

Advances in Fenton and photo-Fenton degradation of anionic surfactant SDBS

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Abstract

Surfactants are widely used in hygiene and cleaning products; however, their persistence in aquatic environments classifies them as emerging contaminants. This study aimed to evaluate the behavior and degradation efficiency of the anionic surfactant Sodium Dodecyl Benzene Sulfonate (SDBS) using Fenton and photo-Fenton Advanced Oxidation Processes (AOPs). Analytical monitoring of pollutant removal was performed using High-Performance Liquid Chromatography (HPLC). To optimize the operational variables – namely reaction time, pH, H_2O_2 and Fe^{2+} concentrations – Response Surface Methodology (RSM) and Analysis of Variance (ANOVA) were applied using Jamovi and RStudio software. The experimental results demonstrated that the photo-Fenton process significantly outperformed the conventional Fenton process, which was driven by UV radiation, promoting the continuous regeneration of Fe^{2+} ions and maximizing the generation of hydroxyl radicals ($\text{HO}\cdot$). The reduced quadratic model for the photo-Fenton system was statistically significant ($p = 0.013$), highlighting reaction time as a critical factor ($p = 0.024$) and indicating a strong negative quadratic effect of iron concentration. The 3D response surfaces confirmed the presence of an optimal intermediate operation region, proving that excessive reagent dosages trigger scavenging effects, which limit further removal efficiency. The Fenton process achieved SDBS removal ranging from 22% to 52%, whereas the photo-Fenton process achieved SDBS removal ranging from 50% to 76%, demonstrating that both processes were effective and that UV irradiation enhanced the oxidative efficiency of the system. Ultimately, this study provides a robust technical framework aligned with the United Nations 2030 Agenda, directly contributing to Sustainable Development Goal 6 (Clean Water and Sanitation) by engineering efficient pathways for the removal of persistent surfactants from wastewater, while also aligning with SDG 12 (Responsible Consumption and Production) and SDG 14 (Life Below Water).

Keywords: advanced oxidation process, photo-Fenton process, Response Surface Methodology (RSM), Sodium Dodecyl Benzene Sulfonate (SDBS), sustainability.

Resumo

Os surfactantes são amplamente utilizados em produtos de higiene e limpeza, porém sua persistência em ambiente aquático os classifica como contaminantes emergentes. Este trabalho teve como objetivo avaliar o comportamento e a eficiência de remoção do surfactante aniônico Linear Dodecilbenzeno Sulfonato de Sódio (SDBS) por meio dos Processos Oxidativos Avançados (POAs) Fenton e foto-Fenton. O monitoramento analítico da degradação do poluente foi realizado recorrendo à Cromatografia Líquida de Alta Performance (HPLC). Para a otimização das variáveis operacionais do processo – nomeadamente o tempo de reação, o pH, e as concentrações de H_2O_2 e de Fe^{2+} –, aplicou-se a Metodologia de Superfície de Resposta (RSM) e a Análise de Variância (ANOVA) com o auxílio dos softwares Jamovi e RStudio. Os resultados experimentais demonstraram que o processo foto-Fenton superou significativamente o Fenton convencional, desempenho este atribuído à radiação UV, que promove a regeneração contínua de íons Fe^{2+} e maximiza a geração de radicais hidroxila ($\text{HO}\bullet$). O modelo quadrático reduzido obtido para o sistema foto-Fenton revelou-se estatisticamente significativo ($p = 0,013$), destacando o tempo de reação como um fator crítico ($p = 0,024$) e evidenciando um forte efeito quadrático negativo para a concentração de ferro. As superfícies de 3D confirmaram a existência de uma região ótima intermédia de operação, comprovando que dosagens excessivas de reagentes desencadeiam efeitos sequestradores (*scavenger*), limitando o incremento da eficiência de degradação. O processo Fenton apresentou remoção de SDBS variando de 22% a 52%, enquanto o processo foto-Fenton atingiu valores entre 50% e 76%, demonstrando que ambos os processos foram eficazes e que a irradiação UV aumentou positivamente a eficiência oxidativa do sistema. Em suma, este estudo fornece uma base técnica robusta alinhada com a Agenda 2030 da Organização das Nações Unidas, contribuindo diretamente para o Objetivo de Desenvolvimento Sustentável 6 (Água Potável e Saneamento) ao propor soluções eficientes para a remoção de surfactantes persistentes em efluentes, estando também alinhado com os ODS 12 (Consumo e Produção Sustentável) e ODS 14 (Proteger a Vida Marinha).

Palavras-chave: Linear Dodecilbenzeno Sulfonato de Sódio (SDBS), Metodologia de Superfície de Resposta (RSM), processo foto-Fenton, processos de oxidação avançados, sustentabilidade.

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List of Abbreviations

AOPs	Advanced Oxidation Processes
ANOVA	Analysis of Variance
AWWA	American Water Works Association
BAC	Biological Activated Carbon
BBD	Box-Behnken Design
BOD	Biochemical Oxygen Demand
CECs	Contaminants of Emerging Concern
COD	Chemical Oxygen Demand
CMC	Critical Micellar Concentration
DAD	Diode-array detector
DBS	Dodecyl benzene sulfonate
EOR	Enhanced Oil Recovery
HO•	Hydroxyl Radical
HOCs	Hydrophobic Organic Compounds
HPLC	High-Performance Liquid Chromatography
LAS	Linear Alkylbenzene Sulfonate
ODS	Translated as SDGs (Sustainable Development Goals)
PTFE	Polytetrafluoroethylene
PS	Persulfate
RSM	Response Surface Methodology
SDBS	Sodium Dodecyl Benzene Sulfonate
SDGs	Sustainable Development Goals
TFA	Trifluoroacetic acid
UN	United Nations
UV	Ultraviolet
WEF	Water Environment Federation
WQI	Water Quality Index
WWTP	Wastewater Treatment Plant

1. INTRODUCTION

Surfactants, also known as surface-active agents, are compounds that modify the surface and interfacial properties of liquids. In addition, they are considered emerging contaminants because they are present in various cleaning products and industrial processes that are disposed of in effluents (Nunes and Teixeira, 2022). Their main characteristic is their ability to alter the surface tension between two liquids or between a liquid and solid surface (Barros et al., 2007). These molecules have a structure consisting of a hydrophilic head that interacts with water and a hydrophobic tail that tends to repel water. This structure enables the formation of micelles and modification of surface interactions, facilitating processes such as emulsification, dispersion, detergency, and wetting (Fatma et al., 2022).

Compounds produced by microorganisms, known as biosurfactants, have attracted attention because they combine surface activity with greater sustainability and biodegradability (Barros et al., 2007). They are notable for their ease of decomposition, making them a more ecological option (Reeve and Fallowfield, 2018). However, most industrial surfactants are synthesized from petroleum-derived products. The use of synthetic surfactants has serious environmental consequences. The presence of surfactants in water bodies can negatively affect aquatic life by interfering with the microbiota and increasing the toxicity of aquatic environments, affecting organisms such as fish and algae (Makala et al., 2023). With more than 15 million tons of surfactants consumed globally each year, approximately 60% of these compounds end up in water bodies, and it is urgent to search for alternatives with a lower environmental impact (Nagtode et al., 2023).

Overall, the removal of surfactants from wastewater remains a challenge because of the chemical stability of several surfactant classes and their low biodegradability rates. The main removal strategies include physical (precipitation, flocculation, electroflocculation, and membrane processes), biological (aerobic and anaerobic degradation), and chemical (oxidation and reduction) processes. Each technique has specific advantages and limitations, and the choice is conditioned by the characteristics of the effluent and the treatment objectives (Nunes and Teixeira, 2022).

In contrast, the Fenton and photo-Fenton Advanced Oxidative Processes have shown promising results compared to other forms of treatment. They are better,

including higher degradation efficiency, no residues, and a wide area for substance treatment. When the Fenton process is coupled with photocatalysis, a hybrid approach is created by increasing the mineralization of pollutants, reducing the production of iron sludge, accelerating the iron oxidation cycle, making it more efficient, and extending the useful life of the photo-generated (Dong et al., 2020).

The environmental problem of inadequate disposal of surfactants in domestic and industrial environments is directly in line with the Sustainable Development Goals (SDGs) proposed by the United Nations (UN) in the 2030 Agenda, which seeks to promote responsible production and consumption, in addition to providing quality sanitation, drinking water and protection of aquatic life (United Nations, 2015).

Within this context, this study aimed to evaluate the potential of the Fenton and photo-Fenton processes for the degradation of synthetic surfactants.

2. OBJECTIVES

2.1. General Objective

To evaluate the behavior and removal efficiency of the Fenton and photo-Fenton processes for the anionic surfactant Sodium Dodecyl Benzene Sulfonate (SDBS), under operational conditions that minimize environmental impacts associated with its presence in effluents.

