INSTITUTO POLITÉCNICO DE BRAGANÇA Escola Superior de Tecnologia e Gestão

OPTIMISING LANDFILL LEACHATE TREATMENT: INTEGRATED COAGULATION/FLOCCULATION AND FENTON APPROACHES

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"Em memória di nha Mãe"

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ABSTRACT

The continuous accumulation of municipal solid waste in landfills has resulted in the generation of significant volumes of leachate, a complex and highly contaminated liquid effluent. This leachate is typically enriched with high concentrations of organic matter, ammonia nitrogen, heavy metals, and recalcitrant compounds such as humic and fulvic acids, which collectively confer low biodegradability and considerable variability in composition. These characteristics pose substantial limitations to conventional treatment technologies, often resulting in inefficient pollutant removal. Due to its potential to cause severe environmental contamination of soil and water bodies, the implementation of advanced and economically feasible treatment solutions is imperative. This study proposed and evaluated an integrated two-stage treatment strategy designed to enhance the efficiency of landfill leachate remediation processes. The proposed treatment procedure was initiated with a coagulation–flocculation (C – F) pre-treatment designed to promote the aggregation and subsequent removal of suspended solids and colloidal organic matter, thereby reducing turbidity and the initial organic load. This step was succeeded by an advanced oxidation process (AOP) based on the Fenton reaction, which relies on the in-situ generation of hydroxyl radicals (•OH) to oxidise refractory organic constituents. Following the C – F stage, a marked reduction in chemical oxygen demand (COD) and a concomitant increase in five-day biochemical oxygen demand (BOD_5) were observed, resulting in a significant improvement in the COD/BOD_5 ratio, a critical parameter for assessing effluent biodegradability. Process optimisation was conducted using Minitab® software, identifying the optimal Fenton conditions at pH 3.4, Fe^{2+} dosage of 8.96 g L^{-1}, and H_2O_2 (30% w/w) volume of 30 mL L^{-1} of leachate. Under these conditions, the COD removal efficiency reached approximately 92%, and the COD/BOD_5 ratio increased from 0.053 to 0.87, indicating a substantial enhancement in biodegradability. The integration of physicochemical and oxidative processes has demonstrated high efficacy in mitigating the complex pollutant matrix of landfill leachate, offering a technically robust and environmentally sustainable strategy for effluent management. The goal was to propose a comprehensive and efficient solution for managing this effluent, supporting environmental sustainability and public health protection.

Keywords: Biodegradability, coagulation–flocculation, environmental sustainability, Fenton process, landfill leachate, wastewater treatment.

RESUMO

A acumulação contínua de resíduos sólidos urbanos nos aterros resulta na geração de volumes significativos de lixiviado, um efluente líquido complexo e altamente contaminado. Este lixiviado apresenta geralmente elevadas concentrações de matéria orgânica, azoto amoniacal, metais pesados e compostos recalcitrantes como os ácidos húmicos e fúlvicos, os quais conferem baixa biodegradabilidade e elevada variabilidade na composição. Estas características impõem limitações substanciais às tecnologias de tratamento convencionais, conduzindo frequentemente a remoções ineficazes dos poluentes. Perante o seu elevado potencial de causar contaminação ambiental grave do solo e da água, torna-se imperativa a implementação de soluções de tratamento avançadas e economicamente sustentáveis. Este estudo propôs e avaliou uma estratégia integrada de tratamento em duas fases, concebida para melhorar a eficiência dos processos de remediação do lixiviado de aterro. O tratamento proposto iniciou-se com uma pré-etapa de coagulação-floculação (C – F), destinada a promover a agregação e subsequente remoção de sólidos suspensos e matéria orgânica coloidal, reduzindo assim a turbidez e a carga orgânica inicial. Seguiu-se um processo de oxidação avançada (AOP) baseado na reação de Fenton, que depende da geração in situ de radicais hidroxilo (•OH) para oxidar compostos orgânicos refratários. Após a etapa de C – F, observou-se uma redução significativa na carência química de oxigénio (CQO) e um aumento concomitante na carência bioquímica de oxigénio a cinco dias (DBO_5), resultando numa melhoria notável da razão DBO_5/CQO – um parâmetro crucial na avaliação da biodegradabilidade dos efluentes. A otimização do processo foi realizada com recurso ao software Minitab®, tendo sido identificadas as condições ótimas da reação de Fenton: pH 3.4, dosagem de Fe^{2+} de 8.96 g L^{-1} e volume de H_2O_2 (30% w/w) de 30 mL L^{-1} de lixiviado. Nestas condições, a eficiência de remoção da CQO atingiu aproximadamente 92% e a razão DBO_5/CQO aumentou de 0.053 para 0.87, evidenciando uma melhoria substancial na biodegradabilidade. A integração de processos físico-químicos e oxidativos demonstrou elevada eficácia na mitigação da complexa matriz poluente do lixiviado de aterro, oferecendo uma solução tecnicamente robusta e ambientalmente sustentável para a gestão deste tipo de efluente. O objetivo foi propor uma abordagem abrangente e eficiente para a gestão deste efluente, contribuindo para a sustentabilidade ambiental e para a proteção da saúde pública

Palavras-chave: Lixiviados de Aterros; Coagulação-Floculação; Processo de Fenton; Biodegradabilidade; Sustentabilidade Ambiental; Tratamento de Águas Residuais.

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AOPs	*Advanced Oxidation Process*	
APA	*Agência Portuguesa do Ambiente*	
	(Portuguese Environment Agency)	
NH_3–N	*Ammoniacal Nitrogen*	mg L^{-1} NH_4
AD	*Anaerobic digestion*	
ANOVA	*Analysis of Variance*	
BOD5/COD	*Biodegradability Index*	
BOD_5	*Biochemical Oxygen Demand over 5 days*	mg L^{-1} O_2
BBD	*Box-Behnken Design*	
COD	*Chemical Oxygen Demand*	mg L^{-1} O_2
C – F	*Coagulation – Flocculation*	
ELV	*Emission Limit Value*	
EU	*European Union*	
MSW	*Municipal Solid residue*	
RSM	*Response surface methodology*	
SER	*State of Environmental Report*	
TS	*Total solids*	g L^{-1}
UR	*Urban Residue*	
UWMS	*Urban Waste Management System*	
WWTP	*Wastewater Treatment Plant*	

1. INTRODUCTION

1.1 Framework

The systematic management of materials at the end of their life cycle constitutes a critical component of environmental sustainability, enabling the mitigation of ecological degradation and preservation of finite natural resources. Adequate treatment or final disposal of post-consumer products is essential to prevent the mobilisation of toxic substances and persistent pollutants into environmental compartments, thereby safeguarding both ecosystem functionality and human health. The implementation of environmentally responsible end-of-life strategies requires strict adherence to regulatory frameworks and the integration of low-impact technological solutions, which include material recovery, recycling, composting, landfilling, incineration, and advanced waste treatment systems. These practices contribute to pollution abatement, resource circularity, and the establishment of resilient socio-environmental systems aligned with the principles of a circular economy. Among the various waste disposal techniques, sanitary landfills remain the predominant method globally for municipal solid waste containment due to their operational simplicity and cost-effectiveness (Bello et al., 2022; Yatoo et al., 2024).

Sanitary landfills are technically engineered systems intended for the final disposal of municipal solid waste through controlled burial. These facilities are meticulously designed to comply with environmental and public health standards and incorporate barrier systems, leachate collection infrastructure, and gas management components to mitigate the adverse effects associated with waste decomposition processes (Filho et al., 2015). Despite continuous improvements in design and operational protocols, sanitary landfilling remains intrinsically associated with considerable environmental liability. Among the most harmful by-products is landfill leachate, which is a highly complex and toxic effluent comprising recalcitrant organic molecules and a diverse array of inorganic contaminants. This leachate originates predominantly from the infiltration of precipitation through the heterogeneous waste matrix, which facilitates the solubilisation and mobilisation of both dissolved and suspended pollutants. Inadequate waste disposal practices, particularly those involving open dumping or non-regulated landfills, exacerbate environmental degradation and intensify public health risk. Due to its long-term persistence and high pollutant load, landfill leachate contributes significantly to aquatic ecosystem deterioration, manifesting through phenomena such as eutrophication, depletion of dissolved oxygen, and heightened ecotoxicological responses in aquatic organisms (Muaz et al., 2015).

As reported by RECICLA (2023), the implementation of sanitary landfills requires extensive spatial allocation and incorporation of robust geoenvironmental engineering controls. These include the application of impermeable liners for subsoil isolation and the deployment of leachate drainage and collection systems engineered to ensure hydraulic efficiency and chemical compatibility. After collection, leachate must be directed to dedicated treatment facilities to enable environmentally compliant management of the complex effluents generated throughout the operational lifespan of the landfill.

The physicochemical profile of landfill leachate reveals pronounced heterogeneity, which is governed by a multitude of variables such as the landfill's operational age, degree of organic matter stabilisation, waste composition, and site-specific hydrometeorological dynamics, particularly precipitation intensity and frequency (Remmas et al., 2023). This compositional variability imposes significant constraints on the formulation of standardised treatment solutions, rendering site-specific process optimisation indispensable.

From a techno-economic perspective, biological treatment processes have traditionally been regarded as the most cost-effective and sustainable alternatives for the remediation of "young" leachates, typically originating from recently established landfills. The efficacy of these processes is intrinsically linked to the biodegradability index of leachate, which is commonly quantified by the BOD/COD ratio. Values exceeding 0.4 indicate a favourable substrate profile for microbial degradation. In contrast, "stabilised" leachates, distinguished by their dark colouration, high concentrations of ammoniacal nitrogen and COD, and a low BOD/COD ratio, exhibit limited biodegradability. The persistence of refractory and cytotoxic compounds in these effluents compromises the performance of conventional biological systems and necessitates the integration of advanced physicochemical and oxidative treatment technologies (Zamri et al., 2017).

Traditional physicochemical treatment strategies for stabilised landfill leachates encompass a range of unit operations, including chemical precipitation, coagulation–flocculation, oxidative chemical processes, and membrane-based separation techniques, such as reverse osmosis. These methods are frequently employed as pretreatment stages to reduce pollutant load and enhance the biodegradability of leachates prior to biological treatment (Kamaruddin et al., 2013, 2015). However, in the context of mature or stabilised leachates – typically associated with aged landfills and characterised by the presence of recalcitrant organics, high ammoniacal nitrogen concentrations, and low BOD_5/COD ratios – the effectiveness of such conventional approaches is markedly constrained.

In response to these limitations, advanced oxidation processes (AOPs) have gained prominence because of their ability to generate nonselective and highly reactive oxidising species, particularly hydroxyl radicals (•OH), which are capable of mineralising persistent organic pollutants. Hermosilla et al. (2009) demonstrated that AOPs offer superior degradation performance compared to traditional physicochemical methods, which often result only in the physical transfer of contaminants rather than their chemical transformation or destruction. Unlike these phase-transfer mechanisms, AOPs facilitate the oxidative breakdown of complex molecular structures into biodegradable intermediates or fully oxidised end products, thereby significantly enhancing downstream treatment (Deng & Englehardt, 2006; Hermosilla et al., 2009).

Given the persistent nature and toxicological burden of stabilised leachates, there is a critical need to develop integrated and cost-effective treatment protocols tailored to these effluents. In this context, the present study proposes a hybridised treatment approach composed of an initial coagulation–flocculation pre-treatment, designed to remove colloidal and particulate organic matter, followed by an advanced oxidation step via the Fenton process. The rationale behind this sequential configuration is to reduce the matrix complexity of the effluent in the pretreatment stage, thereby increasing the efficacy of the oxidative degradation of residual refractory compounds during the subsequent AOP phase.

For the experimental component of this study, stabilised leachate samples were collected from the Urjais sanitary landfill located in the municipality of Vila Flor, northern Portugal. On September 27, 1997, the Urjais facility was commissioned to receive municipal solid waste from the Terra Quente Transmontana region, later expanding its service area to include municipalities from Douro Superior and Terra Fria do Nordeste Transmontano (Resíduos do Nordeste, 2023). The leachate generated at this site exhibited the typical physicochemical profile of a mature effluent, including high concentrations of non-biodegradable organics, ammoniacal nitrogen, and humic substances, underscoring the need for advanced treatment strategies to achieveH effective remediation.

1.2 General Objective

The primary objective of this research was to assess the effectiveness of an integrated physicochemical and advanced oxidation treatment system for the remediation of stabilised landfill leachate originating from the Urjais facility. This study aimed to enhance treatment performance to meet environmental discharge standards or facilitate subsequent treatment stages. This objective was achieved through the sequential application of coagulation–flocculation as a primary conditioning step, followed by an advanced oxidation process based on the Fenton reaction. The optimisation of key operational parameters of the Fenton process, namely hydrogen peroxide concentration and ferrous ion dosage, will be conducted using Response Surface Methodology (RSM), enabling multivariate statistical modelling and the identification of optimal treatment conditions.

1.3 Specific Objective

a) To collect representative samples of stabilised leachate from the Urjais sanitary landfill under controlled conditions for experimental analysis.
b) To conduct an in-depth physicochemical characterisation of the raw leachate, parameters relevant to biodegradability, organic load, and pollutant recalcitrance.
c) To implement and evaluate a coagulation–flocculation pretreatment step aimed at reducing turbidity, suspended solids, and part of the organic fraction.
d) To apply the Fenton oxidation process as a post-treatment stage and assess its efficacy in degrading recalcitrant organic compounds and improving leachate biodegradability.
e) To perform post-treatment characterisation of the effluent in order to quantify reductions in critical parameters such as COD, BOD_5, ammoniacal nitrogen, and assess improvements in the COD/BOD_5 ratio.
f) The quality of the treated effluent was compared against applicable environmental legislation and discharge standards to determine regulatory compliance.

2. STATE-OF-THE-ART

2.1 Urban Waste Management

Throughout the 20th century, rapid technological and scientific advancements coupled with the industrial-scale production of novel materials and intensified consumption patterns have led to a significant rise in waste generation. This escalation is directly correlated with demographic expansion, accelerated urbanisation, and rising per capita consumption. In recent decades, this trend has evolved into a critical environmental concern, demanding strategic, technically grounded, and sustainable waste-management solutions.

According to the European Parliament report entitled Waste Management in the European Union: Data and Statistics, updated in November 2023, the total waste generation within the EU is estimated at approximately 2.2 billion tonnes annually. Notably, 27% of this total corresponds to municipal solid waste (MSW), a significant portion of which is used in landfilling operations.

Under Decree Law No. 178/2006, on September 5, as amended and republished by Decree Law No. 102-D/2020, of December 10, Urban Waste is defined as: “i) Indiscriminate collection and selective collection from households, including paper and cardboard, glass, metals, plastics, bio-waste, wood, textiles, packaging, waste from electrical and electronic equipment, waste from batteries and accumulators, as well as bulky waste, including mattresses and furniture; and ii) Indiscriminate collection and selective collection from other sources, if they are similar to household waste in nature and composition” (Decree law No. 102-D/2020, 2020).

The total generation of municipal solid waste (MSW) in Portugal in 2023 was estimated to be approximately 5.05 million tonnes, representing a slight increase of 0.24% compared to the previous reporting year. This corresponds to a per-capita generation rate of 507 $kg \cdot inhabitant^{-1} \cdot year^{-1}$, equivalent to an average daily production of 1.39 kg per person, as shown in Figure 1 (APA, 2022).

The imperative for effective waste management strategies transcends national boundaries, reflecting a pervasive global environmental and public health challenge. Numerous countries face convergent difficulties in managing escalating volumes of solid waste, exacerbated by urbanisation, industrialisation, and consumption trends. Over the past few decades, conventional waste management practices have predominantly relied on incineration or landfill as final disposal pathways (Read et al., 1997). In the Portuguese context, by the end of the 1990s, the predominant mode of MSW disposal involved non-engineered open-air dumping, accounting for approximately 76% of the total waste deposition. Additionally, so-called “controlled” landfills comprised a further 14%, illustrating a historical dependency on suboptimal disposal practices that contributed significantly to environmental degradation and necessitated the subsequent modernisation of waste infrastructure (Russo, 2005)

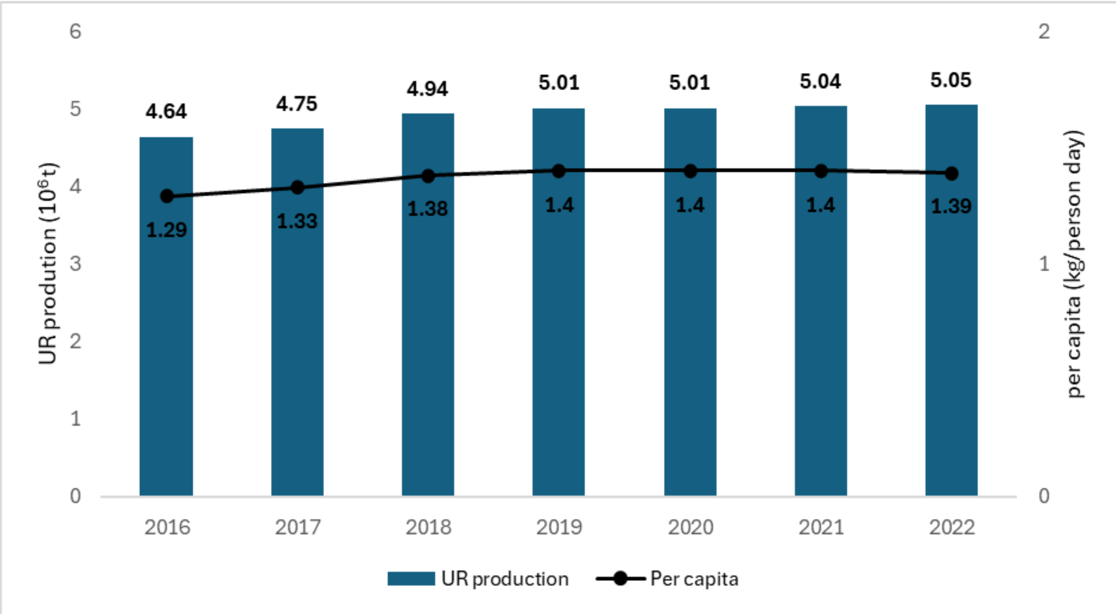

Figure 1. Historical trend in the generation of urban residue (UR) in Portugal. Adapted from APA, 2022.

