructed a combined process of "Denitrification Pretreatment - Heterogeneous Fenton Catalytic Oxidation-Advanced Post-treatment". Engineering practice validation yielded the following key results:

(1) Significant Process Synergy: Pretreatment units (screening, coagulation sedimentation) effectively removed suspended solids, laying the foundation for deep treatment. Synergy between air stripping deammonification and activated carbon adsorption enhanced pre-removal of nitrogen and recalcitrant organics. The core heterogeneous Fenton unit, utilizing a supported iron-based catalyst under optimized conditions (pH 3-5, H_2O_2 1.2x theoretical, HRT 2-3 h), efficiently generated hydroxyl radicals via $\text{Fe}^{3+}/\text{Fe}^{2+}$ cycling on the catalyst surface, achieving broad-spectrum degradation and mineralization of organic pollutants, overcoming the limitations of homogeneous Fenton (narrow pH range, high sludge yield). Post-treatment units (A/O biological treatment, chemical precipitation, filtration/disinfection) ensured stable, compliant effluent quality. The synergistic linkage of all units formed a complete technical chain from pretreatment to advanced purification.

(2) Stable Compliant Effluent: Continuous operational monitoring data demonstrated removal rates of 98% for COD, 98.8% for BOD_5 , 99.3% for ammonia nitrogen, 99.04% for total nitrogen, and 98.6% for suspended solids. TOC degradation exceeded 60%. Effluent quality consistently met all discharge standards specified in Table 2 of GB16889-2024. This validates the combined process's high efficiency in removing concentrated, recalcitrant pollutants from mature landfill leachate, solving a long-standing technical challenge in the industry.

(3) Techno-economic and Environmental Benefits: The recyclability of the supported catalyst in the heterogeneous Fenton unit significantly reduced catalyst consumption and sludge disposal costs compared to homogeneous Fenton, contributing to an overall cost reduction of 17.5%. The entire process adheres to the principles of "reduction, resource recovery, and harmless treatment," minimizing pollutant discharge at the source and preventing secondary pollution of soil and groundwater ecosystems. Aligned with green and low-carbon development, the process holds significant potential for replication and promotion.

In summary, the combined process developed in this study breaks through the technical barriers for treating mature solid waste landfill leachate, achieving a synergistic balance of high purification efficiency, economic viability, and environmental protection. It provides a replicable and promotable technical paradigm for similar projects, holding significant practical value and exemplary significance for advancing landfill leachate treatment technology in China and improving ecological environmental quality. Future research could focus on catalyst long-term stability mechanisms and intelligent process control to further enhance application efficacy.

COMPETING INTERESTS

The authors have no relevant financial or non-financial interests to disclose.

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