2.2. Specific Objectives

- Perform oxidative degradation tests of anionic surfactant SDBS using Fenton and photo-Fenton processes;
- Identify how operational parameters influence the removal efficiency of each process with ANOVA and RSM;
- Quantify the residual concentration of SDBS to determine the efficiency achieved by the oxidation processes;
- Compare the Fenton and photo-Fenton processes, highlighting efficiency gains, limitations, and operational challenges.

3. STATE OF ART

3.1. Classification and Properties of Surfactants

Surfactants are amphiphilic compounds that play a key role in various industrial and environmental applications. Surfactants are classified based on the nature of the polar head of the molecule, into anionic, cationic, nonionic, and amphoteric (Figure 1). In addition, they can be classified as synthetic or natural, depending on their origin and production method (Janoska et al., 2018). Mushtaq et al. (2023) highlight that the selection of surfactants should take into account the minimization of adsorption in the porous medium to optimize their recovery. This factor is also relevant for industrial processes that involve membrane separation and treatment of effluents containing surfactants. In addition, there has been an increase in information on the application of microbial biosurfactants as sustainable alternatives to synthetic surfactants in these processes because of their higher tolerance to extreme conditions and lower environmental impact (Nagtode et al., 2023).

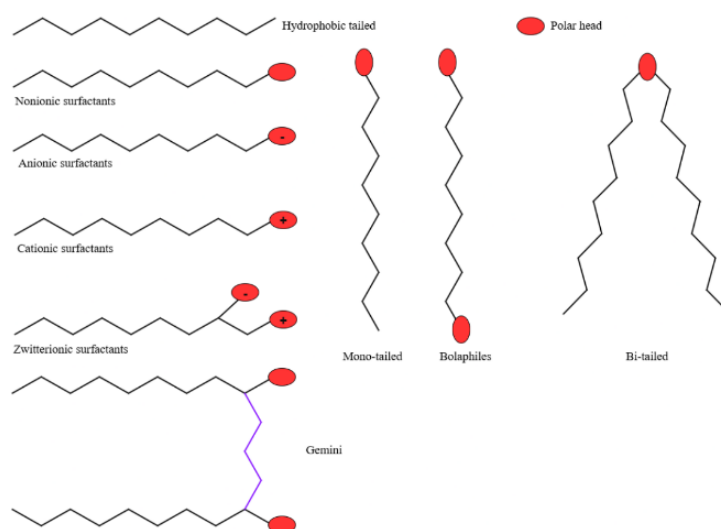


Figure 1. Schematic representation of the surfactants according to their polar head and their hydrophobic chain (Khalfallah, 2024).

Natural surfactants are obtained from plants, animals, and microorganisms through extraction, precipitation, and distillation processes without the need for complex organic synthesis (Raj and Ramamurthy, 2024).

Saponins are the most common plant-based surfactants, with foaming properties, and are used in detergents and cleaning products (Sparg et al., 2004). Examples of plant

sources include *Jatropha curcas*, almond seed, *Vernonia amygdalina*, *Ziziphus spina-christi*, and soap (Gbadamosi et al., 2022).

Animal-based surfactants are widely used in the production of aerated concrete and remediation of contaminated soils (Raj and Ramamurthy, 2024). Examples include poractant alfa and beractant, which are used to treat of respiratory distress syndrome (Dong et al., 2021).

Biosurfactants, produced by microorganisms, have great environmental potential because of their biodegradability and low toxicity. They play an essential role in bioremediation and biosorption and are considered sustainable alternatives to synthetic surfactants (Fardami et al., 2022; Fenibo et al., 2019). Microbial biosurfactants, such as rhamnolipids, surfactin, and sophorolipids, are of increasing interest because they can be produced on large-scale by microorganisms such as yeasts and bacteria (Zhou et al., 2013).

These biosurfactants have also been studied for their use in environmental technologies, such as soil washing, as they are more compatible with the environment and less toxic than synthetic surfactants. Additionally, they are effective in removing hydrophobic organic compounds (HOCs) from contaminated soils (Bezerra et al., 2018).

Synthetic surfactants are widely used in industries because their properties can be modified through chemical processes. They are divided into amphoteric, cationic, nonionic, and anionic surfactants, with a focus on SDBS.

Amphoteric surfactants have pH-dependent loading in solution, making them versatile for foam cleaning and stabilization applications. They are mainly used in shampoos and shower gels, because they offer softness during application and are less irritating to the skin (Baek et al., 2021).

Cationic surfactants, such as quaternary ammonium compounds, possess antimicrobial properties and are widely used in cosmetics, pharmaceuticals, and disinfectants (Pérez et al., 2021, Zakharova et al., 2019). Due to their positive charge, they can interact with the negative charges on surfaces, making them effective in disinfectants and antiseptics.

Nonionic surfactants are preferred in cosmetic and pharmaceutical formulations because of their stability and low toxicity. They are important for the formation of

niosomes, which are lipid structures used as vehicles for the controlled release of pharmaceutical and cosmetic actives (Mahale et al., 2012). Their inability to dissociate in solutions makes them ideal for gentler, non-irritating products.

Anionic surfactants, which account for 70-75% of the world's total surfactants, have excellent performance in removing ionic contaminants and are widely used in detergents (Tamjidi et al., 2021). These surfactants have negatively charged polar heads, making them effective for emulsifying oils and cleaning surfaces.

Linear Alkylbenzene Sulfonate (LAS) is one of the most widely used synthetic anionic surfactants, which contains between 10 and 14 carbons in the linear alkyl chain attached to a benzene sulfonate ring at the *para* position (Hassanzadeh and Jafari, 2020) and is commonly found in household detergents and personal products. At low concentrations it does not significantly affect the environment; however, in large quantities it can be harmful in aqueous media (Yuliana et al., 2025). In large doses, it forms a foam that hinders the operational activity of the treatment and promotes health risks due to the accumulation of pathogens that are carried in the foam blown by the wind (Asok, Fathima and Jisha, 2015). When saturated, aggregates form aqueous micelles, improving cell membrane permeability and causing cell lysis (Wei et al., 2024).

Linear Alkylbenzene Sulfonate (LAS) has low anaerobic biodegradability, and its removal can occur via adsorption (Marinho et al., 2022). This adsorption mechanism has also been observed in studies using oxidized graphite and silica gel as adsorbent materials for cationic surfactants (Koner et al., 2010; Corona et al., 2023).

Sodium Dodecyl Benzene Sulfonate (SDBS) is a surfactant used in detergents, household cleaning products, and industrial processes such as textiles, agriculture, and concrete (Tofan et al., 2026). High concentrations of it can be found in chemical compounds considered foreign to living organisms (xenobiotics). It also affects the mobility of organic compounds and minerals present in soil or sediments, preventing photosynthesis in plants and producing plant growth. When present in water, it can enter fish and cause cancer (Wulandari and Siswanta, 2018).

Several methods have been used to decompose or remove SDBS, including adsorption, photocatalysis with titanium dioxide, ozone oxidation in hydrogen peroxide, ultrasonic irradiation with Fe^{2+} , and biological activity with algae and bacteria. In addition, methods for detecting the concentration of SDBS in water samples include

liquid chromatography with mass spectrometry, indirect atomic absorption spectroscopy, and colorimetry with methylene blue (Gu et al., 2021).

3.1.1 Industrial application

In the pulp and paper industry, compounds such as NALBRITE 2623 and NALCO 8683 are used for cleaning and descaling machines from recycled fibers (Kruszelnicka et al., 2024). These surfactants help ensure the quality of the final product and the efficiency of production processes.

In the petroleum industry, surfactants are applied in Enhanced Petroleum Recovery (EOR). They help reduce the interfacial tension between water and oil, making it easier to recover residual oil from reservoirs. In addition, surfactants help modify the wettability of reservoir rocks, making the process more efficient (Gbadamosi et al., 2022).

In the cosmetics industry, natural surfactants, such as microbial biosurfactants, are increasingly used in products such as shampoos, as they are a more sustainable and environmentally friendly alternative to synthetic surfactants. These natural surfactants are not only more biodegradable but also have greater compatibility with skin and hair (Bezerra et al., 2018). Recently, the literature has highlighted the potential of biosurfactants as multifunctional agents in cosmetic formulations, including antimicrobial properties and increased biocompatibility, making them promising for formulations aimed at sensitive and sustainable consumers (Nagtode et al., 2023). In the cosmetic sector, the adsorption of anionic surfactants on substrates such as silica gel (Koner et al., 2010) and graphite oxides (Corona et al., 2023) has been explored to develop of new, more sustainable formulations. These studies suggest the possibility of replacing synthetic surfactants with biodegradable alternatives, such as microbial biosurfactants.