Within this framework, the Strategic Plan for Municipal Solid Waste (PERSU I), initially approved in 1997 and subject to subsequent updates, was instituted as a foundational policy instrument to guide the national strategy for integrated municipal waste management in Portugal. According to the Portuguese Environment Agency (APA), its implementation catalysed the deployment of a structured set of regulatory and infrastructural measures aligned with the waste management hierarchy. This hierarchical model emphasised, in descending order of priority: (i) waste prevention, through minimisation and reuse; (ii) material and energy valorisation, via recycling and recovery; and (iii) environmentally sound final disposal through engineered containment systems (Russo, 2005; Filho et al., 2015).

Between 1995 and 2005, under the directives established by PERSU I, a comprehensive restructuring of the national waste management infrastructure was undertaken. This led to the systematic closure of non-compliant and environmentally hazardous disposal sites and the concurrent establishment of a network of technically regulated landfills (ERSAR, 2022). As a result, the country transitioned from a system in which only 13 compliant landfills were operational in 1996—serving approximately 26% of the population - to full national coverage by 2004, with 33 sanitary landfills equipped to manage municipal solid waste in accordance with contemporary environmental and public health standards (Russo, 2005).

Decree Law No. 102-D/2020, on December 10, established the legal definition and functional classification of landfills within the Portuguese regulatory framework. According to legislation, a landfill is characterised as an engineered facility designated for the final disposal of waste, whether situated above or below the natural surface level, including subsurface deposition systems. This definition also extends to internal disposal infrastructure operated by waste producers themselves at the point of generation. Moreover, landfills are recognised as permanent facilities utilised for the temporary storage of waste when the storage period exceeds one calendar year (Decree Law No. 102-D/2020, 2020).

Figure 2 depicts the spatial distribution of the 23 officially designated Urban Waste Management Systems (UWMS) across mainland Portugal, based on data updated in 2022. Among these, 12 systems operate under a multi-municipal governance model and are responsible for managing approximately 66% of the total municipal solid waste (MSW) generated nationally. The remaining 11 systems function under inter-municipal arrangements, collectively overseeing the management of the residual waste fraction (APA, 2023).

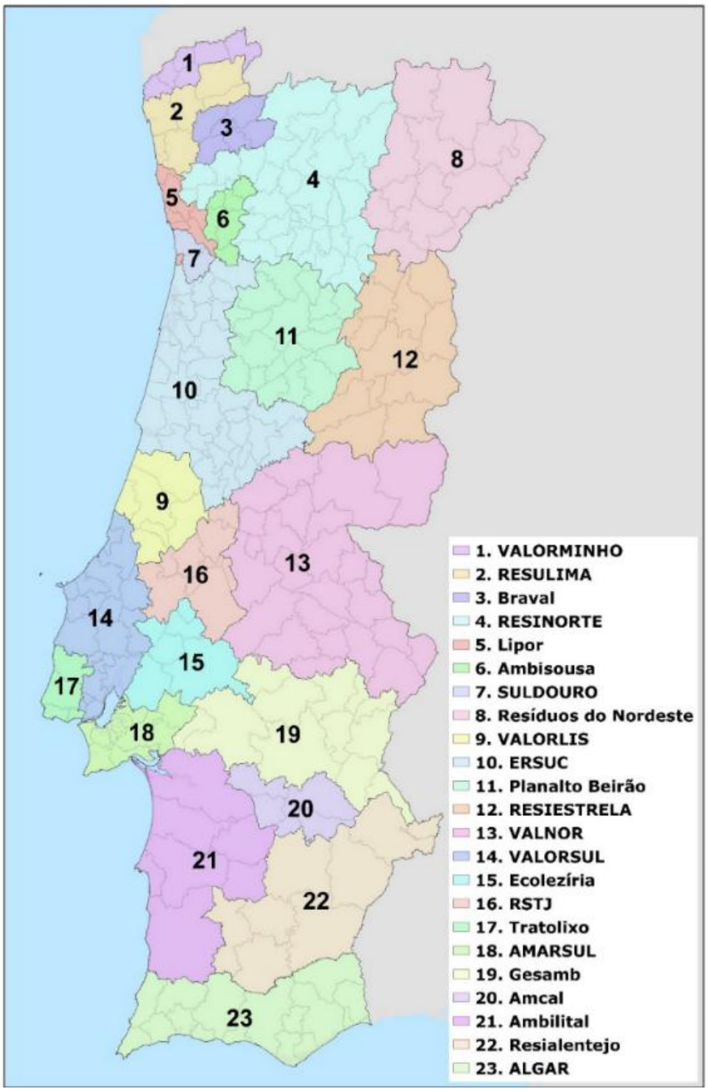

Figure 2. Geographical distribution of the Urban Waste Management Systems (UWMS) across mainland Portugal. Adapted from APA, 2023.

Landfilling of waste derived from undifferentiated collection remains the predominant and most globally adopted strategy for the final disposal of municipal solid waste (MSW). This method is widely regarded as the most cost-effective solution within current waste management frameworks, particularly in regions where selective collection and material recovery systems are not fully operational or economically viable (Gao et al., 2014; Hermosilla et al., 2009; Martins & Boaventura, 2014). Although alternative valorisation technologies such as composting, recycling, and energy recovery have gained relevance in recent years, landfill disposal continues to represent the terminal stage for a significant fraction of waste streams, particularly those that are heterogeneous or contaminated.

According to the State of the Environment Report (SER, 2022), approximately 57% of MSW generated in mainland Portugal is directed to landfill disposal facilities. This figure highlights the persistent structural dependence on landfill as a principal waste management practice at the national level. Figure 3 illustrates the distribution of waste treatment routes in Portugal, with landfilling accounting for the majority of the final waste disposal.

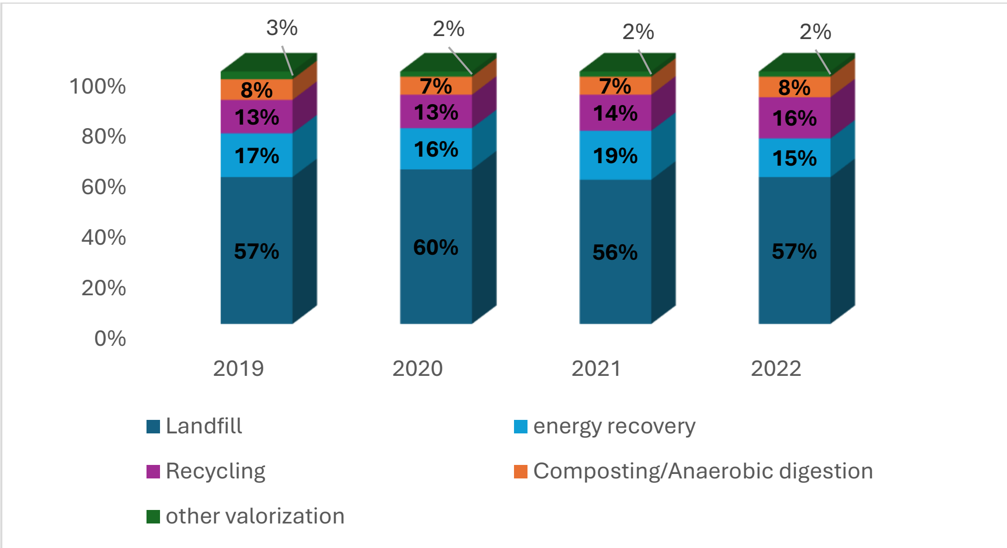

Figure 3. Final destinations of municipal solid waste (MSW) in Portugal between 2019 and 2022. Adapted from APA, (2023).

The inter-municipal waste management entity operating in northern Portugal, Resíduos do Nordeste, is responsible for the operation of an engineered landfill facility authorised for the final disposal of non-hazardous solid waste. This facility constitutes a critical component of the region's integrated municipal solid waste management infrastructure and is designed in accordance with the technical specifications and environmental safeguards established under the national and EU regulatory frameworks for Class II landfills (regulated landfills designed for non-hazardous waste). Figure 4 provides a spatial and functional overview of the facility, highlighting its role in the regional waste management system.

Figure 4. Territorial layout and infrastructure of the Resíduos do Nordeste waste management system in northern Portugal. Adapted from Resíduos do Nordeste, 2023.

A sanitary landfill can be conceptually described as a large-scale biochemical reactor. The primary inputs to this system include municipal solid waste (MSW) and infiltrated rainwater, while its main outputs consist of biogas (primarily methane (CH_4) and carbon dioxide (CO_2)) and leachate. The latter is a result of the degradation of biodegradable organic fractions present in MSW and constitutes one of the principal environmental drawbacks of landfilling operations due to its high contamination potential (Silva, 2014).

2.2 Leachate

As previously discussed, landfilling operations constitute a major environmental liability, primarily due to the continuous generation of leachate. This effluent arises from the percolation of rainwater through the waste mass and subsequent degradation of solid waste via biochemical and physicochemical pathways (Renou et al., 2008). Once produced, leachate may percolate through soil layers, potentially reaching and contaminating surface water bodies and groundwater resources (Tatsi et al., 2003).

Landfill leachate is typically characterised by elevated concentrations of dissolved and suspended pollutants, including biodegradable and refractory organic matter (humic and fulvic acids), heavy metals, ammoniacal nitrogen, and other xenobiotic compounds. Particularly relevant are humic and fulvic acids, which exhibit high chemical stability and low biodegradability (Mandal et al., 2017; Mojiri et al., 2021; Renou et al., 2008). The compositional variability and complexity of leachate are influenced by several interrelated factors, including waste composition and heterogeneity, compaction density, hydrometeorological conditions (precipitation), and the age and biochemical stage of the landfill (Hermosilla et al., 2009; Mandal et al., 2017; Mojiri et al., 2021; Renou et al., 2008; Traid et al., 2022).

Kjeldsen et al. (2002), identify at least four distinct and sequential phases of waste degradation within landfills, each characterised by specific biochemical and physicochemical conditions:

- **Phase I** – Initial Aerobic Phase: Occurs immediately after waste deposition when residual oxygen entrapped within the waste matrix enables limited aerobic microbial activity. Rapid consumption of available oxygen leads to the production of CO_2 and localised exothermic reactions. This phase is short-lived, as the subsequent compaction and covering inhibit further oxygen ingress.

- **Phase II** – Anaerobic Acidogenic Phase: In the absence of oxygen, anaerobic conditions dominate, favouring fermentative metabolic pathways. Acidogenic bacteria convert hydrolysed organic substrates into volatile fatty acids (VFAs), alcohols, lactic acid, hydrogen, and CO_2. This phase is characterised by a marked decrease in pH and an increase in chemical oxygen demand (COD) due to the accumulation of soluble intermediates.

- **Phase III** – Methanogenic Phase**:** Initiated when the pH environment becomes sufficiently buffered to permit the proliferation of methanogenic archaea. These obligate anaerobes metabolise VFAs and other precursors into CH_4 and CO_2. During this stage, the concentration of soluble organics gradually decreased, and the pH stabilised near neutrality, indicating a shift toward biochemical stabilisation.

- **Phase IV** – Stabilisation phase: This terminal phase is marked by the attenuation of methanogenic activity as the availability of biodegradable substrates, primarily carboxylic acids, reaches minimal levels. Consequently, methane production declined, and the pH stabilised at neutral to slightly alkaline values. The landfill system transitions into a biogeochemically inert state with limited microbial turnover and reduced leachate generation, primarily composed of refractory and slowly degradable compounds.

Over time, as the landfill progresses through its biostabilisation trajectory, the leachate composition undergoes significant physicochemical and biological transformations. These temporal dynamics permit the classification of leachates into three primary categories based on the operational age of the landfill: young, intermediate, and stabilised. This classification is based on key indicators such as pH, biochemical oxygen demand (BOD), chemical oxygen demand (COD), and the BOD/COD ratio. As landfill age increases, a consistent decline in BOD_5 and an increase in COD are typically observed, indicating a shift toward lower biodegradability and greater chemical recalcitrance. These patterns are summarised in Table 1, providing a structured framework for the selection of appropriate treatment strategies.

Table 1. Classification of landfill leachate as a function of landfill age and associated physicochemical properties (Mojiri et al., 2021; Renou et al., 2008).

Parameter	Young	Intermediary	Stabilized
Age (year)	< 5	5 – 10	> 10
pH	< 6.5	6.5 – 7.5	>8.5
COD (mg L^{-1})	> 10000	4000 – 10000	< 4000
BOD_5/COD	> 0.3	0.1 – 0.3	< 0.1
Organic compounds	80% volatile fatty acids	5 – 30% Volatile fatty acids + fulvic and humic acids	Fulvic and humic acids
Concentration of heavy metals	Low – medium	–	Low
NH_3-N (mg L^{-1})	< 400	–	> 400
Biodegradability	High	Average	Low

The classification of landfill leachate based on landfill age provides critical insight into its physicochemical evolution and biodegradability. The term "Young" refers to effluents generated during the initial phase of landfill operation (≤ five years). At this stage, the leachate is typically acidic, exhibiting high concentrations of low-molecular-weight organic compounds, predominantly volatile fatty acids (VFAs), which may account for up to 80% of the total organic load, resulting in high biodegradability and elevated BOD/COD ratios.

As landfills transition into the intermediate stage (5 – 10 years), a notable decline in biodegradable organic matter occurs. This is accompanied by a progressive reduction in the BOD/COD ratio, indicating the accumulation of recalcitrant compounds, particularly humic and fulvic acids, which exhibit a low susceptibility to microbial degradation. Simultaneously, the concentration of VFAs decreases, leading to an increase in pH that promotes the establishment of methanogenic conditions, signalling the onset of the third degradation phase.

In the final stage, designated as "mature leachate" (≥10 years), the landfill reached a stabilised state. Additionally, there is a consistent increase in ammoniacal nitrogen concentration, further contributing to the environmental complexity and treatment difficulty of the effluent (Luo et al., 2019; Mojiri et al., 2021; Renou et al., 2008).

2.3 Legal Framework

The discharge or release of landfill leachate into aquatic systems or terrestrial environments is governed by the provisions of Decree-Law No. 236/98 of August 1. This legal instrument establishes a regulatory framework for the discharge of wastewater into surface waters, coastal and territorial waters, groundwater bodies, soil, and public sewage networks. Its primary objective is to ensure the protection of aquatic ecosystems and the preservation of water quality, considering their designated uses, as well as to safeguard public health and soil integrity (decree-Law No. 236/98, 1998).

The decree further stipulates a comprehensive set of Emission Limit Values (ELVs) that must be strictly observed for any wastewater discharge activity. These ELVs are designed to mitigate the introduction of harmful contaminants into the environment and standardise the effluent quality thresholds for regulatory compliance. Table 2 summarises the legally established ELVs applicable to the discharge of effluents, including landfill leachate, into water bodies or soils.

Table 2. ELV in the discharge of wastewater. Adapted from *Decree Law No. 236/98, 1998.*

Parameter	ELV (1)	Expression of results
pH	6.0 – 9.0 (2)	Sorensen Scale
Temperature	Increase in 3ºC (3)	ºC
BOD_5, 20ºC	40	mg L^{-1} O_2
COD	150	mg L^{-1} O_2
TSS	60	mg L^{-1}
Aluminium	10	mg L^{-1} Al
Total iron	2.0	mg L^{-1} Fe
Total manganese	2.0	mg L^{-1} Mn
Smell	Not detectable at 1:20 dilution	-
Cor	Not visible at 1:20 dilution	-
Residual chlorine available		
Free	0.5	mg L^{-1} Cl_2
Total	1.0	mg L^{-1} Cl_2
Phenols	0.5	mg L^{-1} C_6H_5OH
Oils and fats	15	mg L^{-1}
Sulfurets	1.0	mg L^{-1} S
Sulphites	1.0	mg L^{-1} SO_3
Sulphates	2000	mg L^{-1} SO_4
Total phosphorus	10 3 (in waters that feed ponds or reservoirs) 0.5 (in ponds or reservoirs)	mg L^{-1} P
Ammonical nitrogen	10	mg L^{-1} NH_4
Total nitrogen	15	mg L^{-1} N
Nitrates	50	mg L^{-1} NO_3
Aldehydes	1.0	mg L^{-1}
Total Arsenium	1.0	mg L^{-1} As
Total Lead	1.0	mg L^{-1} Pb
Total Cadmium	0.2	mg L^{-1} Cd
Total Chromium	2.0	mg L^{-1} Cr
Hexavalent chromium	0.1	mg L^{-1} Cr (VI)
Total Copper	1.0	mg L^{-1} Cu
Total Nickel	2.0	mg L^{-1} Ni
Total Mercury	0.05	mg L^{-1} Hg
Total cyanides	0.5	mg L^{-1} CN
Mineral oils	15	mg L^{-1}
Detergent (sodium laurel sulfate	2.0 (4) (5)	mg L^{-1}

(1) ELV (Emission Limit Value), understood as a monthly average, defined as the arithmetic mean of daily averages for the days of operation in a month, which must not be exceeded. The daily value, determined based on a representative sample of the wastewater discharged over a twenty-four-hour period, must not exceed twice the monthly average value (the sample over a twenty-four-hour period should be composed taking into account the discharge pattern of the produced wastewater).
(2)The daily average value must, at most, fall within the range of 5.0-10.0.
(3) The temperature of the receiving environment after the discharge of wastewater, measured 30 meters downstream from the discharge point, with the daily average value not exceeding twice the monthly average value.
(4)The daily average value must not exceed twice the monthly average value.
(5) Value related to the discharge from the industrial unit to produce HCH, lindane extraction, or simultaneously, the production of HCH and lindane extraction.

2.4 Leachate Treatment

The management of landfill leachate is critical because of its high pollutant load, which requires effective treatment before environmental discharge. As previously noted, leachate composition is influenced by factors such as the nature of the deposited waste, site-specific hydrogeological conditions, and most notably, landfill age. One of the primary challenges in leachate management is addressing this compositional variability.

The biodegradability index (BOD_5/COD), representing the ratio of Biochemical Oxygen Demand to Chemical Oxygen Demand, is a key indicator used to guide the selection of appropriate treatment strategies. Based on this index and the overall contaminant profile, leachate treatment methods are broadly classified into three main categories (Zamri et al., 2017; Levy & Cabeças, 2006; Mojiri et al., 2021; Renou et al., 2008; Sapkota et al., 2023; Tatsi et al., 2003):

1. **Biological Treatments**
   - *Aerobic processes:* utilise oxygen-dependent microbial activity in systems such as aerated lagoons or aerobic bioreactors to degrade biodegradable organic matter.
   - *Anaerobic processes:* rely upon oxygen-free environments, typically anaerobic lagoons or digesters, to decompose organic matter, generating biogas (primarily methane) as a by-product.
2. **Physicochemical Treatments**
   - *Coagulation/flocculation:* this involves the addition of coagulants and flocculants to destabilise and aggregate suspended particles into removable flocs.
   - *Chemical oxidation:* strong oxidants (hydrogen peroxide and ozone) are used to degrade recalcitrant organic compounds.
   - *Adsorption:* adsorbent materials such as activated carbon are used to capture and remove contaminants.
   - *Ion Exchange:* targets specific ionic pollutants using ion-exchange resins.
   - *Membrane filtration:* application of pressure-driven membrane processes (ultrafiltration, nanofiltration, and reverse osmosis) to separate solutes from water.

- *Chemical Precipitation:* promotes the removal of dissolved substances by converting them into insoluble precipitates through reagent addition.
- *Air stripping:* aeration is used to volatilize and remove gaseous pollutants or oxidise organics.

3. **Hybrid Treatments**
   - Integrated biological–physicochemical systems are frequently employed to improve the overall treatment performance. These may comprise sequential or parallel configurations that target a wide range of contaminants.

When assessing the treatment technology or a combination of technologies for landfill leachate, three fundamental criteria must be considered. These criteria encompass treatment efficacy, the financial investment required for the treatment system, and the environmental repercussions associated with its implementation. A thorough examination of these elements is imperative to ensure the adoption of efficient, economically feasible, and environmentally sound leachate management strategies (Mandal et al., 2017). Figure 5 illustrates the three main criteria recommended for selecting landfill leachate treatment technologies.

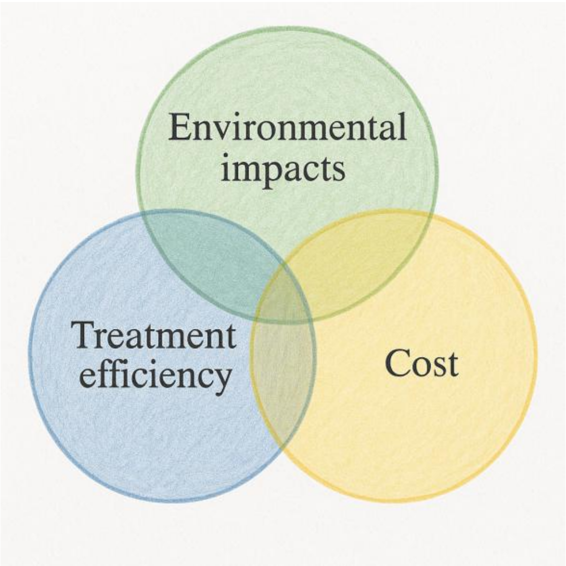

Figure 5. Key criteria for selecting appropriate landfill leachate treatment technologies. Adapted from Mandal et al., 2017.

2.5 Leachate Treatment in Portugal

According to Levy and Santana (2004), mainland Portugal has 37 active sanitary landfills, of which 32 are equipped with leachate treatment plants. These facilities primarily use biochemical treatments to reduce COD, BOD_5, and ammonia ($N\text{-}NH_3$), often in combination with membrane filtration or lagoon systems. As illustrated in Figure 6 and summarised in Table 3, approximately 35% of leachate treatment plants incorporate reverse osmosis as a secondary treatment stage. Physical–chemical methods and activated sludge processes are implemented in approximately 31% of the systems, while approximately 14% discharge leachate directly into municipal wastewater networks.

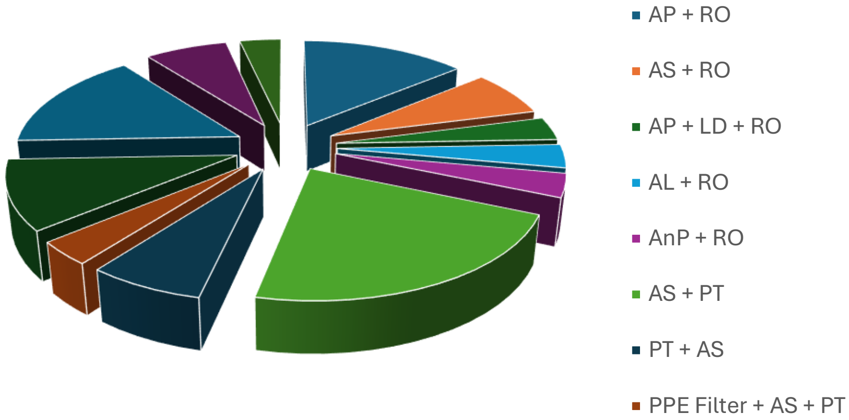

Figure 6. The leachate treatment process in mainland Portugal. Adapted from *Levy & Santana, 2004*.

The most prevalent treatment configuration identified is OD + Connection to Exutor (Oxidation Ditch combined with sewer discharge), accounting for 19% of the surveyed systems. This indicates a preference for integrating biological oxidation processes with a centralised wastewater infrastructure. In contrast, configurations such as AP + LD + RO (aeration pond + lamellar decanter + reverse osmosis) and AS + RO (activated sludge + reverse osmosis) are among the least common, each representing only 3% (Levy & Santana, 2004). These results reflect the diversity of the treatment strategies implemented, although some advanced or hybridised systems are less frequently adopted (Table 3).

Table 3. Leachate treatment facilities in Portugal (Levy and Santana 2004).

Facility/Company	Treatment Process	Discharge
RESIOESTE	Aeration Pond + Reverse Osmosis	Waterline
ALGAR (Barlavento)		Waterline
ALGAR (Sotavento)		Waterline
Cova da beira	Activated Sludge + Reverse Osmosis	Waterline
Raia/Pinhal		Waterline
Planalto Beirão		Waterline
LIPOR II		Waterline
REBAT		Waterline
SULDOURO	Aeration Pond + Lamellar Decanter + Reverse Osmosis	WWTP + Waterline
RESIDOURO	Airy or Anaerobic Lagoon + Reverse Osmosis	Waterline
AM. Distrito de Évora	Anaerobic Ponds + Reverse Osmosis	Waterline
VALSOUSA (Lousada	Activated Sludge + Physicochemical Treatment	Waterline
RESULIMA		WWTP
VALORMINHO		Waterline
ERSUC – Mondego (Coimbra)		WWTP
VALNOR (Avis)		Waterline
SULDOURO	Physicochemical Treatment + Activated Sludge	WWTP + Waterline
RESIURB		Waterline
RESAT		Waterline
BRAVAL	PPE Filter + Activated Sludge + Physicochemical Treatment	WWTP
AMALGA (Beja)		WWTP + Waterline
RESITEJO	Aeration Pond + Physicochemical Treatment	Inoperable
Vale do Douro Norte		Waterline
VALORSUL		WWTP
ERSUC – Baixo Vouga		WWTP
AMARTEJO		Waterline
AMAGRA (Grândola)	Aeration Pond	Zero discharge
AMARSUL (Palmela)		WWTP
VALSOUSA (Penafiel)		WWTP
AMCAL (Cuba)	Aeration Pond + Macrophyte Pond	Waterline
VALORLIS		WWTP
AMTRES	Oxidation Ditch + Connection to Exutor	WWTP
ERSUC – Baixo Mondego	Discharge in municipal ETAR	WWTP
Amave (Santo Tirso) – SIDVA		WWTP
Amave (Gonça) – SIDVA		WWTP
Terra Fria/Terra Quente/Douro Superior		WWTP
AMARSUL (Seixal)		WWTP

2.6 Treatment Process

2.6.1 Coagulation/Flocculation

Coagulation/flocculation is one of the most widely used physicochemical pretreatment methods for leachate derived from aged and stabilised landfills. This process has shown significant effectiveness in removing various contaminants, including non-biodegradable organic compounds, suspended solids, colloidal particles, turbidity, colour, and heavy metals. The overall efficiency of coagulation–flocculation is highly dependent on the nature of the leachate, particularly the specific contaminants present, as well as the type and dosage of coagulant and flocculant employed (Sapkota et al., 2023).

According to Levy and Cabeças (2006), the theoretical foundation of physicochemical treatment through coagulation/flocculation is the neutralisation of electrostatic repulsion among particles in the effluent to be treated. This neutralisation step enhances particle aggregation, thereby facilitating subsequent removal.

In leachate treatment, commonly used coagulants include ferric chloride ($FeCl_3$), ferric sulfate ($Fe_2(SO_4)_3$), aluminium sulfate (alum), and polyaluminum chloride (PAC), all of which are effective in charge neutralisation and initial floc formation (Mao Rui et al., 2012). Typical flocculants include polyacrylamide (PAM), available in various ionic forms (anionic, cationic, nonionic), which assist in bridging particles to form larger flocs. Natural alternatives such as chitosan and starch-based polymers are also employed for their biodegradability and low environmental impact (Maćczak et al., 2020). The choice of coagulant–flocculant combination depends on the leachate's characteristics, particularly pH, organic load, and suspended solids content.

Two distinct chemical agents are employed in the coagulation–flocculation process, as illustrated in Figure 7. The coagulant is first added to a rapid mixing chamber to promote the destabilisation of the colloidal particles present in the effluent. This chemical destabilisation triggers the initial aggregation of colloids and suspended matter. Subsequently, a flocculant is introduced to further enhance floc growth. This phase involves a hydrodynamic mechanism that facilitates contact between destabilised particles, thereby promoting the formation of larger and more settleable flocs (Levy & Cabeças, 2006).

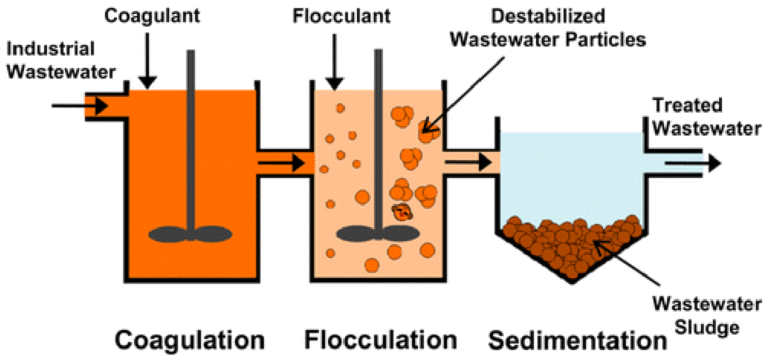

Figure 7. Schematic representation of coagulation–flocculation process (Werjen, 2023).

2.6.2 Advanced Oxidation Process (AOPs)

Chemical oxidation is widely applied in the treatment of effluents containing refractory compounds such as landfill leachate. This technique involves the use of strong oxidants such as ozone (O_3) or hydrogen peroxide (H_2O_2), which induce chemical transformations in complex pollutants. Among these, advanced oxidation processes (AOPs) are particularly effective in degrading persistent organic contaminants commonly found in stabilised leachates (Amor et al., 2015; Hermosilla et al., 2009; Levy & Cabeças, 2006; Renou et al., 2008). AOPs operate through redox mechanisms, transferring electrons between oxidising and reducing agents. According to Levy and Cabeças (2006), hazardous compounds are transformed into less-harmful substances during wastewater treatment.

Lopez et al. (2003) define AOPs by oxidation mechanisms that produce hydroxyl radicals in significant quantities, thereby influencing the treatment of water and wastewater. The hydroxyl radical (HO•) plays a pivotal role in the degradation of pollutants and is one of the most reactive free radical groups ($HO• + H+ + e^- \rightarrow H_2O$; E0 = 2.73 V) (Umar et al., 2010).

Various systems fall under the category of AOPs, with many employing strategic combinations, such as the simultaneous use of two oxidants, ($O_3 + H_2O_2$); the presence of a catalyst associated with an oxidant (Fe2+ + H_2O_2); the use of an oxidant together with irradiation (H_2O_2 plus UV); the combination of an oxidant with a photocatalyst (H_2O_2 plus TiO_2 plus hv); and the association of an oxidant with ultrasound (H_2O_2 plus ultrasound) (Lopez et al., 2003).

These systems are commonly characterised by high energy consumption, primarily owing to the operation of devices such as ozonators, UV lamps, and ultrasound generators, which results in considerably elevated treatment costs. Notably, the Fenton process is an exception to this. In this method, the combination of Fe^{2+} with H_2O_2 generates hydroxyl radicals (OH•) in a highly economical manner (Lopez et al., 2003).

The Fenton reaction, initially observed by Fenton in 1894, relies on electron transfer between hydrogen peroxide (H_2O_2) and a metal ion, typically ferrous iron (Fe^{2+}), which acts as a catalyst. The interaction between H_2O_2 and Fe^{2+} generates hydroxyl radicals, enabling the oxidative breakdown of organic matter without external energy input.(Umar et al., 2010). This process is represented by the following reactions (Equations 1-8) (Deng & Englehardt, 2006; Hermosilla et al., 2009; Umar et al., 2010):

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH^\bullet \qquad K1 = 70.0\ M^{-1}s^{-1} \qquad (1)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^\bullet + H^+ \qquad K2 <<< k1 \qquad (2)$$

$$H_2O_2 + OH^\bullet \rightarrow HO_2^\bullet + H_2O \qquad K3 = 3.3 * 10^7\ M^{-1}s^{-1} \qquad (3)$$

$$Fe^{2+} + OH^\bullet \rightarrow Fe^{3+} + OH^- \qquad K4 = 3.2 * 10^8\ M^{-1}s^{-1} \qquad (4)$$

$$Fe^{3+} + HO_2^\bullet \rightarrow Fe^{2+} + O_2H^+ \qquad K5 < 2.0 * 10^3\ M^{-1}s^{-1} \qquad (5)$$

$$Fe^{2+} + HO_2^\bullet + H^+ \rightarrow Fe^{3+} + H_2O_2 \qquad K6 = 1.20 * 10^6\ M^{-1}s^{-1} \qquad (6)$$

$$HO_2^\bullet + HO_2^\bullet \rightarrow H_2O_2 + H^+ \qquad K7 = 8.3 * 10^5\ M^{-1}s^{-1} \qquad (7)$$

$$HO_2^\bullet + H_2O_2 \rightarrow OH^\bullet + H_2O + O_2 \qquad K8 = 3.0\ M^{-1}s^{-1} \qquad (8)$$

The oxidation of ferrous ions (Fe^{2+}) to ferric ions (Fe^{3+}) initiates and catalyses the decomposition of hydrogen peroxide (H_2O_2), resulting in the rapid formation of hydroxyl radicals (•OH) as shown in Equations (1) – (7). This process, which involves a redox cycle between Fe^{2+} and Fe^{3+}, is most efficient under acidic conditions, where the availability of H^+ ions enhances the dissociation of H_2O_2 and maximises radical generation.