Biosurfactants are also effective in environmental technologies such as soil washing. They are used to remove hydrophobic organic compounds (HOCs) from contaminated soils, offering a more environmentally friendly alternative to synthetic surfactants. This application has gained prominence, especially because of the biodegradability and low toxicity of biosurfactants (Zhou et al., 2013).

3.1.2 Environmental impact

Surfactants play a crucial role in various industries; however, their overuse raises significant environmental concerns. The release of these compounds into water bodies, soils, and ecosystems can lead to a number of detrimental impacts on aquatic and terrestrial organisms (Balson et al., 2002).

Aerobic and anaerobic biodegradation of surfactants have different efficiencies. Ríos et al. (2024) point out that certain surfactants, such as anionics, tend to accumulate in the environment under anaerobic conditions, which can result in prolonged environmental impacts.

Surfactants primarily affect aquatic organisms through interactions with their respiratory structures, such as epithelial membranes. This interaction can destabilize these structures, alter cell permeability, promote cell lysis, and compromise the respiration of organisms (Balson et al., 2002). Studies have indicated that anionic and cationic surfactants have a greater denaturing effect than neutral surfactants, with cationic surfactants being the most toxic to fish, invertebrates, and algae (Cserhádi, Forgács and Oros, 2002).

In addition to their direct toxicity, surfactants can affect the bioavailability of pollutants in aquatic environments. The formation of micelles influences the sorption and desorption of toxic substances, increasing the interaction between microplastics and aquatic organisms, which can amplify the negative impact on ecosystems (Guerranti et al., 2021).

The bioaccumulation of surfactants in organisms is a concern, especially for those with a high affinity for phospholipid membranes, such as cationic surfactants (Kierkegaard et al., 2021). These compounds tend to accumulate in fish and other aquatic organisms, increasing their toxicity in the food chain.

Anionic surfactants can also cause structural changes in proteins and destabilize enzymes and cell membranes, resulting in toxicity in animals and humans (Cserhádi, 2002). In addition, the toxicity of surfactants is enhanced by their hydrophobic properties, which facilitate their interaction with sensitive cellular structures (Badmus et al., 2021).

Surfactants pose a risk to terrestrial ecosystems. When present in the soil, they can be toxic to microorganisms essential for maintaining fertility, compromising processes such as the decomposition of organic matter and nutrient fixation (Lavanya and Machado, 2024). They can also directly affect plant growth by causing root damage and inhibiting photosynthesis (Borah et al., 2023).

The presence of long-chain surfactants and aromatic compounds in the soil reduces biodegradability, favoring persistence in the environment and increasing long-term negative impacts (Lavanya and Machado, 2024). This recalcitrant behavior reinforces the need for advanced treatment technologies, such as advanced oxidative processes (AOPs), which can promote the complete mineralization of these compounds and minimize ecological and public health risks (Rizzo et al., 2019, Shrivastava and Mategaonkar, 2024).

In addition to their environmental impact, surfactants pose a risk to human health. Analyses indicate that prolonged contact with surfactants can cause dermatitis, respiratory irritation and, in some cases, oral ulcerations (Lavanya and Machado, 2024). Anionic surfactants, such as linear alkylbenzene sulfonates (LAS), can reduce the body's resistance to environmental stress and affect vital metabolic processes (Badmus et al., 2021).

Therefore, it is essential to adopt strategies to minimize the impact of surfactants on the environment and human health, and encourage the development of more sustainable alternatives and efficient processes for the treatment and degradation of these compounds.

3.2. Surfactant Treatment

The treatment of effluents containing surfactants is one of the main challenges faced by the sanitation sector and industry. Due to the widespread use and structural diversity of these compounds, their presence in wastewater can compromise the efficiency of conventional treatment systems and generate significant environmental impacts (Palmer and Hatley, 2018).

The treatment should be effective over a wide range of concentrations. Among the most commonly used methods, biodegradation in biological systems is particularly noteworthy, especially in domestic sewage treatment. In these processes,

microorganisms use surfactants as a source of energy or nutrients, or even by cometabolism through different metabolic pathways (Ríos et al., 2024). However, the chemical structure of the surfactant and environmental conditions (aerobic or anaerobic) directly influence the biodegradation mechanism of the surfactant (Marinho et al., 2022).

Linear alkylbenzene sulfonate (LAS) surfactants, which are anionic compounds widely used in detergents, have a removal efficiency of up to 99.9% under aerobic conditions. However, its biodegradation under anaerobic conditions is significantly reduced, and its removal is predominantly attributed to anaerobic sludge adsorption. In addition, studies have indicated that high concentrations of LAS can inhibit biogas production by up to 50%, possibly due to its toxicity to methanogenic and acidogenic microorganisms (Marinho et al., 2022).

Adsorption has also been widely studied as a treatment method. The results indicate that the removal of cationic surfactants from silica gel can be potentiated under high pH conditions and in the presence of salts, while graphite oxide is an outstanding adsorbent material for anionic surfactants in laundry effluents (Koner et al., 2010; Corona et al., 2023).

Other physicochemical removal methods include nanofiltration (Kertész et al., 2008) and the use of selective membranes to retain cationic surfactants in industrial effluents (Klimonda and Kowalska, 2021). Likewise, it has been successfully used for the removal of the anionic surfactant CL80, reducing its concentration by 96% (Kertész et al., 2008). Membrane-based purification techniques are efficient alternatives for removing surfactants from industrial wastewater treatment. The use of reverse osmosis has been shown to be highly effective for the removal of fluorinated surfactants, with retention coefficients between 99.94% and 99.97% (Klimonda and Kowalska, 2021). Although the removal rate is high with this method, the production and maintenance costs make it a costly process.

In recent years, Advanced Oxidative Processes (AOPs) have emerged as promising alternatives for the removal of surfactants, as they are more efficient in the degradation of recalcitrant compounds than conventional methods. These processes can reduce treatment time and achieve better water quality indices, constituting a viable option in scenarios with a growing demand for sustainable solutions (Shrivastava and Mategaonkar, 2024).

3.2.1 Advanced Oxidation Processes (AOPs)

The development of Advanced Oxidation Processes (AOPs) has increased over the last few decades, with increasingly diverse applications. Despite these advances, the application of AOPs to effluents from urban wastewater treatment plants (WWTP) remains challenging. To overcome this limitation, bench and pilot-scale studies using realistic matrices, such as urban WWTP effluents, have been recommended (Rizzo et al., 2019). However, the lack of specific regulations for the removal of Contaminants of Emerging Concern (CECs) and the presence of substances that act as hydroxyl radical scavengers ($\text{HO}\bullet$) in wastewater compromise the efficiency of degradation.

AOPs involve the production of highly oxidative chemical species, such as hydroxyl ($\text{OH}^\cdot$) and sulfate ($\text{SO}_4^\cdot$) radicals, which are responsible for attacking and mineralizing pollutants in water. Technologies, such as ultraviolet (UV) radiation, ozone (O_3), and hydrogen peroxide (H_2O_2), have been shown to be effective in treating wastewater containing complex organic compounds (Nunes and Teixeira, 2022).

In particular, the application of hydroxyl radicals ($\text{HO}\bullet$) and other radicals formed in AOPs has been prominent in HOC degradation. These processes generate CO_2 , water, and inorganic compounds from the mineralization of pollutants, and are considered an effective solution to replace traditional oxidation technologies, such as the use of potassium permanganate (KMnO_4), potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$), and sodium persulfate ($\text{Na}_2\text{S}_2\text{O}_8$), which only partially oxidize organic compounds and can result in secondary sources of pollution (Krystynik, 2021).

Despite their high efficiency, AOPs face challenges, mainly related to the selectivity of the generated radicals. Free radicals, such as hydroxyl radicals ($\text{HO}\bullet$), although effective in destroying a wide range of pollutants, are susceptible to interference from inorganic ions and organic adjuvants in the effluent. This can result in poor performance and high chemical consumption (Wang et al., 2025).

In this context, the search for solutions that improve the performance of AOPs is the focus of research, and this factor reinforces the need to use other processes, such as the Fenton and photo-Fenton methods, which have demonstrated efficiency in the degradation of recalcitrant compounds.

Among the various types of AOPs, Fenton-based processes are low-cost, high-efficiency, and applicable methods for the removal of antibiotics and other organic

compounds from wastewater. This process involves the combination of ferrous ions (Fe^{2+}) with hydrogen peroxide (H_2O_2), generating hydroxyl radicals ($\text{HO}\cdot$), which are highly oxidizing species capable of promoting the mineralization of contaminants (Befenzi et al., 2024).