The Fenton reagent system ($Fe^{2+} + H_2O_2 + H^+$) has several notable advantages: (i) both reagents are inexpensive and environmentally benign; (ii) the homogeneous reaction mechanism avoids mass transfer limitations; (iii) no external energy source is required for catalyst activation; and (iv) the process is simple to implement on a technical scale (Lopez et al., 2003).

Moreover, hydrogen peroxide decomposes into water and oxygen, posing minimal risk of residual toxicity in the treated effluent. This feature aligns with environmental sustainability, as many microorganisms naturally degrade H_2O_2 during metabolic processes (Levy & Cabeças, 2006).

3. EXPERIMENTAL METHODOLOGY

In this study, a comprehensive physicochemical characterisation of landfill leachate was performed, including the determination of parameters such as pH, Chemical Oxygen Demand (COD), Biochemical Oxygen Demand over 5 days (BOD_5), total ammonia, electrical conductivity, and total solids. This section presents the standard calibration curves employed and details the optimisation of operational parameters for the coagulation–flocculation and Fenton processes, with the aim of enhancing treatment efficiency. All experimental procedures were performed at the Chemical Processes Laboratory of the School of Technology and Management, Polytechnic Institute of Bragança.

3.1 Leachate characterisation

Leachate samples were collected from the Urjais Landfill during two distinct sampling campaigns conducted during different seasons to capture potential variations in effluent composition. Manual sampling was performed directly from the raw leachate bypass tank (Figure 8) to ensure the representative capture of the untreated effluent. Samples were collected in 20-litre containers and stored at 4 °C in a refrigerator until analysis. This strategy enabled a reliable assessment of seasonal fluctuations and ensured that subsequent treatment evaluations reflected the real operational conditions.

Figure 8. Collection of raw leachate samples for physicochemical analysis.

Physicochemical characterisation of raw leachate listed in Table 4 was based on the protocols outlined in the *Standard Methods for the Examination of Water and Wastewater* (19th Edition), published by the American Public Health Association (APHA), American Water Works Association (AWWA), and Water Environment Federation (WEF) (Clesceri et al., 1995).

Table 4. Standard analytical methods employed for the physicochemical characterisation of raw landfill leachate.

Parameter	Method	Description
pH	-	Measure of the acidity or alkalinity of the leachate, indicating the concentration of hydrogen ions present.
Conductivity	-	The leachate's ability to conduct an electric current,
COD	5220 D	Closed Reflux Calorimeter Method.
BOD_5	5210 B	Standardised respirometry method using the OxiTop (WTW) equipment.
Total solids	2540 Solids	gravimetric
Total ammonia	4500 – NH_3	Nesslerization

3.1.1 Chemical Oxygen Demand (COD)

Chemical Oxygen Demand (COD) is a fundamental parameter used to quantify the amount of oxidisable organic and inorganic matter present in water and wastewater. It represents the quantity of oxygen required to chemically oxidise these substances under standardised conditions. As stated by the amount of oxidant consumed during the process is expressed in terms of oxygen equivalents.

The analysis was conducted using the closed reflux colourimetric method (Standard Methods, section 5220D), was selected. This method uses a JASCO V-530 spectrophotometer configured at a wavelength of 600 nm. Owing to the high COD levels in the raw leachate, sample dilution was required to bring measurements within the 0 – 1000 mg O_2 L^{-1} analytical range.

A calibration curve was constructed using potassium hydrogen phthalate (KHP) as the standard, where 1 mg of KHP corresponds to 1.176 mg O_2 L^{-1} (Figure 9).

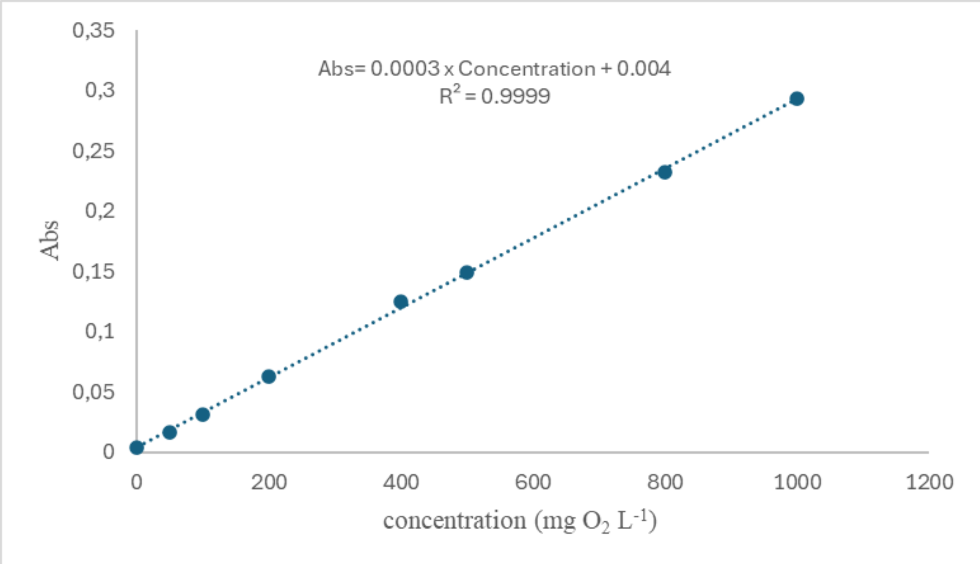

Figure 9. Calibration curve for COD determination using standard solutions.

With an R^2 value of 0.9999, the calibration curve demonstrates a strong linear correlation, confirming the validity of the equation (9) for COD determination within the range of 0 – 1000 mg O_2 L^{-1}.

$$COD, mg\ O_2L^{-1} = \frac{Abs - 0.004}{0.0003} \tag{9}$$

The Chemical Oxygen Demand (COD) removal efficiency was calculated using Equation (10), which quantifies the reduction in contaminant concentration after treatment:

$$\text{Removal efficiency (\%)} = \frac{inicial\ COD\ concentration\ (\text{mg}\ O_2L^{-1}) - final\ COD\ concentration\ (\text{mg}\ O_2L^{-1})}{inicial\ COD\ concentration\ (\text{mg}\ O_2L^{-1})} \tag{10}$$

This equation provides a standardised method for assessing the effectiveness of the treatment process in decreasing organic pollutant load.

3.1.2 Biochemical Oxygen Demand (BOD_5)

Biochemical Oxygen Demand (BOD) is a key parameter for quantifying the biodegradable organic load in wastewater and assessing treatment efficiency (Clesceri et al., 1995).

According to the *Standard Methods for the Examination of Water and Wastewater* (Clesceri et al., 1995), the BOD test measures the molecular oxygen consumed during the microbial oxidation of organic matter and the oxidation of certain inorganic compounds (sulfides and ferrous iron) over a specified period.

Various methods are employed to determine Biochemical Oxygen Demand (BOD), including measurements of oxygen consumption over different incubation periods, such as 60 to 90 days, 5 days (BOD_5), or continuous oxygen uptake, depending on the analytical requirements.

BOD_5, the most applied index, represents the oxygen demand over a 5-day incubation at 20 °C. In this study, BOD_5 was determined following Standard Method 5210-B using the OxiTop® respirometric system. This method quantifies the decrease in dissolved oxygen (DO) concentration between the initial and final readings, reflecting the extent of organic matter biodegradation within the test period.

3.1.3 Total Solids

Total Solids (TS) encompasses all dissolved and suspended organic and inorganic substances in a sample. In landfill leachate analysis, TS serves as a critical parameter for assessing the overall pollutant load and monitoring the treatment performance.

Quantification of TS followed the gravimetric method described in the Standard Method 2540 B, involving the following:

1. Dispensing a known volume of leachate into a pre-dried, pre-weighed Petri dish;
2. The sample was dried at 105 °C to evaporate the moisture.
3. Cooling in a desiccator and reweighing the dish;
4. The TS concentration was calculated based on the weight difference, normalised to the sample volume (eq.11).

$$TS\ (gL^{-1}) = \frac{m_{final} - m_{initial}}{V} \tag{11}$$

where:

- m_{final}, mass of the Petri dish with dried residue (g);
- $m_{initial}$, mass of the Petri dish (g);
- V, sample volume (L).

The total solids in the leachate were categorised based on their physical state and chemical composition. Total Suspended Solids (TSS) comprise particulate matter retained on a filter, whereas Total Dissolved Solids (TDS) represent the fraction that passes through the filter. This classification enables the distinction between particulate and soluble phases. Furthermore, solids are also characterised by their volatility: Volatile Solids (VS) indicate the organic fraction quantified by ignition at 550 °C, whereas Fixed Solids (FS) denote the inorganic residue remaining post-ignition.

3.1.4 Total ammonia

Total ammonia quantification encompasses both ammonia (NH_3) and ammonium (NH_4^+) species in aqueous solutions. In this study, the direct Nesslerization method was employed. This technique relies on the reaction between Nessler reagent and ammonia under alkaline conditions, producing a yellow-coloured complex. The intensity of the resulting colour, indicative of the ammonia concentration, was measured spectrophotometrically at 400 – 425 nm.

Owing to the potential interference from the intrinsic colour and turbidity of the leachate, sample dilution was applied to ensure analytical accuracy. Quantification was achieved through a calibration curve (Figure 10) constructed from standard solutions ranging from 0 to 1.0 mg L^{-1} $N – NH_4^+$.

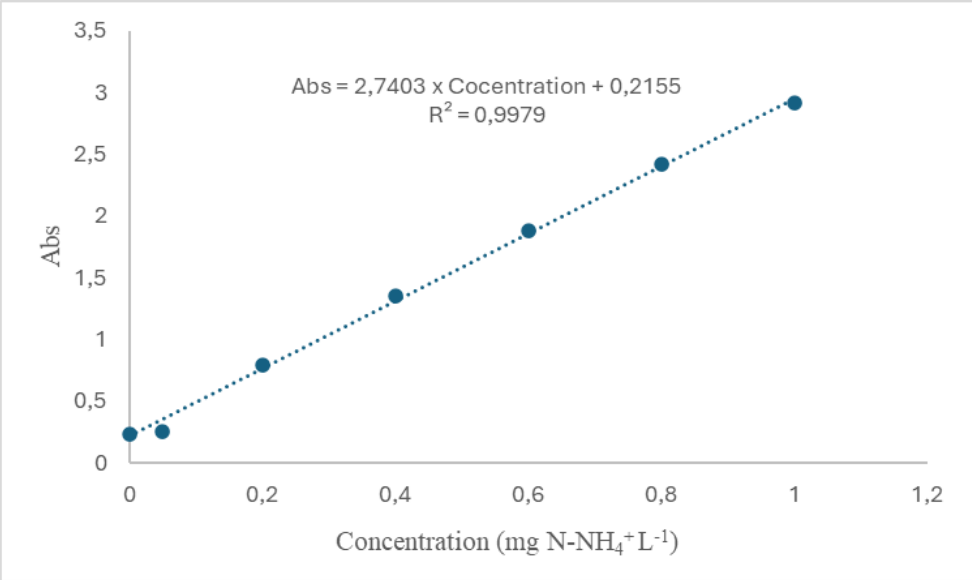

Figure 10. Calibration curve for total ammonia determination using standard solutions.

The ammonia concentration is expressed in mg N-NH_4^+ L^{-1} and was calculated using the standard curve based on Equation (11):

$$\text{mg N} - NH_4{}^{+}\text{L}^{-1} = \frac{(\text{abs}-0.2155)}{2.7403} \tag{12}$$

3.2 Coagulation/Flocculation

In each test, 300 mL of raw leachate was transferred to a beaker, and RIFLOC 1815 was added at a predetermined dosage. The pH was adjusted to the optimal value of 5 using NaOH or 95% H_2SO_4. Rapid mixing was conducted at 150 rpm for 3 min, followed by slow mixing at 20 rpm for 15 min to facilitate floc formation under low-shear conditions. Flocculation was achieved without the addition of a secondary flocculant.

The assays were conducted at bench scale using a standard jar-test apparatus (Figure 11). After mixing, the suspension was allowed to settle for 24 h to promote gravitational sedimentation. Phase separation was then carried out (Figure 12), and a supernatant aliquot was collected for the analysis of organic matter and total solid removal.

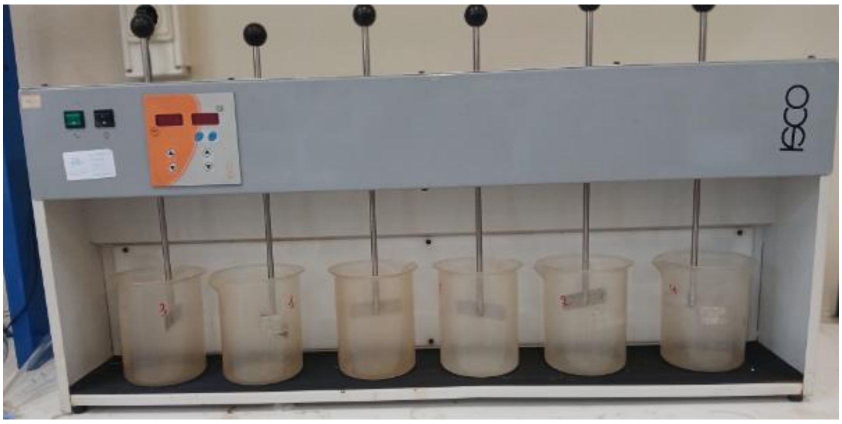

Figure 11. Jar-test apparatus used for assessing coagulant efficiency and floc settling under controlled mixing conditions.

Figure 12. Leachate samples following the coagulation–flocculation treatment, illustrating distinct phase separation between the clarified supernatant and the sedimented floc layer.

3.3 Fenton trials

The Fenton process comprises four fundamental stages: oxidation, neutralisation, flocculation, and sedimentation (Figure 13). The efficiency of this advanced oxidation process is strongly influenced by several operational parameters, including the pH, reagent concentrations (H_2O_2 and Fe^{2+}), reaction time, and reagent dosage. To systematically investigate the effects of these variables and optimise treatment performance, Response Surface Methodology (RSM) was employed. Additionally, Analysis of Variance (ANOVA) was conducted to assess the statistical significance of the model and individual factors, providing a robust framework for interpreting experimental results and identifying optimal process conditions.

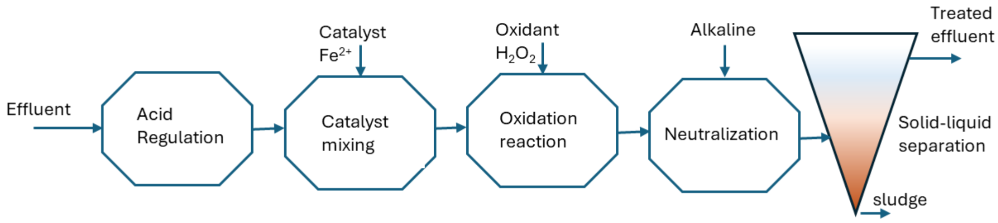

Figure 13. Flow diagram of the Fenton treatment process of landfill leachate.

Following coagulation–flocculation pre-treatment, the clarified supernatant was subjected to Fenton oxidation. The process was performed under continuous magnetic stirring to maintain homogeneous reaction conditions. Ferrous ions (Fe^{2+}) were introduced as the catalytic species, followed by the gradual addition of hydrogen peroxide (H_2O_2) using a burette. This controlled addition was essential to sustain reagent availability throughout the 30-minute reaction period while minimising excessive foaming. Upon completion of the reaction, the process was quenched by increasing the pH to 11 using sodium hydroxide (NaOH) 6 N, thereby inducing the precipitation of iron hydroxides and associated solids. The treated effluent was subsequently transferred to a volumetric cylinder for sludge volume assessment and left undisturbed for 24 h to ensure adequate sedimentation. The stages of this treatment are shown in Figure 14.

Figure 14. Fenton oxidation process applied after coagulation–flocculation: (A) gradual H_2O_2 addition under continuous stirring; (B) foam generation and reaction progression; (C) sedimentation following pH adjustment to 11 and a 24-hour settling period.

Response Surface Methodology (RSM) was implemented to optimise the Fenton oxidation process and identify the optimal conditions for achieving maximum treatment efficiency. This approach enabled the minimisation of experimental runs and reduced the consumption of chemical reagents, while maintaining analytical robustness. Among the available RSM techniques, the Box–Behnken design and Central Composite Design (CCD) were selected because of their proven efficacy in evaluating nonlinear interactions and establishing optimal operating conditions.

These methods facilitated the assessment of the interactive effects among the three critical independent variables – hydrogen peroxide dosage (H_2O_2), ferrous ion dosage (Fe^{2+}), and pH – on the response variable, namely COD removal efficiency. The system behaviour was modelled using a second-order polynomial equation (Equation 13), which accurately describes the response surface and enables the identification of the most favourable treatment conditions (Wu et al., 2010).

$$Y = \beta_0 + \sum \beta_i X_i + \sum \beta_{ii} X_i^2 + \sum_i \sum_j \beta_{ij} X_i X_j \quad (13)$$

where Y represents the predicted response influenced by the variables X, $\beta_0$is a constant; β_i denotes the linear coefficient for factor i; β_{ii} the quadratic coefficient; and β_{ij} the interaction coefficient between factors i and j.

Subsequently, the variables were encoded as X_1 (H_2O_2), X_2 (Fe^{2+}), and X_3 (pH), with Y indicating the percentage of COD removal.

3.3.1 pH

The Fenton reaction, which employs ferrous ions (Fe^{2+}) and hydrogen peroxide (H_2O_2) to generate highly reactive oxidising species, is strongly pH dependent. This parameter significantly affects iron speciation, hydroxyl radical generation, and overall oxidation efficiency.

The optimal pH range for the Fenton process generally lies between 2.5 and 3.0. Under these acidic conditions, both Fe^{2+} and Fe^{3+} coexist in solution, promoting the formation of reactive intermediates such as $[Fe(OH)]^{2+}$ and $[Fe(OOH)]^{2+}$, which enhance the production of hydroxyl radicals (•OH), the primary oxidising agents responsible for organic matter degradation (Salgado et al., 2013; Walling et al., 2021).

In practical applications, such as leachate treatment, the optimal pH range may vary slightly depending on the matrix composition, typically ranging from 2.5 to 4.5 for raw leachates and up to pH 6.0 for biologically pretreated leachates (Salgado et al., 2013).

Several inhibitory effects were observed at low pH values (below 2.5). A high concentration of H^+ ions can scavenge hydroxyl radicals, reducing their availability for oxidation reactions. Under these conditions, Fe^{2+} ions form stable $[Fe(H_2O)_6]^{2+}$ complexes that are less reactive and hinder the formation of reactive species. Additionally, the regeneration of Fe^{2+} from Fe^{3+} becomes inefficient, thereby interrupting the catalytic cycle required for continuous radical production. At pH levels below 2.2, the system may shift from hydroxyl radical-driven oxidation to other pathways, such as reactions involving oxoiron (IV) species, which exhibit reduced oxidative potential (Lu et al., 2018; Walling et al., 2021).

Conversely, at high pH values (above 4.0), iron begins to precipitate predominantly as $Fe(OH)_3$ and other hydroxide forms, which reduces its solubility and drastically reduces its catalytic activity. The solubility of Fe^{3+} decreases by up to two orders of magnitude compared with that of Fe^{2+} under near-neutral pH conditions, rendering it ineffective as a catalyst. Simultaneously, H_2O_2 undergoes non-radical decomposition, producing O_2 and H_2O, and the redox potential of •OH decreases, limiting its oxidative capability. Above this pH, iron exists primarily in insoluble oxides or colloidal forms, thereby reducing the efficiency of the Fenton process (Lu et al., 2018; Salgado et al., 2013).

3.3.2 Temperature and Reaction Time

The present study adopted a reaction time of 30 min for the Fenton oxidation process, which was conducted at ambient temperature. This choice is supported by findings in the literature, indicating that a 30-minute duration is generally sufficient for achieving substantial pollutant removal.

For example, Mohamed (2022) reported that a 30-minute Fenton reaction resulted in 77.4% COD reduction and 95.4% removal of oil and grease (O&G) in wastewater treatment. Extending the reaction to 50 min led to only marginal gains, suggesting that additional reaction time does not proportionally enhance the treatment efficiency.

Similarly, Krupińska (2024) demonstrated that in groundwater treatment applications, increasing the oxidation time from 15 to 30 min significantly improved the removal of Total Organic Carbon (TOC) and Dissolved Organic Carbon (DOC), and further extending the duration to 60 min yielded only incremental benefits, reinforcing the conclusion that 30 min represents an optimal compromise between effectiveness and operational feasibility.

Given these findings, the 30-minute reaction time was considered adequate for this investigation, offering a balance between treatment performance and energy efficiency. Operating at room temperature also increases process simplicity and practical scalability, as no external heating is required.

3.3.3 H_2O_2:COD Ratio

Kinetic studies by Lucas & Peres (2009) on the treatment of olive mill wastewater using Fenton's reagent indicated that the theoretical dose of hydrogen peroxide required for the complete oxidation of organic matter can be estimated from the stoichiometric weight ratio between H_2O_2 and the Chemical Oxygen Demand (COD). This approach assumes the complete mineralisation of organic compounds, as expressed in Equation 14.

$$1\ \mathrm{g\ COD} = 1\ \mathrm{g\ O_2} = 0.03125\ \mathrm{mol\ O_2} = 0.0625\ \mathrm{mol\ H_2O_2} = 2.125\ \mathrm{g\ H_2O_2} \qquad (14)$$

Similarly, Deng & Englehardt (2006) in their study on landfill leachate treatment via the Fenton process, they reported a theoretical mass ratio of removable COD to H_2O_2 of 470.6:1000. This implies that 1000 mg/L of H_2O_2 can theoretically oxidise 470.6 mg/L of COD.

3.3.4 H_2O_2:Fe^{2+} Ratio

Ferrous ions (Fe^{2+}) play a crucial role in the generation of hydroxyl radicals (•OH) through the Fenton reaction (Equation 3), which are the primary oxidising species responsible for the degradation of organic contaminants. However, when present in excess, Fe^{2+} can lead to unwanted reactions, particularly recombination with hydroxyl radicals to form Fe^{3+}, as illustrated in Equation 4 (Deng & Englehardt, 2006). This scavenging effect diminishes the availability of •OH for the target oxidation reactions, thereby impairing the overall efficacy of the process. Thus, maintaining a carefully optimised Fe^{2+} concentration is essential for maximising radical yield while limiting radical depletion.

The optimal molar ratio of H_2O_2 to Fe^{2+} is highly dependent on the specific physicochemical characteristics of the leachate. According to Zhang et al. (2006) a molar ratio of 3:1 (H_2O_2:Fe^{2+}) is optimal in a continuous stirred-tank reactor configuration. Conversely, Traid et al. (2022), in their study involving the Fenton process post-biological nitrification of leachate, they found a markedly higher optimal ratio of 50:1, demonstrating how process context significantly influences reagent stoichiometry

3.3.5 Response Surface Methodology

Response Surface Methodology (RSM) was employed to systematically evaluate the influence of different molar ratios of H_2O_2 to Fe^{2+} on treatment performance. The central experimental point was established at a molar ratio of 5:1, and structured variation across the defined levels (Table 5) was applied. This statistical approach enables the identification of optimal process conditions through the generation of predictive models that account for factor interactions, thereby enhancing the treatment efficiency and experimental reproducibility.

The experimental modelling, statistical analyses, and graphical outputs for multivariate interpretation were performed using **Minitab® version 21.4.1 (64-bit)**. Within the framework of the Response Surface Methodology (RSM), an experimental design was developed to explore the relationships between three critical process variables: hydrogen peroxide concentration, ferrous ion concentration, and pH.

Table 5. Levels of factor variation for experimental design.

Level	H_2O_2 (30% w/w)		$FeSO_4.7H_2O$		pH
	Factor	Amount (mL)	ratio	Amount (g)	
+1	1.5	1.5		0.448	4
0	1.0	0.9	5:1	0.269	3
-1	0.5	0.3		0.0896	2

Note: The concentrations of H_2O_2 and Fe^{2+} were established based on the COD concentration measured after the coagulation-flocculation pretreatment (COD = 4.105 g L^{-1}), and a ratio of 5:1 indicates that 1 g of Fe^{2+} is required for 5 g of H_2O_2. All reagent calculations were based on a working sample volume of 50 mL, with corrections made according to the hydrogen peroxide purity (30% w/w). Additionally, the molar mass of $FeSO_4 \cdot 7H_2O$ was accounted for when calculating the required ferrous ion dosage to ensure stoichiometric accuracy in reagent preparation.

Fifteen experimental runs were conducted, incorporating coded levels corresponding to the minimum (−1), central (0), and maximum (+1) values of the variables. The experimental matrix followed the Box–Behnken design, and three central replicates were included to evaluate model reliability and estimate experimental error. All experiments were performed in duplicate to ensure statistical robustness and reproducibility (Table 6).

Table 6. Experimental matrix based on the Box–Behnken Design for optimising COD removal by the Fenton process.

Run	**Level**	**Factor**		
	----	**H_2O_2 (mL)**	**Fe^{2+} (g)**	**pH**
1	--0	0.3	0.090	3
2	+-0	1.5	0.090	3
3	-+0	0.3	0.448	3
4	++0	1.5	0.448	3
5	-0-	0.3	0.269	2
6	+0-	1.5	0.269	2
7	-0+	0.3	0.269	4
8	+0+	1.5	0.269	4
9	0--	0.9	0.090	2
10	0+-	0.9	0.448	2
11	0-+	0.9	0.090	4
12	0++	0.9	0.448	4
13	000	0.9	0.269	3
14	000	0.9	0.269	3
15	000	0.9	0.269	3
16	--0	0.3	0.090	3
17	+-0	1.5	0.090	3
18	-+0	0.3	0.448	3
19	++0	1.5	0.448	3
20	-0-	0.3	0.269	2
21	+0-	1.5	0.269	2
22	-0+	0.3	0.269	4
23	+0+	1.5	0.269	4
24	0--	0.9	0.090	2
25	0+-	0.9	0.448	2
26	0-+	0.9	0.090	4
27	0++	0.9	0.448	4
28	000	0.9	0.269	3
29	000	0.9	0.269	3
30	000	0.9	0.269	3

This approach allowed for a systematic evaluation of the effects of different variables, ensuring the selection of optimal conditions for maximum pollutant removal. Statistical analysis provided insights into the interactions between factors such as hydrogen peroxide dosage, ferrous ion concentration, and pH, which are crucial for the effectiveness of the Fenton reaction.

3.4 Case Study

The Urjais Landfill, operated by Resíduos do Nordeste, is a managed solid waste disposal facility that generates both biogas and leachate, the latter of which constitutes the primary effluent investigated in this study. Upon generation, the leachate was conveyed to a homogenization pond to ensure compositional uniformity and facilitate subsequent treatment operations.

Following homogenization, the leachate was treated using a reverse osmosis (RO) system. This process yields a permeate, which may be discharged into the receiving water body, if it complies with regulatory discharge standards. Alternatively, the permeate can be directed to a municipal wastewater treatment facility (ETAR) for additional treatment or recirculated into the landfill to support internal moisture regulation and enhance biological stabilisation. The RO process also produces a concentrated retentate, which is subsequently transferred to a retention pond for further management

Table 7 presents the characteristics of the leachate sampled at different times throughout the year, reflecting seasonal variations and providing essential data to support the design and optimisation of the treatment strategy.

Physicochemical characterisation of leachate samples collected during distinct seasonal periods revealed notable variability influenced by hydrometeorological conditions. While pH values remained relatively stable across both sampling intervals, indicating minimal influence of seasonal shifts on acid–base equilibrium, substantial variations were observed in other key parameters.

The electrical conductivity (EC) was markedly higher during the dry (sunny) season (41 mS cm^{-1}) than during the wet (rainy) season (29 mS cm^{-1}). This difference is primarily due to the reduced dilution caused by lower precipitation and increased evapotranspiration, which concentrates the soluble ionic species in the leachate.

Table 7. Physicochemical properties of leachate samples collected during the two distinct sampling periods.

Parameter	Unit	Sampling 1	Sampling 2
Calendar	Day/Months/Year	14/02/2024 (rainy day)	25/06/2024 (sunny day)
pH	Sorensen Scale	8.3	8.3
Conductivity	mS cm^{-1}	29	41
COD	mg L^{-1} O_2	14987	19560
BOD_5	mg L^{-1} O_2	1025	1036
BOD_5/COD	-	0.07	0.05
Total solids	g L^{-1}	28	39
Total ammonia	mg L^{-1} NH_4	-	196

Likewise, the organic pollutant load, measured through Chemical Oxygen Demand (COD) and Biochemical Oxygen Demand (BOD_5), was higher under dry conditions – recorded at 19560 mg L^{-1} and 1036 mg L^{-1}, respectively – compared to 14987 mg L^{-1} COD and 1025 mg L^{-1} BOD_5 during the rainy season. This suggests that lower inflows during dry periods contribute to the accumulation and concentration of organic constituents.

The total solid content followed a similar trend, increasing from 28 g L^{-1} in the rainy season to 39 g L^{-1} in the sunny season, further confirming the concentration effect due to reduced leachate dilution.

According to the classification criteria outlined in Table 1, the leachate exhibits hybrid characteristics, aligning partially with both "new" and "stabilised" leachate typologies. Elevated COD levels and low ammoniacal nitrogen suggest a new leachate profile, while the alkaline pH (~8.3) and low BOD/COD ratio are indicative of stabilised leachate, which is typically rich in refractory organics, such as humic and fulvic substances.

These findings underscore the need for seasonally adaptive treatment strategies. In the wet season, dilution may facilitate treatment by lowering pollutant concentrations, whereas during dry periods, intensified or multi-stage treatment becomes essential to address elevated organic and solid loads. Therefore, a comprehensive knowledge of seasonal dynamics is critical for designing robust and responsive leachate management systems.

4. RESULTS AND DISCUSSION

4.1 Coagulation-Flocculation Treatment

In pursuit of improving the physicochemical treatability of stabilised landfill leachate, a coagulation–flocculation (C-F) pre-treatment was conducted as a preparatory stage prior to advanced oxidation. This approach aimed to enhance the removal of suspended solids and high-molecular-weight organic compounds, thereby reducing the chemical oxygen demand (COD) and improving the leachability of the leachate.

The experimental assessment focused on the comparative performance of two distinct coagulants applied under the natural pH of the leachate (~8.3): RIFLOC 1815, a polyamine-based organic coagulant, and ferric chloride ($FeCl_3$), a conventional inorganic salt that is widely employed in industrial and municipal wastewater treatment. RIFLOC 1815 is formulated as an aqueous solution containing 25–50% of a polymer derived from 1,2-ethylenediamine, (chloromethyl) oxirane, and N-methylhexanamine, as well as approximately 18% polyaluminum chloride (Cristóvão et al., 2012). Its hybrid composition is designed to promote charge neutralisation, bridging mechanisms, and effective destabilisation of colloidal particles.

Conversely, $FeCl_3$ acts primarily through hydrolysis and the formation of insoluble ferric hydroxides, facilitating the agglomeration and sedimentation of the dispersed matter. Despite its widespread application, its efficiency is highly sensitive to pH, often requiring acidic conditions for optimal floc formation.

The efficacy of each coagulant was determined based on the percentage reduction in COD, which serves as a critical indicator of the treatment performance. The results summarised in Table 8 provide a quantitative basis for selecting the most appropriate coagulant for subsequent integration with the Fenton oxidation process.

Table 8. Removal efficiencies obtained with different dosages of RIFLOC 1815 and Ferric Chloride ($FeCl_3$) at natural leachate pH.

Coagulant	Dosage	Unit	Removal efficiency (%)
RIFLOC 1815	1	mL	44.8
$FeCl_3$	2	g L^{-1}	2.2
	4	g L^{-1}	13.4

The organic coagulant RIFLOC 1815 demonstrated superior coagulation performance, achieving a COD removal efficiency of 44.8% at a dosage of 1 mL, in contrast to ferric chloride ($FeCl_3$), which yielded only 13.4% removal efficiency at a substantially higher dosage (4 g L^{-1}). These results highlight the enhanced efficacy of RIFLOC 1815 for the coagulation–flocculation pre-treatment of stabilised landfill leachate.

The greater performance of RIFLOC 1815 is likely attributable to its polyamine-based molecular structure, which enhances electrostatic charge neutralisation, promoting the effective aggregation of colloidal and dissolved organic matter. Conversely, the limited performance of $FeCl_3$ under the same conditions may be linked to the physicochemical characteristics of the leachate and/or suboptimal pH at which the initial tests were conducted.

To further elucidate the behaviour of $FeCl_3$, additional coagulation trials were performed under controlled acidic conditions (pH 5), a range known to improve its performance due to increased solubility and formation of ferric hydroxide complexes. The results of these trials, presented in Table 9, provide a comparative assessment of removal efficiency at various dosages, facilitating a more comprehensive evaluation of $FeCl_3$'s applicability under optimised conditions.

Table 9. Evaluation of removal efficiency at pH 5 with various coagulant dosages.