However, the process efficiency is heavily dependent on the pH. In an alkaline medium, iron (II) hydroxides are formed, and the decomposition of H_2O_2 is accelerated, which reduces the availability of hydroxyl radicals. However, in media with a very low pH, the active H_2O_2 concentration is affected by the formation of stable H_3O_2^+ ions. Thus, optimizing the reaction conditions is key to ensuring process efficiency (Možar et al., 2024).

These reactions can be modified using UV radiation to form the photo-Fenton process, which regenerates Fe^{2+} from Fe^{3+} , increases the generation of radicals, and enhances the degradation of recalcitrant pollutants (Ahmed et al., 2024). A representation of the Fenton and photo-Fenton processes is illustrated in Figure 2.

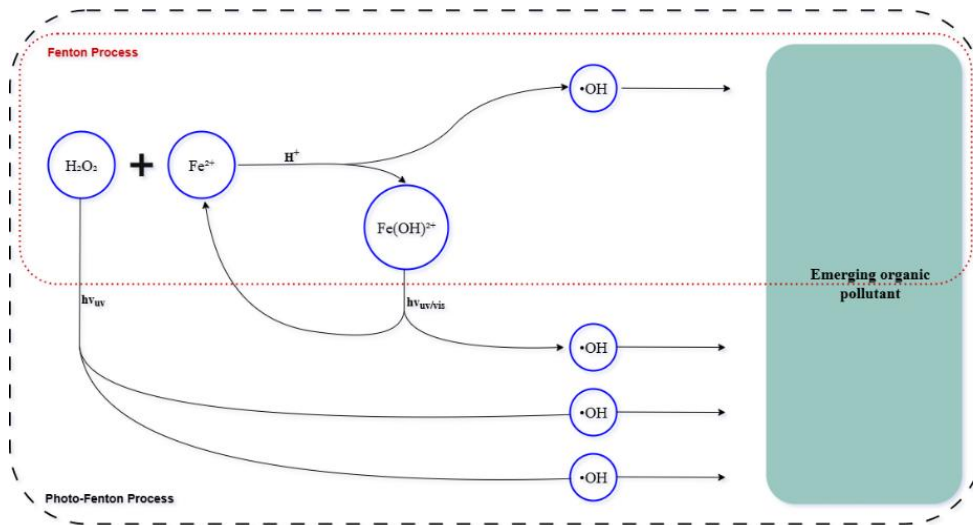


Figure 2. Representation of the Fenton and photo-Fenton processes (Možar et al., 2024).

In addition, solar photo-Fenton processes have proven to be an advantageous option for the treatment of industrial effluents, as they reduce electricity costs by using solar radiation to generate the radicals necessary for the degradation of organic pollutant. Studies have shown that the combination of photo-Fenton with complementary processes (coagulation, flocculation, and ozonation) can achieve up to 90% removal of biochemical oxygen demand (BOD) and chemical oxygen demand (COD) from industrial wastewater (Yuste-Córdoba et al., 2024).

Some studies have been conducted on Fenton and photo-Fenton processes; using the degradation of anionic surfactants or organic compounds, varying operational parameters such as pH, concentration of H_2O_2 and Fe^{2+} , and reaction time. Table 1 presents the abstracts of some of these studies.

Table 1. Summary of operational parameters, efficiencies, and limitations of Fenton and photo-Fenton processes in recent studies.

Author	Surfactant/Effluent	Process	Operational Parameters				Efficiency	Limitations/Observations
			pH	Fe ²⁺	H ₂ O ₂	Time		
Ayedi et al. (2025)	Anthracene (ANT) and benzo[a]pyrene (BaP).	Fenton and photo-Fenton	3.0	2.5-10 mg L ⁻¹	60-240 mg L ⁻¹	180-360 min	photo-Fenton: BaP - 85% and ANT - 70%. Fenton: BaP - ≈100% and ANT - 70%	Excess of hydrogen peroxide concentration (≈30%); pH control near to 3;
Giraldo et al. (2022)	Tannery wastewater	Fenton and photo-Fenton	4.0	0.333 g L ⁻¹	17 mL (30% v/v)	120 min	Maximum removal of TOC and COD: 66.15% and 35.15%	pH manipulation closer to neutral; low COD removal; Optimal results for wastewater decontamination and energy savings (photo-Fenton as sunlight);
Li et al. (2022)	Sodium oleate (NaOL)	Fenton	2.0 - 3.0	0.15 mmol L ⁻¹	1.4 mmol L ⁻¹	60 min	NaOL: 98.99%	Control of hydrogen peroxide concentration; pH control between 2-3;
Ranara et al. (2025)	Synthetic Wastewater (ortho-toluidine)	photo-Fenton	-	0.4730 mM	9 mM	-	Great COD removal: 57.22%	Don't control pH and time; show optimal solutions to be applied using the cost;
Yuste-Córdoba et al. (2024)	Cork Boiling Wastewater	Solar photo-Fenton	2.8 - 3.0	30±5 mg L ⁻¹	300±50 mg L ⁻¹	180-480 min	Removal of COD: 48-91%. Removal of TPC: 45-96%. Removal of COD after decantation: 74-97%	Long range of removal COD; formation of recalcitrant phenolic by-products; climate variations; need additional polishing; Long time process;

Operational parameters play a decisive role in the efficiency of Fenton and photo-Fenton processes because they determine both the degradation rates and economic feasibility. Ayedi et al. (2025), for instance, reported nearly complete removal of BaP and about 70% of ANT, but highlighted limitations such as the excess of H_2O_2 and the strict control required at acidic pH. Ranara et al. (2025) also demonstrated COD removals above 80%; however, the use of artificial radiation significantly increased energy demand and costs. Similarly, in another photo-Fenton study, the treatment costs ranged from 147 to 2087 USD m^{-3} , with optimized conditions achieving 57.2% COD removal at 707.4 USD m^{-3} . In all cases, parameters such as acidic pH, concentration of H_2O_2 , and dosage of Fe^{2+} were shown to be critical, not only for efficiency but also for avoiding side reactions and the formation of unwanted by-products.

3.3. Sustainability and Future Prospects for Surfactant Treatment

The growing environmental concerns and impacts associated with the improper disposal of surfactants in water bodies have driven the development of more sustainable and effective treatment technologies. In this context, Advanced Oxidative Processes (AOPs) have emerged as promising alternatives to the limitations of conventional methods, especially in regions with a high incidence of annual solar radiation. In these locations, photocatalytic AOPs are competitive, although many of these processes are still at an early stage of technological readiness, making direct comparisons with established methods difficult (Rizzo et al., 2019). However, the application of AOPs requires attention to the formation of oxidative by-products with potential biological effects, from both contaminants and dissolved organic matter.

Among the AOPs, persulfate (PS)-based processes are highly efficient for the degradation of surfactants in aqueous matrices. However, the effectiveness of these processes is strongly conditioned by operational factors, such as the pH of the solution, type of activation used (UV radiation, heat, ultrasound, among others), concentration of PS and the pollutant, and the composition of the actual matrix (Nunes and Teixeira, 2022). Another emerging approach involves the use of ultrasound to promote the degradation of surfactants. Sonocatalysis can be combined with other oxidative methods, such as the use of periodate and persulfate, resulting in synergistic treatments with greater efficacy (Merouani et al., 2024).

In the case of the Fenton process and its variants (photo-Fenton, sono-Fenton, and electro-Fenton), although there is already recognized scientific evidence of their efficiency in the degradation of recalcitrant micropollutants, there is still no consolidated version on an industrial scale without operational restrictions. This motivates the continuation of research aimed at improving the performance and applicability of these processes on a real scale (Ziembowicz and Kida, 2022).

In sustainable innovation, biosurfactants – amphiphilic molecules produced by microorganisms or extracted from plants – have gained attention as ecological alternatives to synthetic surfactants. These compounds are characterized by their low toxicity, high biodegradability, and superior efficacy under extreme pH and temperature conditions. In addition, they have lower critical micellar concentrations (CMC), which enhances their action at low concentrations (Nagtode et al., 2023). However, the large-scale production of biosurfactants faces economic and technical barriers, such as high purification costs and downstream processing challenges, which limit their immediate industrial viability.

Several Studies have explored the production of these compounds from renewable raw materials and biological sources, although their broader application is still limited by the cost associated with extraction and purification (Lavanya and Machado, 2024).

3.3.1 Sustainable Development Goals

The growing concern over environmental pollution has intensified the search for sustainability-oriented strategies, particularly after the establishments of the Sustainable Development Goals (SDGs) in 2015 as part of the United Nations 2030 Agenda, a global framework composed of 17 goals and 169 targets designed to address major environmental, economic, and social challenges while promoting poverty reduction, planetary protection, and improved living standards by 2030 (United Nations, 2015). Nevertheless, progress toward the SDGs remains uneven across countries, particularly in developing regions, where socioeconomic disparities and structural constraints influence the implementation of the 2030 Agenda (Medina-Hernández, 2024). Within this context, the transition toward more efficient management practices aligned with circular economy principles depends not only on technological progress, but also on stronger public policies and regulatory frameworks. In the case of surfactant treatment, this discussion is particularly related to SDG 6, which focuses on water quality and

sanitation; SDG 12, which centers on responsible consumption and production; and SDG 14, which is dedicated to the protection of aquatic ecosystems.