Coagulant	Dosages	Units	Removal efficiencies (%)
RIFLOC 1815	1	mL	73
$FeCl_3$	2	g L^{-1}	61
	4	g L^{-1}	78

Although ferric chloride ($FeCl_3$) exhibited higher COD removal efficiency at a concentration of 4 g L^{-1}, RIFLOC 1815 was selected as the coagulant for subsequent experimentation because of its biopolymeric nature, biodegradability, and reduced environmental burden compared to conventional inorganic coagulants. Additionally, RIFLOC 1815 achieved a comparable removal efficiency (73%) at a markedly lower dosage, underscoring its technical viability and ecological advantage as a sustainable alternative for the coagulation–flocculation pretreatment of landfill leachate.

Following its selection, a series of targeted experiments was conducted to determine the optimal operational conditions for the RIFLOC 1815 application. The first parameter investigated was pH, which is a critical factor influencing coagulation kinetics, charge neutralisation, and floc formation. To isolate its effect, experiments were performed using a fixed coagulant volume of 1 mL while the pH was systematically varied. The aim was to identify the pH range yielding the maximal COD removal efficiency, thereby establishing the foundational conditions for subsequent dosage optimisation and integration with advanced oxidation processes, as illustrated in Figure 15.

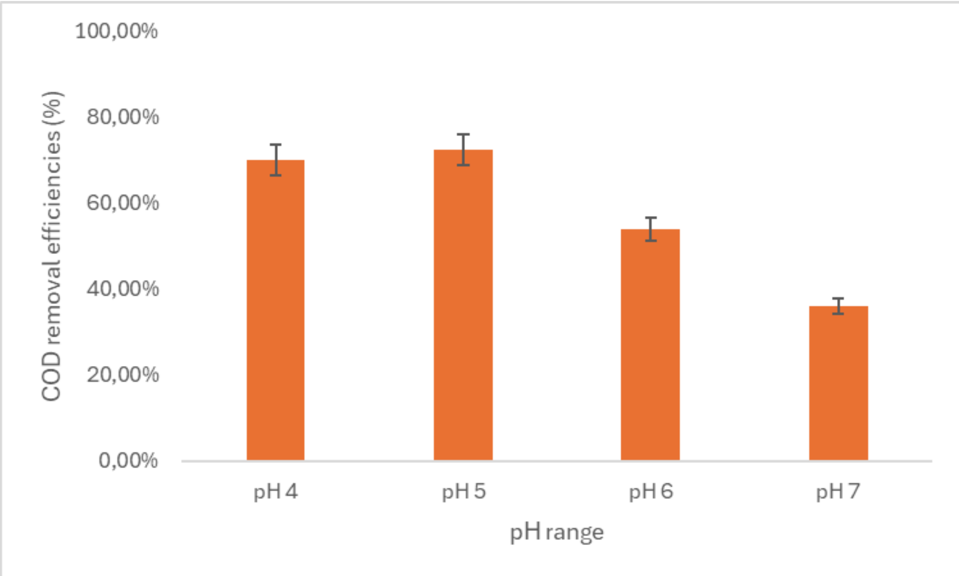

Figure 15. Effect of pH on COD removal efficiency with a constant RIFLOC 1815 dosage (1 mL).

The results presented in Figure 15 reveal that the highest COD removal efficiency (~73%) was attained at pH 5, suggesting that RIFLOC 1815 exhibited optimal performance under slightly acidic conditions. This outcome is consistent with the mechanism of charge neutralisation, wherein moderate acidity promotes the efficient destabilisation of colloidal particles and subsequent floc formation. At pH levels below 5, a progressive decline in removal efficiency was observed, likely due to over-acidification, which disrupts coagulation dynamics, potentially increasing the solubility of certain organic fractions and weakening inter-particle interactions.

The next phase of the investigation focuses on optimising the coagulant dosage while maintaining the previously identified optimal pH of 5 to further enhance the treatment performance. As illustrated in Figure 16, various RIFLOC 1815 concentrations were evaluated to determine the minimum dosage required to achieve maximum COD removal efficiency. This step is critical not only for maximising treatment efficacy but also for ensuring cost-effectiveness and minimising chemical consumption, thereby improving the overall sustainability and operational viability of the coagulation–flocculation process in landfill leachate management.

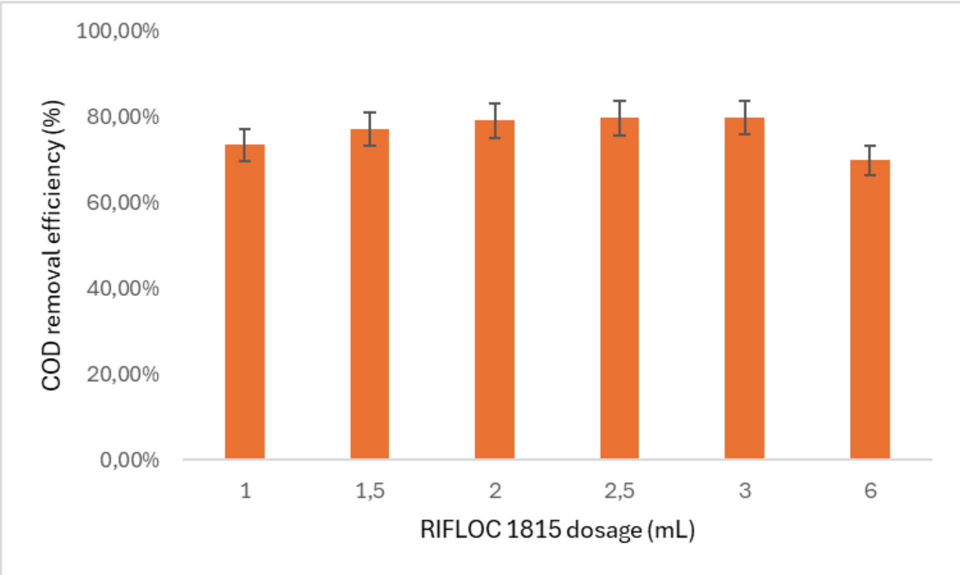

Figure 16. COD removal efficiency as a function of RIFLOC 1815 coagulant dosage.

The results in Figure 16 demonstrate that the application of 3 mL of RIFLOC 1815 resulted in the highest COD removal efficiency among the tested dosages. Therefore, this volume was selected as the optimal coagulant dosage for subsequent coagulation–flocculation pretreatment. Further increases in dosage beyond this value did not yield significant improvements in the removal efficiency and may lead to diminished performance. This decline can be attributed to charge neutralisation saturation, followed by charge reversal phenomena, where excessive coagulant concentrations destabilise floc structures or promote the redispersion of colloidal particles due to electrostatic repulsion or steric hindrance.

4.2 Fenton Approach

Subsequent to physicochemical pre-treatment, which significantly reduced the organic load and turbidity, the treated leachate underwent Fenton oxidation, targeting the removal of residual refractory organic compounds through advanced oxidative mechanisms.

Table 10 details the experimental matrix employed in the Fenton treatment phase, listing the independent process variables (H_2O_2 concentration, Fe^{2+} dosage, and pH), along with the response variable (Y), defined as the experimentally determined COD removal efficiency (%). For each experimental run, the table also includes the corresponding predicted values of COD removal as calculated from the fitted second-order polynomial model (Equation 15).

These data support the response surface methodology applied in this study and serve as the foundation for process optimisation, enabling a comprehensive evaluation of the individual and interactive effects of the operational variables on the Fenton process performance.

Table 10. Experimental input parameters and model-estimated responses for Chemical Oxygen Demand (COD) removal using Fenton oxidation.

	Factors			**Y – COD removal efficiency (%)**	**Predicted COD removal (%)**
Run	**H_2O_2 (mL)**	**Fe^{2+} (g)**	**pH**		
1	0.3	0.090	3	22.8	24.1
2	1.5	0.090	3	35.1	34.4
3	0.3	0.448	3	41.5	41.3
4	1.5	0.448	3	56.3	58.5
5	0.3	0.269	2	27.5	27.2
6	1.5	0.269	2	34.0	38.4
7	0.3	0.269	4	34.6	34.2
8	1.5	0.269	4	48.8	50.6
9	0.9	0.090	2	18.2	17.0
10	0.9	0.448	2	43.7	38.9
11	0.9	0.090	4	26.0	27.8
12	0.9	0.448	4	47.3	47.3
13	0.9	0.269	3	44.5	44.5
14	0.9	0.269	3	42.0	44.5
15	0.9	0.269	3	46.4	44.5
16	0.3	0.090	3	26.8	24.0
17	1.5	0.090	3	34.7	34.4
18	0.3	0.448	3	40.3	41.3
19	1.5	0.448	3	59.3	58.5

Table 10. Experimental input parameters and model-estimated responses for Chemical Oxygen Demand (COD) removal using Fenton oxidation (cont.).

Run	Factors			Y – COD removal efficiency (%)	Predicted COD removal (%)
	H_2O_2 (mL)	Fe^{2+} (g)	pH		
20	0.3	0.269	2	25.1	27.2
21	1.5	0.269	2	41.5	38.4
22	0.3	0.269	4	34.9	34.2
23	1.5	0.269	4	54.2	50.6
24	0.9	0.090	2	16.0	17.0
25	0.9	0.448	2	36.7	38.9
26	0.9	0.090	4	27.0	27.8
27	0.9	0.448	4	47.0	47.3
28	0.9	0.269	3	47.8	44.5
29	0.9	0.269	3	43.1	44.5
30	0.9	0.269	3	43.0	44.5

Thirty experimental runs were performed, wherein the concentrations of hydrogen peroxide (H_2O_2), ferrous ions (Fe^{2+}), and pH were systematically varied as independent variables according to the levels established by the factorial design of experiments. An experimental matrix was constructed to enable a robust evaluation of both the individual and interaction effects among these process parameters.

The regression model, expressed in Equation (15), is formulated as a second-order polynomial equation that includes linear, quadratic, and interaction terms associated with the independent variables. This structure enables a detailed characterisation of the system's behaviour, capturing both the primary effects and the curvature of the response surface. As such, the model functions as a predictive tool for estimating COD removal efficiency under varying operating conditions, thereby supporting the optimisation and control of the Fenton oxidation process applied to stabilised landfill leachate.

$$\begin{aligned} Y(\%) = {} & -0.617 + 0.0063H_2O_2 + 1.354\mathrm{Fe}^{2+} + 0.4498\mathrm{pH} + 0.000(H_2O_2)^2 - 1.521(\mathrm{Fe}^{2+})^2 \\ & - 0.06873pH^2 + 0.1597H_2O_2 \times \mathrm{Fe}^{2+} + 0.0219H_2O_2 \times \mathrm{pH} \\ & - 0.0339\mathrm{Fe}^{2+} \times \mathrm{pH} \end{aligned} \tag{15}$$

To rigorously assess the accuracy, reliability, and predictive robustness of the developed regression model, a set of critical statistical indicators was analysed. Table 11 presents the model summary, which includes the coefficient of determination (R^2), adjusted R^2, predicted R^2, and the standard error of the regression (S). These parameters collectively provide insights into the model's explanatory power, its capacity to generalise to new data, and the consistency of residual variability.

In addition, the Prediction Error Sum of Squares (PRESS) value was reported, offering a quantitative measure of the prediction error under cross-validation conditions. A low PRESS value indicates that the model has high predictive capability and is not overfitted to the experimental dataset.

Furthermore, Variance Inflation Factor (VIF) values for all independent variables were included to assess the presence of multicollinearity. VIF values close to 1 confirm that the predictor variables are statistically independent, thereby enhancing the interpretability and numerical stability of the model coefficients.

Collectively, these metrics validate the statistical adequacy of the regression model for describing and predicting COD removal efficiency in the context of Fenton-based leachate treatment.

Table 11. Statistical evaluation of regression model fit and predictor variable independence for cod removal efficiency.

Y – COD removal (%)	
S (standard error for the regression)	0.0250643
R^2 (%)	96.4%
Adjusted R^2 (%)	94.8%
PRESS (Prediction Error Sum of Squares)	0.0293755
Predicted R^2 (%)	91.6%
Individual Variables	
Term	**VIF**
Constant	-
H_2O_2	1.00
Fe2+	1.00
pH	1.00
$(H_2O_2)^2$	1.01
$(Fe^{2+})^2$	1.01
$(pH)^2$	1.01
$H_2O_2 \times Fe^{2+}$	1.00
$H_2O_2 \times pH$	1.00
$Fe^{2+} \times pH$	1.00

The results of the regression analysis indicate a highly robust model with a coefficient of determination (R^2) of 96.4%, demonstrating that the model explains a substantial portion of the total variability in COD removal efficiency. The adjusted R^2 value of 94.8% further confirms the adequacy of the model by accounting for the number of predictors and sample size, thus avoiding overfitting. In addition, the predicted R^2 of 91.6% suggests strong external validity and generalizability of the model to new data points that were not included in the calibration set.

The Prediction Error Sum of Squares (PRESS) statistic was notably low, indicating minimal predictive error and reinforcing the capacity of the model to produce reliable outcomes under varied experimental conditions.

The analysis also confirmed the absence of multicollinearity, as evidenced by the Variance Inflation Factor (VIF) values close to 1, ensuring that the predictor variables operate independently within the regression framework. This independence among variables is critical for preserving the integrity of the coefficient estimates and the interpretability of individual effects.

Taken together, these metrics confirm the high predictive power, statistical reliability, and structural soundness of the regression model in describing the COD removal behaviour in response to variations in the Fe^{2+} concentration, H_2O_2 dosage, and pH within the defined experimental range.

Table 12 presents the detailed ANOVA results, which evaluate the statistical significance of the model as a whole and for each individual predictor term. This includes essential diagnostic indicators, such as degrees of freedom (DF), sum of squares (SS), mean square (MS), F-statistics, and corresponding p-values, enabling a rigorous assessment of each model component and facilitating the identification of statistically significant effects for model refinement.

Table 12. ANOVA results for the regression model.

Source	DF	Seq SS	Contribution (%)	Adj SS	Adj MS	F-Value	P-Value
Model	9	0.337704	96.41	0.337704	0.037523	59.73	0.000
Linear	3	0.284253	81.15	0.284253	0.094751	150.83	0.000
H202	1	0.076093	21.72	0.076093	0.076093	121.13	0.000
Fe2+	1	0.171210	48.88	0.171210	0.171210	272.53	0.000
pH	1	0.036950	10.55	0.036950	0.036950	58.82	0.000
Square	3	0.049426	14.11	0.049426	0.016475	26.23	0.000
$(H_2O_2)^2$	1	0.000527	0.15	0.000000	0.000000	0.00	0.999

Table 12. ANOVA results for the regression model (cont).

Source	DF	Seq SS	Contribution (%)	Adj SS	Adj MS	F-Value	P-Value
$(Fe^{2+})^2$	1	0.014018	4.00	0.017534	0.017534	27.91	0.000
$(pH)^2$	1	0.034881	9.96	0.034881	0.034881	55.52	0.000
2-Way Interaction	3	0.004025	1.15	0.004025	0.001342	2.14	0.128
$H_2O_2 \times Fe^{2+}$	1	0.002353	0.67	0.002353	0.002353	3.75	0.067
$H_2O_2 \times pH$	1	0.001378	0.39	0.001378	0.001378	2.19	0.154
$Fe^{2+} \times pH$	1	0.000294	0.08	0.000294	0.000294	0.47	0.502
Error	20	0.012564	3.59	0.012564	0.000628	-	-
Lack-of-Fit	3	0.001451	0.41	0.001451	0.000484	0.74	0.543
Pure Error	17	0.011113	3.17	0.011113	0.000654	-	-
Total	29	0.350269	100.00	-	-	-	-

Analysis of variance (ANOVA) demonstrated that the regression model developed for predicting COD removal efficiency was highly statistically significant, as indicated by a global F-value of 59.73 with a p-value < 0.001. This confirms that the collective influence of the predictor variables – Fe^{2+}, H_2O_2, and pH – is substantial in explaining the observed variability in COD removal performance.

Among the first-order (linear) terms, the relative contributions to the total model variation were as follows: Fe^{2+} accounted for 48.88%, followed by H_2O_2 with 21.72%, and pH with 10.55%. All linear terms were highly significant ($p < 0.001$), confirming their dominant role in determining the efficiency of the Fenton reaction under the studied conditions.

Concerning quadratic effects, both $(pH)^2$ and $(Fe^{2+})^2$ were statistically relevant, contributing 9.96% and 4.00% to the total variation, respectively, suggesting nonlinear dependencies in the response surface. In contrast, the $(H_2O_2)^2$ term contributed only 0.15% and was statistically non-significant ($p = 0.999$), indicating that within the tested range, the relationship between COD removal and H_2O_2 dosage remained primarily linear.

The interaction terms were collectively responsible for only 1.15% of the explanatory power of the model, underscoring their minimal influence relative to the main effects. $H_2O_2 \times Fe^{2+}$ exhibited marginal significance ($p = 0.067$), whereas $H_2O_2 \times pH$ ($p = 0.154$) and $Fe^{2+} \times pH$ ($p = 0.502$) were deemed to be statistically non-significant. This reinforces the conclusion that system behaviour is predominantly governed by additive main effects rather than synergistic or antagonistic interactions between variables.