For example, the adoption of advanced oxidation processes (AOPs), such as the use of hydrogen peroxide or ozone, has been discussed from the perspective of urban sustainability. Studies have indicated significant reductions in water quality indices, such as the Water Quality Index (WQI), after 120 min of treatment with AOPs, which may represent a more sustainable alternative to conventional methods, especially in densely populated urban areas. In addition, the simplicity of operation and maintenance of these technologies favors their implementation in line with the Sustainable Development Goals (SDGs), such as SDG 6, which aims to improve water quality and increase effluent recycling by 2030 (Shrivastava and Mategaonkar, 2024).

Therefore, the future prospects for the treatment of surfactants point to the integration of sustainable technologies, optimization of existing processes, and continuous investment in research on green alternatives, such as biosurfactants.

4. MATERIALS AND METHODS

In this study, samples with SDBS were prepared in the laboratory, and experiments were conducted at the Laboratory of Chemical Processes at the Polytechnic Institute of Bragança.

4.1. Chemical and Reagents

Sodium Dodecyl Benzene Sulfonate (SDBS) was used as a model anionic surfactant. It was supplied as dodecylbenzenesulfonic acid, sodium salt, technical grade (Thermo Scientific, CAS 25155-30-0, MW= 348.48 g mol⁻¹). A stock solution of SDBS was prepared by dissolving 1 g of the solid in deionized water and stored under refrigeration. Working solutions at 100 mg L⁻¹ were freshly prepared by diluting the stock solution before each experiment.

Hydrogen peroxide (30 w/w) was used as an oxidant in the Fenton and photo-Fenton processes. Ferrous sulfate heptahydrate (FeSO₄·7H₂O, 99%) was employed as the source of Fe²⁺ ions. Sodium sulfite (Na₂SO₃, 99%) was used to quench the residual hydrogen peroxide at the end of the reaction.

Hydrochloric acid (HCl, 0.086 N) and sodium hydroxide (NaOH 0.1 N) solutions were used to adjust the pH of the SDBS solutions to the desired values. All the aqueous solutions were prepared using deionized water.

For HPLC analyses, acetonitrile, trifluoroacetic acid (TFA, 99%), and ultrapure water were used as mobile phase constituents. Before chromatographic analysis, all samples were filtered through 0.45 µm membrane filters (PTFE).

4.2. Experimental Design and Statistical Analysis

The effects of four operational variables on the degradation of SDBS by Fenton and photo-Fenton processes were constructed using the Box-Behnken design (BBD).

The independent variables were reaction time, pH, H₂O₂ concentration, and Fe²⁺ concentration. To evaluate the Box-Behnken design each variable was investigated at three coded levels (-1, 0, +1), corresponding to actual values of 3.0, 3.5, and 4.0 for pH; 20, 40, and 60 min for reaction time; 5, 10, and 15 mg L⁻¹ for H₂O₂ concentration; and 0.5, 1.0, and 1.5 mg L⁻¹ for Fe²⁺, respectively. The resulting design comprised 27 runs,

including three replicates at the central point (pH 3.5, reaction time 40 min, H₂O₂ 10 mg L⁻¹ and 1.0 mg Fe²⁺ L⁻¹) to allow the estimation of the experimental error and evaluation of the reproducibility of the system. The experimental matrix is presented in Table 2

Table 2. Box-Behnken design with uncoded variables.

Run	Reaction Time (min)	pH	H ₂ O ₂ (mg L ⁻¹)	Fe ²⁺ (mg L ⁻¹)	Run	Reaction Time (min)	pH	H ₂ O ₂ (mg L ⁻¹)	Fe ²⁺ (mg L ⁻¹)
1	40	3.0	5	1.0	14	40	3.5	5	1.5
2	40	3.0	15	1.0	15	40	3.5	15	0.5
3	40	4.0	5	1.0	16	40	3.5	15	1.5
4	40	4.0	15	1.0	17	20	3.5	5	1.0
5	40	3.0	10	0.5	18	20	3.5	15	1.0
6	40	3.0	10	1.5	19	60	3.5	5	1.0
7	40	4.0	10	0.5	20	60	3.5	15	1.0
8	40	4.0	10	1.5	21	20	3.5	10	0.5
9	20	3.0	10	1.0	22	20	3.5	10	1.5
10	60	3.0	10	1.0	23	60	3.5	10	0.5
11	20	4.0	10	1.0	24	60	3.5	10	1.5
12	60	4.0	10	1.0	25	40	3.5	10	1.0
13	40	3.5	5	0.5	26	40	3.5	10	1.0
14	40	3.5	5	1.5	27	40	3.5	10	1.0
15	40	3.5	15	0.5					

Response Surface Methodology (RSM) and Analysis of Variance (ANOVA) were used to analyze the experimental data responses for surfactant degradation. ANOVA and RSM were performed using the JAMOVI 2.7.29 software. For the analysis, the level of confidence was set to be at least 95% (alfa value lower than 5%). The results were then adjusted for the second-order model Equation (1).

$$Y_i = \beta_0 + \sum_{i=1}^k \beta_i X_i + \sum_{i=1}^k \beta_{ii} X_i^2 + \sum_{i < j} \beta_{ij} X_i X_j \quad (1)$$

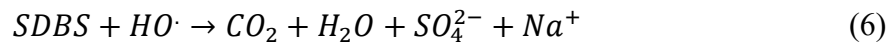
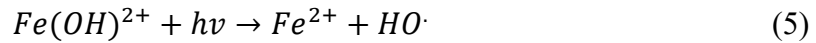
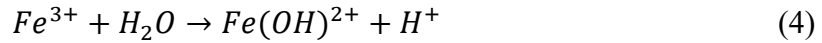
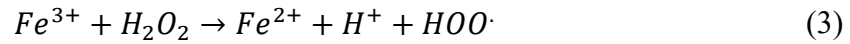
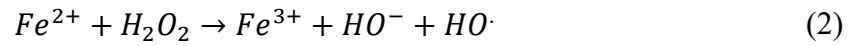
where β_0 , β_i , β_{ii} , and β_{ij} are the regression coefficients for the terms of interception, linear, square, and interaction, respectively. X_i and X_j are independent variables.

The significance of the model and each regression coefficient was assessed using ANOVA; based on the F and p-values. Non-significant terms ($p > 0.05$) were removed

stepwise when necessary, and the model was refitted to improve parsimony without compromising the quality of the fit. The adequacy of the final model was evaluated using the coefficient of determination (R^2), adjusted R^2 , and the lack-of-fit test. Response surface and contour plots were constructed to visualize the effects and interactions of the significant factors on SDBS degradation.

4.3. Fenton and photo-Fenton

The degradation of SDBS was investigated using Fenton and photo-Fenton processes. The main reactions involved in these processes are presented in Equations (2–5) and the Equation (6) shows the theoretical degradation of SDBS by these processes.



4.3.1 Fenton process

Fenton experiments were performed in a 100 ml beaker operated in batch mode with a magnetic stirrer to ensure homogeneous mixing. For each run, 100 mL of SDBS solution with an initial concentration of 100 mg L⁻¹ was transferred into the reactor. The pH was adjusted to the desired value by adding a small volume of NaOH and HCl solution and monitored using a pH meter.

After pH adjustment, the required volume of FeSO₄ solution was added to obtain the iron concentration according to the experimental design. The Fenton reaction was then initiated by adding the appropriate volume of H₂O₂ to obtain the target

concentration and when added the reaction time was set to zero. The process was maintained under constant stirring at room temperature for the selected reaction time.

At the end of the reaction time, aliquots were withdrawn and immediately quenched by adding 3 mL of sodium sulfite solution to consume the remaining H_2O_2 and stop the Fenton reaction.

4.3.2 Photo-Fenton process

Photo-Fenton experiments were conducted in a 1 L beaker with a magnetic stirrer, an external UV lamp, and a pump, using 1 L of SDBS solution at 100 mg L^{-1} . The solution pH was adjusted to the desired value using HCl and NaOH, and the required amount of FeSO_4 solution was added, as in the Fenton experiments. The reactor was continuously stirred.