The lack-of-fit test, with a p-value of 0.543, confirmed that the model did not deviate significantly from the experimental data, thereby validating its adequacy. Furthermore, the low pure error contribution of 3.17% attests to the experimental reproducibility and enhances the credibility of the model.

These statistical outcomes are visually supported by the residual diagnostics presented in Figure 17, which collectively affirm the robustness, predictive capacity, and suitability of the model for guiding the optimisation of Fenton process parameters in the context of stabilised landfill leachate treatment.

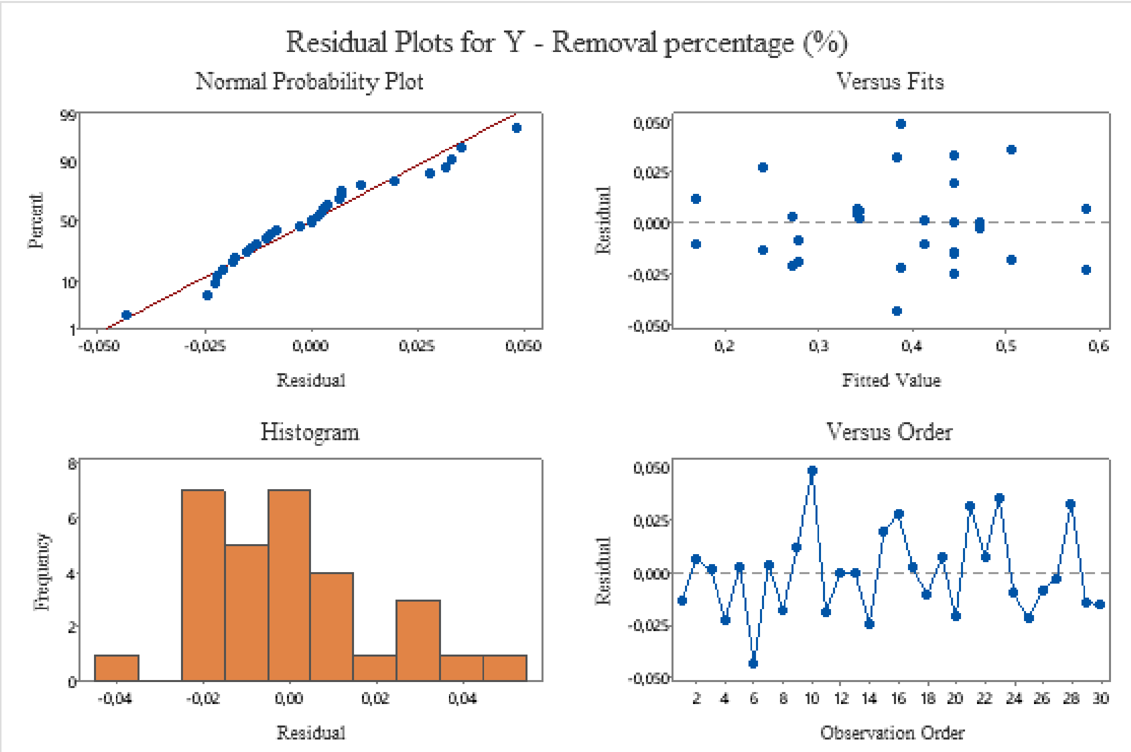

Figure 17. Residual analysis plots for the regression model developed to predict COD removal efficiency in the Fenton process.

The normal probability plot of the residuals revealed that the data points aligned closely with the reference line, indicating that the assumption of normality was satisfied. This conclusion is further supported by the residual histogram, which approximates a bell-shaped distribution without a significant skewness or kurtosis.

The plot of residuals versus fitted values demonstrates a homogeneous spread of residuals without evident patterns or funnel-shaped structures, thus satisfying the condition of homoscedasticity. Furthermore, the residuals versus observation order exhibited no temporal or systematic trends, supporting the independence of errors and confirming the absence of autocorrelation within the data.

Collectively, these diagnostic plots validated the adequacy of the regression model and its underlying assumptions, supporting its application for predictive and optimisation purposes. Minor deviations between experimental and predicted values may stem from intrinsic experimental variability or uncontrolled environmental factors. However, they fell within acceptable statistical boundaries and did not compromise the integrity of the model.

4.2.1 Optimisation Strategy

Based on the results of the regression analysis and diagnostic validation, the model was applied to determine the optimal operational parameters for maximising COD removal efficiency. Optimisation was conducted using response surface methodology (RSM), which integrates second-order polynomial modelling and multivariate analysis to identify the most favourable regions within the experimental design space.

Contour plots (Figures 18, 19, and 20) were constructed to visually represent the interaction effects between key process variables, namely Fe^{2+} and H_2O_2 dosage and pH, on COD removal performance. These plots facilitate the visual identification of synergistic interactions, operational thresholds, and regions of optimal treatment efficiency, thus providing critical insights for process refinement.

The combined analysis of these plots allows for the delineation of an operational window that maximises pollutant degradation while minimising chemical reagent usage, thereby informing both the experimental validation phase and the potential scale-up scenarios.

The contour plot presented in Figure 18 reveals key trends associated with the interactive effects of Fe^{2+} and hydrogen peroxide concentrations on the oxidative removal of chemical oxygen demand (COD) during the Fenton process. When the pH was maintained at its optimal catalytic value (3.0), the plot demonstrated a strong positive correlation between reagent concentration and removal efficiency; COD degradation increased consistently with elevated levels of both Fe^{2+} and H_2O_2.

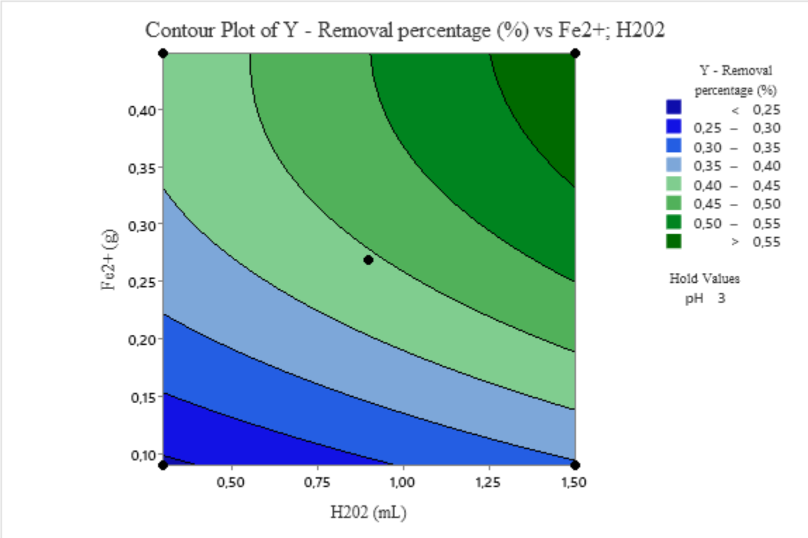

Figure 18. Response surface contour plot illustrating the combined influence of Fe^{2+} and H_2O_2 dosages on COD removal efficiency.

The optimal removal region, defined by COD reductions exceeding 55%, was observed when Fe^{2+} and H_2O_2 dosages exceeded 0.40 g and 1.25 mL, respectively. Within this domain, the system benefits from maximised hydroxyl radical generation resulting from the efficient catalytic decomposition of H_2O_2 in the presence of ferrous ions.

Notably, the steep efficiency gradient observed as Fe^{2+} dosages increase from 0.10 to 0.25 g, particularly when accompanied by elevated H_2O_2, suggests a nonlinear enhancement effect, wherein the catalytic availability of Fe^{2+} acts as a limiting factor in radical propagation at lower concentrations. Once this threshold is surpassed, the system enters a more reactive regime where oxidative degradation is significantly accelerated.

The curvilinear configuration of the contour lines suggested a pronounced synergistic interaction between Fe^{2+} and H_2O_2. This implies that the incremental benefit of increasing one reagent is magnified when the other is also present at elevated levels, underscoring the necessity of jointly optimising both variables. Such synergism enhances the availability and stability of hydroxyl radicals, thereby increasing the overall oxidative potential and pollutant degradation efficiency of the system.

These findings reinforce the importance of precise stoichiometric control in the Fenton reaction and highlight the need for integrated multivariate optimisation approaches to avoid excess reagents while ensuring maximal contaminant removal.

The contour plot presented in Figure 19 delineates the interactive effects between the reaction pH and hydrogen peroxide dosage on the chemical oxygen demand (COD) removal efficiency during the Fenton oxidation process under a fixed Fe^{2+} dosage of 0.269

g. The graphical distribution of the iso-efficiency lines reveals a distinct region of optimal performance (>50% COD removal) located at moderately acidic pH values (3.5–4.0), coupled with an H_2O_2 dosage exceeding 1.25 mL.

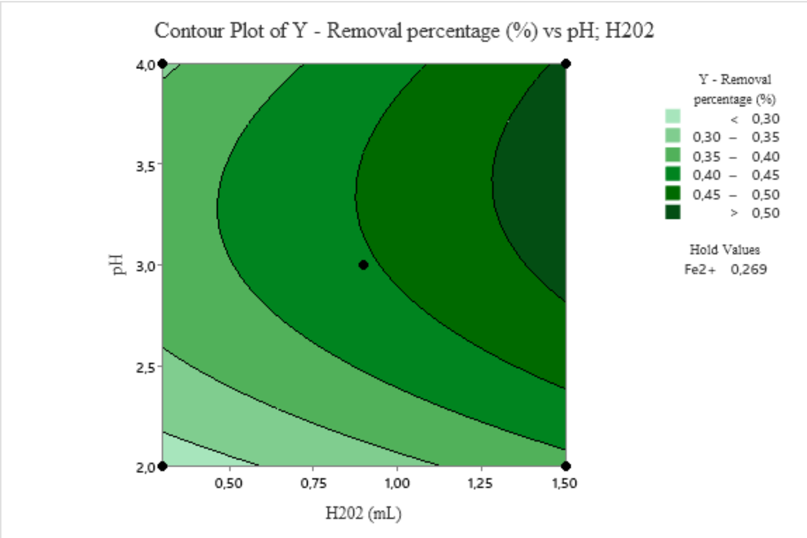

Figure 19. Response surface contour plot illustrating the influence of pH and H_2O_2 dosage on COD removal efficiency.

A pronounced sensitivity to pH was evident, as a progressive increase in removal efficiency was observed when the pH was shifted from 2.0 to the optimal range. This behaviour reflects the enhanced catalytic decomposition of H_2O_2 and increased generation of hydroxyl radicals (• OH) under controlled acidic conditions. However, the spatial configuration of the contour lines also reveals a diminishing marginal benefit at H_2O_2 dosage beyond 1.25 mL, suggesting saturation kinetics or radical scavenging effects, where excess H_2O_2 reacts non-productively with •OH radicals, forming hydroperoxyl radicals (HO_2•), thus decreasing overall oxidative efficiency.

The diagonal orientation of the contour lines further implies a compensatory relationship between the two variables; higher pH values partially offset lower oxidant dosages and broaden the operational envelope for effective treatment. This interaction suggests that within certain bounds, moderate adjustments in one parameter may mitigate suboptimal settings of the other, providing practical flexibility in system design and real-time process control.

These findings reinforce the importance of multivariate optimisation and support the need for precision in adjusting the pH and oxidant load to achieve maximum treatment efficacy while minimising reagent overuse and associated costs or secondary impacts.

The contour plot depicted in Figure 20 offers a quantitative two-dimensional visualisation of the combined effect of the pH and Fe^{2+} concentration on the oxidative performance of the Fenton process under a fixed H_2O_2 dosage of 0.9 mL.

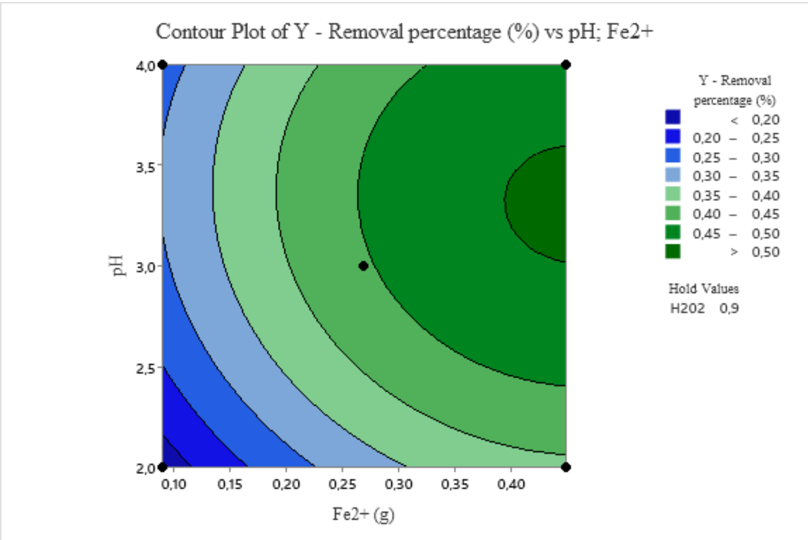

Figure 20. Response surface contour plot illustrating the influence of pH and Fe^{2+}.

The H_2O_2 dosage was kept constant to isolate and examine the interactions between the remaining two independent variables. The analysis revealed that the maximum COD removal efficiency occurred within a narrow acidic pH window (approximately 3.0–3.5). This range coincides with the optimal operational envelope for hydroxyl radical (•OH) generation, given the dual requirements for Fe^{2+} stability and H_2O_2 catalytic decomposition.

The efficiency significantly declines at pH levels outside this range. At lower pH values (<2.5), excess protonation reduces the availability of hydroxyl radicals by enhancing H_2O_2 stability and suppressing Fe^{2+}/Fe^{3+} redox cycling. At a higher pH (>4.0), Fe^{2+} tends to precipitate as ferric hydroxide [$Fe(OH)_3$], thus limiting radical formation and rendering the system catalytically inactive.

Moreover, a distinct threshold effect was observed for the Fe^{2+} dosage, with the performance dropping sharply when Fe^{2+} falls below 0.20 g. This threshold reflects the minimum catalytic load required to sustain a sufficient oxidative potential for contaminant degradation. Conversely, Fe^{2+} dosage above 0.35 g, when coupled with pH values in the optimal range, yields COD removal efficiencies consistently exceeding 50%, suggesting a synergistic interaction between proton availability and ferrous ion activation.

These findings are further substantiated by the three-dimensional response surface plots in Figure 21, which provide a more comprehensive spatial representation of variable interactions. The surfaces confirmed the nonlinear behaviour and complex interdependence between Fe^{2+}, H_2O_2, and pH. Notably, the diminishing marginal returns of increasing H_2O_2 dosage beyond a certain point are observed, likely due to •OH radical scavenging by excess peroxide ($H_2O_2 + \bullet OH \rightarrow HO_2\bullet + H_2O$), which reduces the oxidative efficiency.

Collectively, the graphical analyses underscore the critical importance of maintaining precise control over reaction conditions to optimise treatment efficacy. The narrow operational window and nonlinear interaction effects reinforce the necessity of response surface methodology (RSM) and desirability-based optimisation strategies to achieve high-performance, cost-effective Fenton-based treatment systems for mature landfill leachates.

The 3D surface plots presented in Figure 21 illustrate the relationships discussed earlier in the contour plots but provide an enhanced visual representation of the interaction effects between variables. These surfaces clearly show how COD removal efficiency varies with changes in Fe^{2+}, H_2O_2, and pH levels. Each plot reinforces the trends previously identified, such as the strong influence of Fe^{2+} concentration, optimal pH range, and diminishing returns of H_2O_2 at higher levels, while offering a more intuitive understanding of the process behaviour in three-dimensional space.