The reaction time was initiated by switching on the UV lamp and simultaneously adding the volume of H_2O_2 solution needed to reach the target concentration. The UV source was a UVC-BRIGHT ultraviolet water sterilizer equipped with a 14 W low-pressure mercury lamp emitting at approximately 253 nm. The solution was continuously recirculated from the reservoir through the UVC chamber and back to the reservoir using a peristaltic pump (Watson Marlow 120S) at 200 rpm (Figure 3).

At predetermined reaction times, samples were collected and the reaction was quenched by adding 3 mL of sodium sulphite solution as described for the Fenton process.



Figure 3. Experimental setup for the photo-Fenton process.

4.4. High-Performance Liquid Chromatography

The residual concentrations of SDBS in the Fenton and photo-Fenton samples were determined using high-performance liquid chromatography (HPLC). All samples were filtered through hydrophobic PTFE syringe filters with a pore size of 0.45 μm . An aliquot of 20 μL of each filtered sample was manually injected into a Jasco PU-4180 pump system operated at a flow rate of 1.0 mL min^{-1} and a pressure between 11 and 12 MPa.

Chromatographic separation was conducted on an EC 250/4 NUCLEODUR 100-5 C18 ec column. The mobile phase consisted of pure water containing 0.05% (v/v) trifluoroacetic acid (solvent A) and acetonitrile (solvent B) in isocratic mode with 40% A and 60% B. Detection was performed using a diode-array detector (DAD, Jasco MD-4010) set at 223 nm.

Quantification was based on an external calibration curve constructed from standard solutions of SDBS prepared in the same mobile phase composition as the samples. The peak areas at 223 nm were plotted against the known SDBS concentrations to obtain the equation (Figure 4), which was used to calculate the residual SDBS concentration in the treated samples. The method provided good linearity over the working range, and no interfering peaks were observed at the retention time of SDBS under the selected chromatographic conditions. Representative HPLC chromatograms of the calibration standards and the synthetic SDBS solution are provided in Appendix A (Figures A1 and A2), respectively.

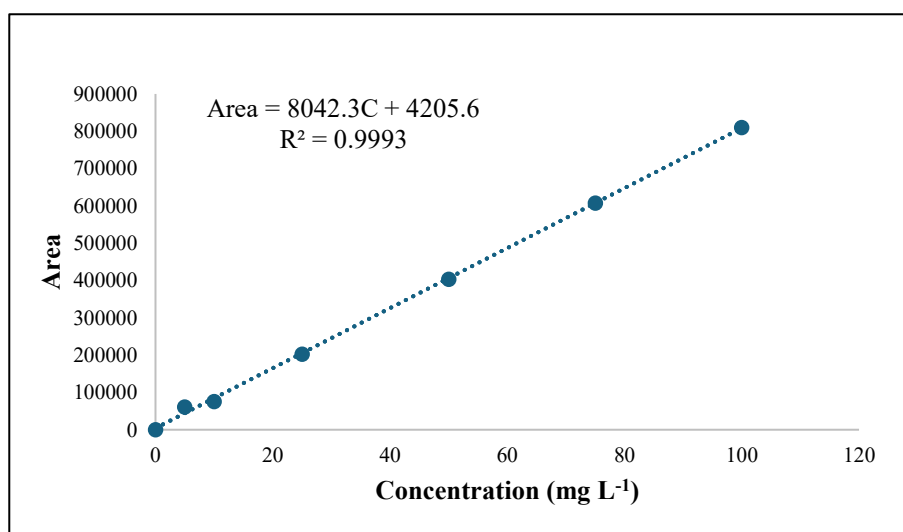


Figure 4. Calibration curve of SDBS in the range of 0-100 mg L^{-1} .

5. RESULTS AND DISCUSSION

5.1. SDBS Removal by Fenton Process

Table 3 shows the responses for SDBS degradation in Fenton obtained after the laboratory tests. The removal efficiencies varied between 22% and 52%, indicating that within the investigated ranges of the parameters, the process was able to achieve only partial degradation of the surfactant. The highest SDBS removal was 52.1%, respectively, in Run 27 (pH 3.5, reaction time 40 min, H₂O₂ 10 mg L⁻¹ and Fe²⁺ 1 mg L⁻¹). The chromatogram corresponding to the best Fenton condition is presented in Appendix A (Figure A3).

Table 3. SDBS removal by Fenton process.

Run	Reaction Time (min)	pH	H ₂ O ₂ (mg L ⁻¹)	Fe ²⁺ (mg L ⁻¹)	Removal (%)
1	40	3.0	5	1.0	35.8
2	40	3.0	15	1.0	40.1
3	40	4.0	5	1.0	42.1
4	40	4.0	15	1.0	43.7
5	40	3.0	10	0.5	29.6
6	40	3.0	10	1.5	33.4
7	40	4.0	10	0.5	28.5
8	40	4.0	10	1.5	29.5
9	20	3.0	10	1.0	44.1
10	60	3.0	10	1.0	40.1
11	20	4.0	10	1.0	48.4
12	60	4.0	10	1.0	45.3
13	40	3.5	5	0.5	22.4
14	40	3.5	5	1.5	26.5
15	40	3.5	15	0.5	40.6
16	40	3.5	15	1.5	36.1
17	20	3.5	5	1.0	37.2
18	20	3.5	15	1.0	39.8
19	60	3.5	5	1.0	33.8
20	60	3.5	15	1.0	46.4
21	20	3.5	10	0.5	28.9
22	20	3.5	10	1.5	31.1
23	60	3.5	10	0.5	27.9
24	60	3.5	10	1.5	40.4
25	40	3.5	10	1.0	43.5
26	40	3.5	10	1.0	30.2
27	40	3.5	10	1.0	52.1

The experimental data for the Fenton process was fitted to a second-order polynomial model, including the main effects, quadratic terms and two-way interactions of the coded factors: reaction time (B), pH (C), H₂O₂ concentration (D), and Fe²⁺ concentration (E). Table 5 presents the ANOVA table with the parameters and full model analysis obtained from the Jamovi software.

The full quadratic model yielded a coefficient of determination (R²) of 0.705, indicating that approximately 70% of the variability in SDBS degradation was explained by regression. However, the adjusted R² was only 0.360, and the global F-test and p-value were not statistically significant at the 5% level (F=2.04; p= 0.111). Therefore, the model was over-parameterized for the available number of experimental samples.

Table 4. Full model ANOVA table (Fenton).

	Estimate	t	p
Intercept	0.417	11612	<0.001
B	0.004	0.205	0.841
C	0.012	0.686	0.506
D	0.042	2330	0.038
E	0.016	0.913	0.379
B²	0.006	0.238	0.816
C²	0.003	0.111	0.913
D²	-0.018	-0.661	0.521
E²	-0.107	-3969	0.002
B * C	0.002	0.071	0.944
B * D	0.026	0.83	0.423
B * E	0.027	0.854	0.41
C * D	-0.007	-0.213	0.835
C * E	-0.007	-0.229	0.823
D * E	-0.022	-0.715	0.488
R²	Adjusted R²	F-test	p-value
0.705	0.36	2.04	0.111

With the full model ANOVA table (Table 4), only the linear effect factor D (H₂O₂ concentration; 0.038) and the quadratic effect factor E² (Fe²⁺ concentration; 0.002) were statistically significant (p<0.05). All other terms presented high p-values, indicating that, with this saturated model, their individual contributions were not statistically different from random variability.

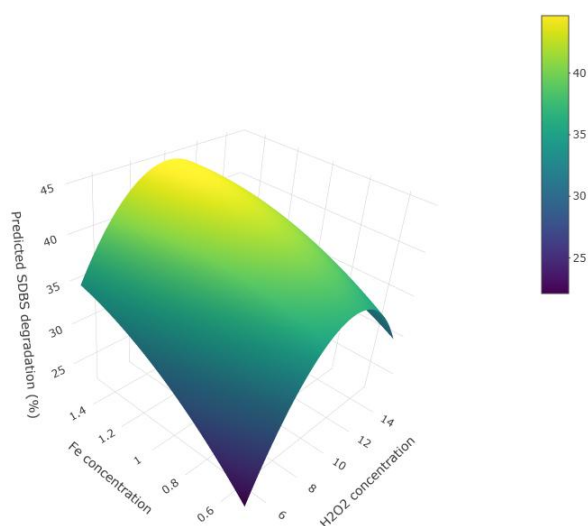
Table 5. Simplified model ANOVA table (Fenton).