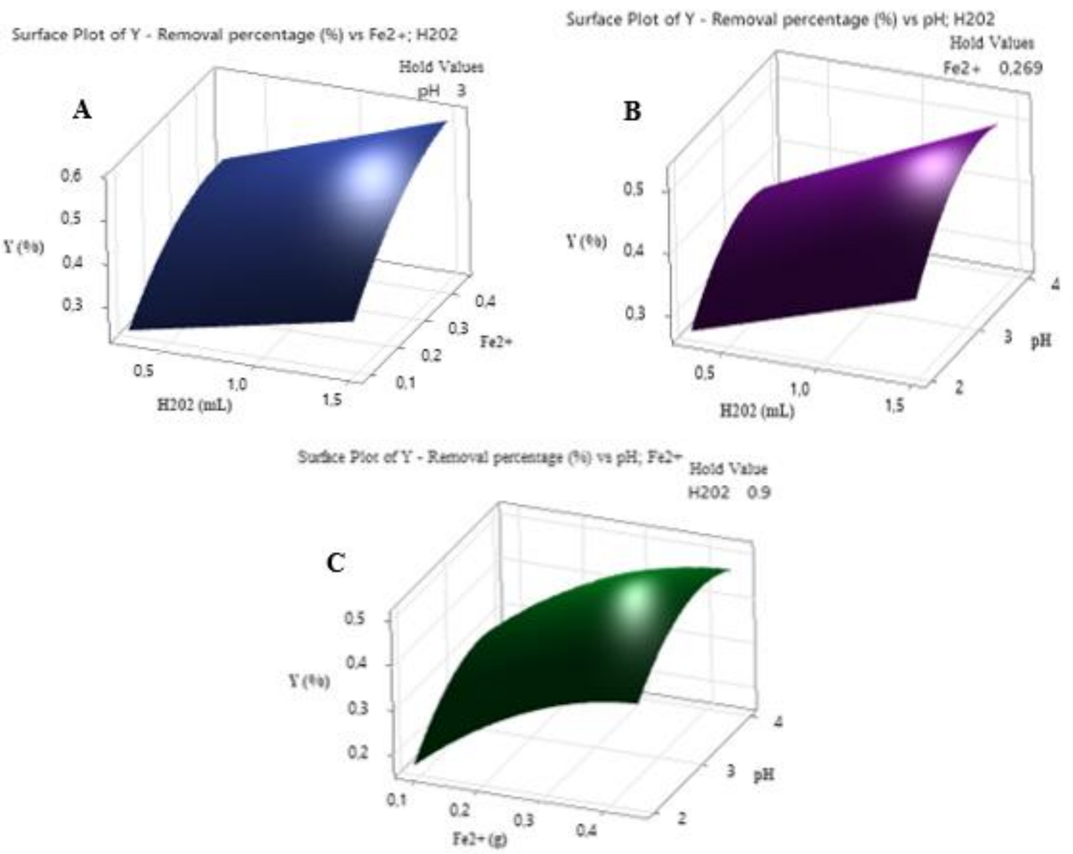

Figure 21. Three-dimensional response surface plots illustrating the interaction effects of operational variables on COD removal efficiency in the Fenton oxidation process: (A) Fe^{2+} and H_2O_2 at fixed pH 3.0; (B) pH and H_2O_2 at fixed Fe^{2+} = 0.269 g; and (C) pH and Fe^{2+} at fixed H_2O_2 = 0.9 mL.

In alignment with the central objective of this study, to optimise the key operational parameters governing the Fenton oxidation process for stabilised landfill leachate treatment, statistical models derived from factorial experimental design were employed to identify the conditions yielding maximal treatment efficiency. Optimisation was conducted via response surface methodology (RSM) using Minitab® software, based on a quadratic polynomial regression model correlating COD removal efficiency with independent variables (pH, Fe^{2+}, and H_2O_2).

The model predicted a maximum COD removal efficiency of 59.64% under the following optimal conditions: pH 3.4, with a hydrogen peroxide (H_2O_2) dosage of 30 mL L^{-1} and a ferrous ion (Fe^{2+}) dosage of 8.96 g L^{-1} of leachate. The corresponding desirability function value was 0.9918, indicating a near-ideal solution within the defined experimental design space. This high desirability score reflects the robustness of the model and its predictive capacity for optimal performance, providing strong justification for subsequent experimental validation under these precise conditions.

Figure 22 displays the optimisation desirability profile, which visually represents the predicted COD removal response as a function of the three operational factors. The response surfaces (Figure 21) reveal notable interaction effects, particularly between the pH and reagent concentrations, emphasising the process's high sensitivity to acidic conditions and the stoichiometric balance between Fe^{2+} and H_2O_2. These results reinforce the critical importance of fine-tuned control over both pH and oxidant/catalyst dosages in maximising the efficiency of hydroxyl radical generation and contaminant degradation in complex effluents, such as landfill leachate.

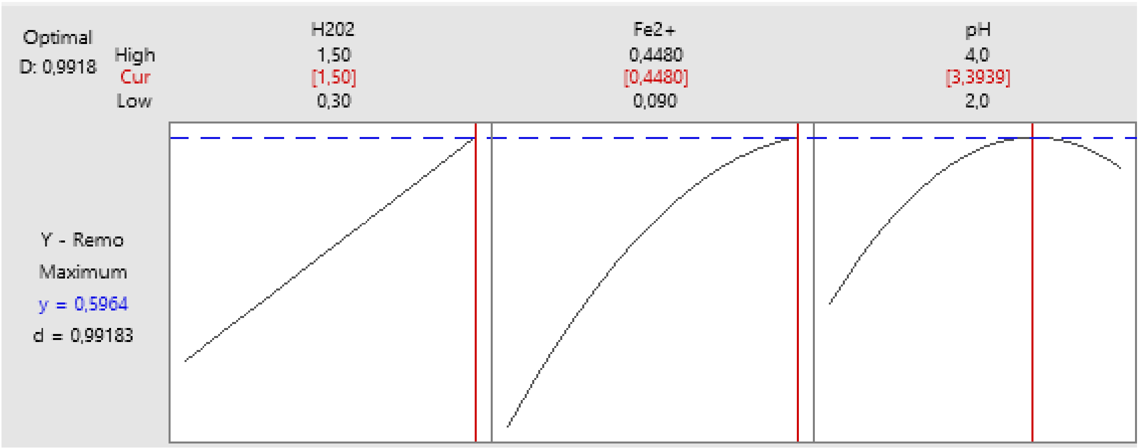

Figure 22. Response surface optimisation of COD removal efficiency through the Fenton oxidation process.

Following the identification of the optimal operating conditions through statistical modelling, an experimental validation was conducted to verify the predictive accuracy and practical applicability of the optimised parameters. The procedure replicated the previously established standard operating protocol, ensuring methodological consistency and enabling a direct performance comparison.

Stabilised landfill leachate previously subjected to coagulation–flocculation pretreatment was decanted, and 50 mL of the resulting supernatant was allocated for the Fenton oxidation stage. The reaction was carried out under the following optimised conditions determined by the model: pH 3.4, ferrous ion dosage of 8.96 g L^{-1} (supplied as $FeSO_4 \cdot 7H_2O$), and hydrogen peroxide (30% w/w) dosage of 30 mL L^{-1} of leachate.

The pH of the solution was carefully adjusted using concentrated H_2SO_4 under continuous magnetic agitation to ensure homogeneity and prevent localised pH gradients.

Fe^{2+} was then introduced to initiate the catalytic cycle, followed by the gradual addition of H_2O_2 via a calibrated burette over a 30-minute interval. This controlled dosing strategy was employed to maintain a stable oxidant concentration, enhance radical availability, and mitigate the formation of excessive foam, which could interfere with the mass transfer and mixing efficiency.

Upon completion of the reaction period, the oxidation process was quenched by increasing the pH to 11 using NaOH, promoting the precipitation of ferric hydroxides [$Fe(OH)_3$] and ensuring the complete removal of soluble iron species. The mixture was then left under quiescent conditions for 24 h to facilitate gravitational settling and solid–liquid separation.

The clarified supernatant was subsequently recovered and analysed for residual COD, BOD_5, total solids, ammoniacal nitrogen, and other relevant parameters. The results, detailed in Table 13, provide a quantitative assessment of the treatment performance under optimised Fenton conditions and serve as a critical reference point for process validation and potential scale-up.

Table 13. Final characterisation of the treated leachate.

Parameter	Units	Raw Leachate Sample	Pre–treatment Coagulation/flocculation	Fenton process
Calendar	Day/Months/Year	25/06/2024 (sunny day)	-	-
pH	Sorensen Scale	8.29	5.5	11
Conductivity	mS/cm	40.7	-	49.5
COD	mg L^{-1} O_2	19560	4105	1542
COD removal	%	-	79%	92%
BOD_5	mg L^{-1} O_2	1036	1242	1343
BOD_5 / COD	-	0.053	0.30	0.87
Total solids	g L^{-1}	39	-	61
Total ammonia	mg L^{-1} NH_4	196	-	184

The analytical results summarised in Table 13 elucidate the progressive transformation of leachate quality across each treatment stage, from the raw effluent through coagulation–flocculation (CF) to the post-Fenton oxidation phase. The raw leachate exhibited physicochemical characteristics typical of mature landfill effluents, with extremely elevated concentrations of chemical oxygen demand (COD: 19560 mg L^{-1}), biochemical oxygen demand (BOD_5: 1036 mg L^{-1}), and total solids (39 g L^{-1}), confirming its recalcitrant nature and limited biodegradability.

The CF pretreatment step induced a significant reduction in COD of 4105 mg L^{-1}, representing a removal efficiency of approximately 79%. Simultaneously, an unexpected increase in BOD_5 to 1242 mg L^{-1} was observed, suggesting the preferential elimination of refractory organic compounds and a relative enrichment of biodegradable fractions. This shift resulted in a substantial improvement in the BOD_5/COD ratio, indicating an enhanced biological treatability. Additionally, the process induced a pH reduction to 5.5, which is inherently favourable to the Fenton process, thereby minimising the requirement for supplementary acidification and contributing to operational optimisation.

Subsequent application of the Fenton oxidation process under optimised conditions (hydrogen peroxide (H_2O_2) dosage of 30 mL L^{-1} and a ferrous ion (Fe^{2+}) dosage of 8.96 g L^{-1} of leachate, and pH 3.4) further enhanced treatment efficacy. COD levels declined sharply to 1542 mg L^{-1}, achieving a cumulative removal efficiency of approximately 92% relative to the raw leachate. Concurrently, BOD_5 concentrations rose to 1343 mg L^{-1} and the BOD_5/COD ratio improved to 0.87, clearly indicating substantial oxidative breakdown of recalcitrant organics and a transition toward an effluent that is more amenable to downstream biological treatment processes.

Despite improvements in organic load reduction and biodegradability, a substantial increase in total solids was recorded following the Fenton process (61 g L^{-1}). This anomalous result is most likely attributable to the formation of poorly settled precipitates, primarily ferric hydroxides ($Fe(OH)_3$), and other insoluble by-products generated during post-oxidation pH neutralisation (to pH 11 with NaOH). Although intended for removal via sedimentation, these compounds may have remained suspended or existed as fine colloidal particles that were inadequately separated prior to sampling, thereby contributing to the elevated solid measurement. Qualitative visual assessment (Figure 14) suggested effective clarification, indicating that analytical discrepancies may stem from insufficient decantation, procedural artefacts, or incomplete phase separation during sample handling.

In terms of nitrogenous species, total ammoniacal nitrogen concentrations remained largely unaltered across all treatment stages, confirming the limited efficacy of both the CF and Fenton processes in ammonia removal. Similar observations were reported by Renou et al., (2008), who highlighted the inefficiency of physicochemical treatments in removing ammoniacal nitrogen from landfill leachates. This reinforces the necessity of implementing complementary or sequential technologies, such as biological nitrification, air stripping, and ion exchange, for comprehensive nitrogen management and regulatory compliance.

Although the integrated C–F and Fenton system demonstrated pronounced effectiveness in organic pollutant removal and biodegradability enhancement, the final treated effluent did not fully comply with the discharge standards established under Decree-Law No. 236/98. Several key parameters, particularly those associated with nitrogen and solid content, exceeded the Emission Limit Values (ELVs) delineated for environmental release (Table 2). Therefore, further posttreatment or system integration is recommended to meet legislative thresholds and ensure environmental safety.

4.3 Sludge Generation and Management

The sequential application of coagulation–flocculation (CF) and Fenton advanced oxidation for stabilised landfill leachate treatment results in the generation of distinct sludge streams with varying physicochemical characteristics and volumetric yields. During the CF stage, a high sludge production rate was recorded: approximately 200 mL of sludge was generated per 300 mL of raw leachate processed, reflecting the effective aggregation and removal of suspended and colloidal matter through destabilisation and charge neutralisation mechanisms.

In contrast, the Fenton process, operating under optimised conditions, yielded an average sludge volume of 14 mL per 50 mL of treated effluent, with an observed variability between 9 and 17 mL. The sludge resulting from this oxidative stage predominantly comprised iron hydroxide precipitates ($Fe(OH)_3$), formed during the neutralisation phase post-reaction, along with oxidised and partially mineralised organic residues.

The solid residues from both treatment steps present distinct vaporisation pathways, contingent upon their elemental composition, contamination profile, and physico-mechanical properties. The sludge generated during CF pretreatment, which is characteristically rich in organic matter and flocculant-derived precipitates, demonstrates potential for anaerobic digestion (AD), provided it exhibits adequate biodegradability and low concentrations of inhibitory substances. Literature reports on analogous matrices suggest biogas yields reaching up to 350 m^3 per tonne of volatile solids, with energy recoveries around 850 kWh (Grosser & Neczaj, 2018). The performance of AD systems is strongly influenced by factors such as substrate-to-inoculum ratio, retention time, organic loading rate, and operational temperature (preferably within the mesophilic range of 35–39 °C). Preconditioning strategies, such as thermal or oxidative pretreatment, may further enhance the hydrolysis rates and methane yield.

Alternatively, CF sludge enriched in inorganic flocculant by-products (e.g., aluminium hydroxides) can be employed in construction materials, specifically as a partial replacement for cement or fine aggregates in concrete formulations. Empirical studies have demonstrated that replacement levels of 5 – 10% are compatible with structural performance requirements, preserving the compressive strength while contributing to material circularity. However, higher substitution ratios have been associated with increased porosity, diminished mechanical resistance, and durability. Thermal activation (~300 °C) has shown promise in improving the pozzolanic reactivity and binding capacity of such residues, while simultaneously reducing their moisture sensitivity (Kaish et al., 2021).

In contrast, due to its low biodegradability and potential enrichment in heavy metals or transformation products, Fenton sludge is largely unsuitable for biological valorisation routes such as AD or land application. Nonetheless, its mineralogical composition supports restricted integration into non-load-bearing construction components, such as pavers, bricks, or base layers in civil works, where substitution levels must be carefully controlled (typically ≤10%) to preserve the structural integrity and prevent leachate-related environmental risks. In this context, standardised leaching tests (e.g., TCLP, EN 12457) are essential to verify compliance with environmental safety criteria (Kaish et al., 2021; Mandlik et al., 2018).

Integrating sludge management into the overall treatment strategy under a circular economy paradigm not only promotes the valorisation of secondary materials but also contributes to resource recovery, energy generation, and reduction of final disposal volumes. This aligns with contemporary waste governance models prioritising environmental sustainability, regulatory compliance, and operational efficiency in landfill leachate treatment systems.

5. CONCLUSION

This study investigated the efficacy of a sequential treatment strategy comprising coagulation–flocculation followed by Fenton oxidation for the remediation of stabilised landfill leachate. The initial characterisation of the raw effluent revealed a high contaminant burden, notably elevated levels of chemical oxygen demand (COD), biochemical oxygen demand over five days (BOD_5), and total solids, thus necessitating the application of advanced multibarrier treatment approaches.

Coagulation–flocculation pretreatment using RIFLOC1815 proved effective in achieving a substantial reduction in COD while simultaneously enhancing BOD_5 levels, which translated into a marked improvement in the BOD/COD ratio, a critical parameter indicative of increased biodegradability. Furthermore, the acidifying effect of this pretreatment facilitated alignment with the optimal acidic pH range required for the Fenton reaction, thereby reducing the demand for chemical acidification and enhancing operational efficiency.

Subsequent application of the Fenton advanced oxidation process, optimised through statistical modelling via Minitab® software, established ideal operating conditions at pH 3.4, with a hydrogen peroxide (H_2O_2) dosage of 30 mL L^{-1} and a ferrous ion (Fe^{2+}) dosage of 8.96 g L^{-1} of leachate. Under these conditions, the system achieved a COD removal efficiency of approximately 92% and further enhancement of biodegradability, with the BOD/COD ratio increasing to 0.87. These findings underscore the dual functionality of the Fenton process: effective mineralisation of refractory organics and improved amenability of the effluent to downstream biological treatments.

Nevertheless, an unexpected increase in total solids was observed post-treatment, likely due to the formation and partial suspension of iron hydroxide precipitates following the final pH adjustment to alkaline values (pH $\approx$ 11). Although a visual reduction in turbidity was noted, gravimetric analyses suggested the need for improved solid–liquid separation techniques to avoid overestimation of residual solids.

Ammoniacal nitrogen concentrations remained largely unaffected by the treatment sequence, highlighting the necessity for complementary post-treatments, such as air stripping, ion exchange, or biologically mediated nitrification, to achieve comprehensive nitrogen removal and meet discharge standards.

From an economic perspective, while the proposed approach demonstrated high treatment efficacy, the associated costs, particularly for chemical reagents such as H_2O_2

and Fe^{2+} salts, must be critically assessed. Optimising reagent dosing and exploring options for iron recovery or reuse could contribute to cost reductions. Furthermore, integrating this physicochemical-oxidative system with biological post-treatment may enhance overall cost-effectiveness, process sustainability, and compliance with regulatory discharge thresholds.

In conclusion, the combined coagulation–flocculation and optimised Fenton processes demonstrated high efficiency in treating mature landfill leachate. Nonetheless, improvements in solid management and nitrogen removal are necessary to comply with discharge regulations and to ensure full environmental and economic sustainability.

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