	Estimate	t	p
Intercept	0.413	31.520	<0.001
D	0.042	2.859	0.009
E	0.016	1.121	0.274
E²	-0.105	-5.359	<0.001
R²	Adjusted R²	F-test	p-value
0.624	0.575	12.7	<0.001

The simplified ANOVA table (Table 5) shows a satisfactory fit, with $R^2 = 0.624$ and adjusted $R^2 = 0.575$, and a highly significant overall regression ($p < 0.001$). The linear effect of D was positive and significant, whereas the quadratic effect of E^2 was negative but highly significant. This indicates that hydrogen peroxide enhanced surfactant degradation within the studied range, and Fe exhibited a clear curvature effect, revealing an optimal concentration region. The principal equation with the reduced method is shown in Equation (6).

$$Y_i = 0.413 + 0.042D + 0.016E - 0.105E^2 \quad (6)$$

A 3D plot (Figure 5) was constructed to show the behavior of SDBS degradation against H_2O_2 and Fe^{2+} concentrations.

**Figure 5.** 3D response surface of SDBS degradation (Fenton).

The 3D response surface exhibited a curved profile, with higher SDBS degradation predicted in the region combining higher H_2O_2 concentrations with intermediate Fe^{2+}

levels, indicating that process performance depends on a balanced dosage of oxidant and catalyst. The nonlinear shape of the surface was consistent with the significant quadratic effect of iron concentration identified in the reduced model, revealing an optimum Fe^{2+} range beyond which additional iron does not enhance and may even reduce degradation efficiency due to scavenging effects. Within the studied domain, increasing H_2O_2 generally promoted SDBS degradation, but the response surface shows that this benefit is maximized only when Fe^{2+} remains close to its optimal level

5.2. SDBS Removal by photo-Fenton Process

The photo-Fenton experiments showed a wider and higher degradation range than the conventional Fenton process, with SDBS removal values varying from 50% to 76% under different conditions. As presented in Table 6, Run 27 also achieved the highest SDBS removal (75.54%) under the conditions: pH 3.5, reaction time of 40 min, H_2O_2 concentration of 10 mg L^{-1} and Fe^{2+} concentration of 1 mg L^{-1} . The chromatogram corresponding to the best photo-Fenton condition is presented in Appendix A (Figure A4).

This suggests that the combined effect of hydrogen peroxide, iron and UV irradiation significantly increased the system's oxidative efficiency. These results indicate that irradiation positively affected the degradation process by promoting the photoreduction of Fe^{3+} to Fe^{2+} , thus facilitating the regeneration of ferrous ions and sustaining hydroxyl radical production during the photo-Fenton reaction.

Table 6. SDBS removal by photo-Fenton process.

Run	Reaction Time (min)	pH	H ₂ O ₂ (mg L ⁻¹)	Fe ²⁺ (mg L ⁻¹)	Removal (%)
1	40	3.0	5	1.0	74.2
2	40	3.0	15	1.0	65.8
3	40	4.0	5	1.0	74.4
4	40	4.0	15	1.0	71.6
5	40	3.0	10	0.5	56.8
6	40	3.0	10	1.5	55.9
7	40	4.0	10	0.5	53.7
8	40	4.0	10	1.5	54.3
9	20	3.0	10	1.0	55.6
10	60	3.0	10	1.0	62.2
11	20	4.0	10	1.0	54.2
12	60	4.0	10	1.0	64.7
13	40	3.5	5	0.5	49.5
14	40	3.5	5	1.5	60.5
15	40	3.5	15	0.5	65.2
16	40	3.5	15	1.5	66.0
17	20	3.5	5	1.0	69.2
18	20	3.5	15	1.0	57.0
19	60	3.5	5	1.0	62.0
20	60	3.5	15	1.0	66.0
21	20	3.5	10	0.5	52.0
22	20	3.5	10	1.5	53.3
23	60	3.5	10	0.5	70.9
24	60	3.5	10	1.5	69.9
25	40	3.5	10	1.0	67.2
26	40	3.5	10	1.0	66.8
27	40	3.5	10	1.0	75.5

As in the Fenton process, the photo-Fenton process, Table 7 presents the ANOVA table with the parameters and the full model analysis obtained using Jamovi software. The experimental data of this process were elaborated using a second-order polynomial model including the main effects, quadratic terms and two-way interactions of the coded factors B, C, D and E.

The initial quadratic model evaluated for the photo-Fenton process did not show a statistically significant overall fit at the 5% level, with an R^2 of 0.573, an adjusted R^2 of 0.075, and a non-significant test ($p = 0.408$). The model explained part of the response variation, but its predictive capacity was limited. With all the terms tested in the full model, only the quadratic term related to iron concentration (E^2) was statistically

significant ($p = 0.023$), showing that the response was strongly influenced by the non-linear behavior of Fe rather than by the simple linear effects of the other factors.

Table 7. Full model ANOVA table (photo-Fenton).

	Estimate	t	p
Intercept	0.704	16.134	<0.001
B	0.046	2.125	0.055
C	0.002	0.09	0.93
D	0.002	0.069	0.946
E	0.01	0.463	0.651
B²	-0.048	-1.460	0.17
C²	-0.04	-1.213	0.248
D²	0.009	0.27	0.792
E²	-0.085	-2.604	0.023
B * C	0.01	0.266	0.795
B * D	0.041	1.099	0.293
B * E	-0.006	-0.152	0.882
C * D	0.014	0.383	0.708
C * E	0.004	0.101	0.922
D * E	-0.026	-0.7	0.497
R²	Adjusted R²	F-test	p-value
0.573	0.075	1.15	0.408

According to the simplified ANOVA table (Table 8), the retained terms in the reduced model were the intercept, factor B, factor E, and the quadratic term E². Factor B remained statistically significant ($p = 0.024$), whereas linear term E was not significant ($p = 0.603$). The negative coefficient associated with E² indicates a curve response, suggesting the existence of an optimum iron concentration within the studied domain, above which the degradation efficiency decreases.

Table 8. Simplified model ANOVA table (photo-Fenton).

	Estimate	t	p
Intercept	0.662	38.629	<0.001
B	0.046	2.419	0.024
E	0.01	0.528	0.603
E²	-0.069	-2.702	0.013
R²	Adjusted R²	F-test	p-value
0.369	0.286	4.48	0.013

Although the reduced model was statistically significant overall ($F = 4.48$ and $p = 0.013$), its coefficients of determination were moderate ($R^2 = 0.369$ and adjusted $R^2 =$

0.286). This means that the model captured the main tendency of the system, but not all the experimental variability. Therefore, the reduced equation is useful for identifying the principal trend and optimum region but should be interpreted with caution when used for prediction. The principal equation with reduced method is shown in Equation (7).

$$Y_i = 0.662 + 0.046B + 0.01E - 0.069E^2 \quad (7)$$

A 3D plot (Figure 6) was constructed to show the behavior of SDBS degradation against reaction time and Fe^{2+} concentration.

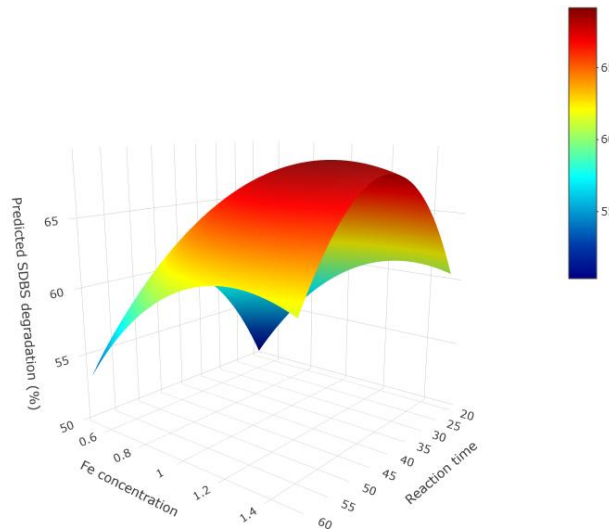


Figure 6. 3D response surface of SDBS degradation (photo-Fenton).

The 3D response surface exhibited a curved profile with higher degradation values observed in the intermediate region of the experimental domain, indicating that the process performance depends on an optimal balance between the evaluated variables. The nonlinear shape of the surface was consistent with the significant quadratic effect of iron concentration, suggesting an optimum Fe level. Increasing the iron dosage or reaction time does not necessarily improve the degradation efficiency, as the response tends to level off or decrease under excessive conditions.

5.3. Comparison between Fenton and photo-Fenton Processes

A comparison between the Fenton and photo-Fenton processes showed that both systems were able to degrade SDBS but with different performance profiles. The photo-Fenton process achieved the highest experimental removal compared to the Fenton process,

indicating that UV radiation enhanced the oxidative capacity of the system (Miranzadeh et al., 2016). This behavior is consistent with the role of light in the regeneration of Fe^{2+} and increases the formation of reactive radicals, which generally improves the oxidation of recalcitrant organic compounds (Aslam, 2024). The photo-Fenton process was more efficient than the Fenton process for pollutant removal using UV irradiation because of the enhanced Fe^{2+} regeneration and hydroxyl radical formation. However, the results clearly demonstrate that increasing the reagent dosage does not necessarily lead to a higher removal efficiency. pH, Fe^{2+} dosage, and H_2O_2 concentration are decisive factors for optimizing the process (Senguttuvan et al., 2025).

From a statistical standpoint, both processes showed curvature in the response surface, indicating the presence of optimal operating regions rather than a linear increase in degradation with the reagent dosage. In the photo-Fenton case, the reduced model was statistically significant ($p = 0.013$), with B and E^2 as the main influential terms, whereas the Fenton model displayed a different response pattern and a stronger overall fit to the experimental data.

6. CONCLUSIONS

This study aimed to evaluate how Fenton and photo-Fenton Advanced Oxidation Processes (AOPs) degrade SDBS, a common and persistent pollutant. HPLC was used to carefully track the degradation in both chemical systems. Both methods successfully broke down SDBS, but they showed different levels of effectiveness.

The photo-Fenton process performed better than the standard Fenton process. It achieved higher removal efficiency. This improved performance is due to UV radiation, which helps regenerate Fe^{2+} ions from Fe^{3+} and creates more reactive hydroxyl radicals. These radicals are crucial for breaking down the tough surfactant structure.

For the Fenton process, SDBS removal ranged from 22% to 52%. The best results were seen at pH 3.5, a reaction time of 40 minutes, 10 mg L^{-1} of H_2O_2 , and 1.0 mg L^{-1} of Fe^{2+} . In contrast, the photo-Fenton process achieved SDBS removal from 50% to 76% under similar conditions, with the highest degradation in Run 27. This clearly shows that while both processes work, photo-Fenton is more effective, confirming the benefit of UV light.

Statistical analysis using RSM and ANOVA helped us understand the process variables. For the photo-Fenton system, the quadratic model was significant ($p = 0.013$). Iron concentration had a strong negative quadratic effect in both systems. This means that there is an optimal range for degradation, not just a continuous increase with more reagents. The 3D response surfaces confirmed that maximum degradation happens within a specific intermediate region.

Our findings also showed that simply increasing the amount of reagents or reaction time does not always lead to better removal. Therefore, carefully adjusting pH, Fe^{2+} , and H_2O_2 concentrations is key to optimizing the process.

From an environmental view, this research supports Sustainable Development Goal 6 (Clean Water and Sanitation) by focusing on water treatment strategies. It also relates to Goal 12 (Responsible Consumption and Production) by promoting better pollutant management, and Goal 14 (Life Below Water) by helping reduce harmful discharges and protect aquatic life.

7. Future Work

The following recommendations are proposed for future work:

- Perform the optimization over wider parameters range, including different Fe^{2+} and H_2O_2 concentrations;
- Compare different quantification methods for the same experimental tests;
- Investigate other anionic surfactants to compare degradation behavior under the same conditions;
- Investigate the possibility of using the solar photo-Fenton process as more sustainable alternative;
- Compare real wastewater containing surfactant with the synthetic surfactant solutions;

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Appendices

Appendix A. HPLC chromatograms related to SDBS analysis.

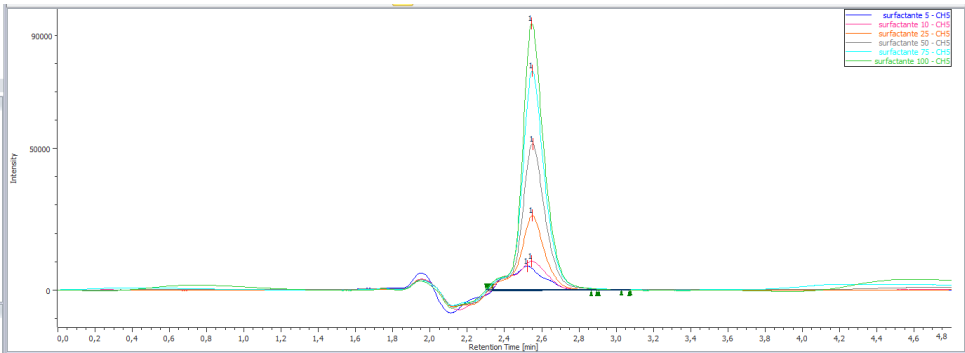


Figure A1. HPLC chromatograms of SDBS standards.

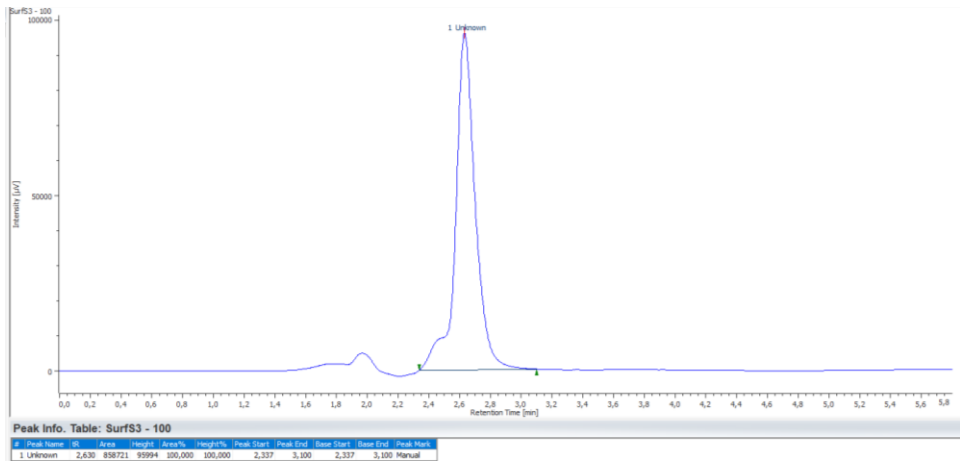


Figure A2. HPLC chromatogram of synthetic SDBS solution.

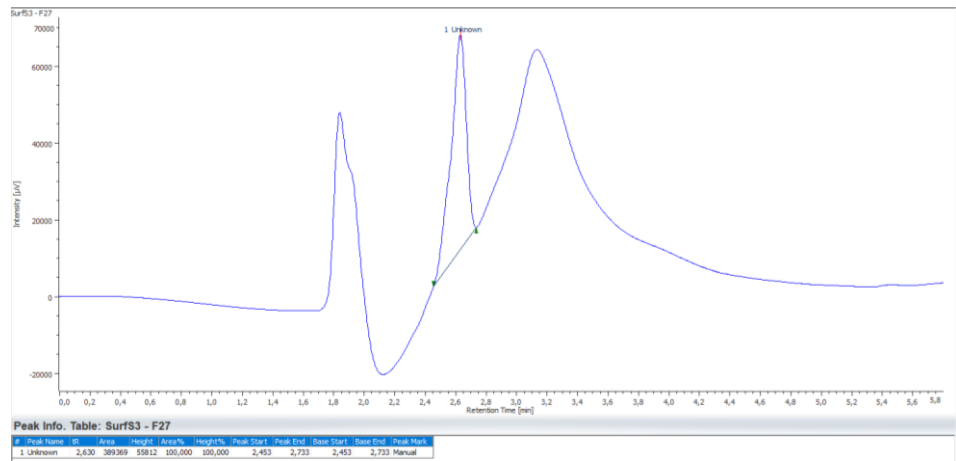


Figure A3. HPLC chromatogram of the best Fenton condition.

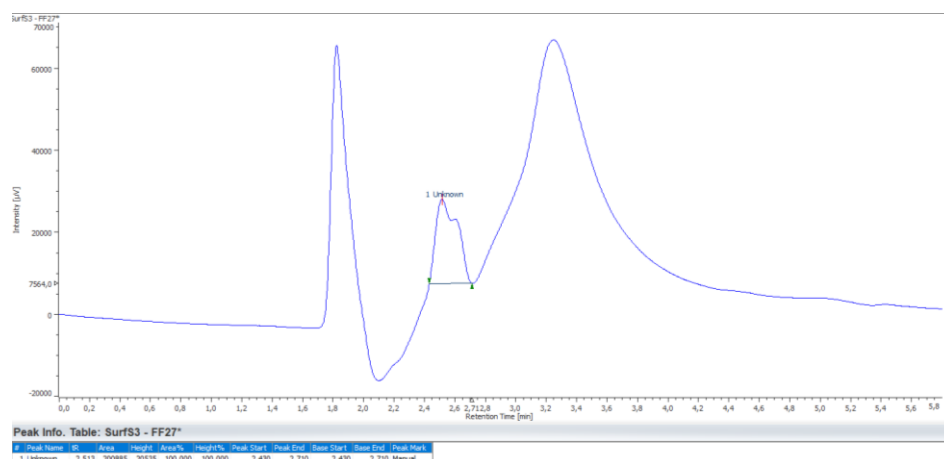


Figure A4. HPLC chromatogram of the best photo-Fenton condition.