Instituto Politécnico de Bragança
Escola Superior de Tecnologia e Gestão

SURFACTANT REMOVAL FROM INDUSTRIAL EFFLUENTS BY MORINGA SEED-ASSISTED COAGULATION AND PHOTO-FENTON OXIDATION

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Master's dissertation presented to the Escola Superior de Tecnologia e Gestão of Instituto Politécnico de Bragança to obtain a Master's degree in Chemical Engineering.

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Bragança, 2026

This thesis is first and foremost dedicated to my parents, whose love, sacrifices, and unwavering support made this journey possible. In addition, I dedicate this work to my entire family for their unwavering support and faith in me.

To my friends who stood by me throughout this journey, offering support, understanding, and strength—thank you. To everyone who helped me along the way, and even to those who smiled at me and offered words of encouragement, your kindness meant more than you know.

Finally, I dedicate this thesis to myself for the perseverance, resilience, and determination to keep going despite every challenge.

"dedicatory"

ACKNOWLEDGEMENTS

First and foremost, I want to sincerely thank **Prof. Ramiro José Espinheira Martins**, my supervisor, for all of his help, support, and encouragement during this project. Their knowledge, tolerance, and helpful criticism have greatly influenced this work and improved my comprehension of scientific study.

I would also like to extend my heartfelt thanks to **my colleagues and classmates**, whose collaboration, discussions, and moral support made this journey both productive and enjoyable. Working alongside such dedicated individuals has been a source of great inspiration and motivation.

My sincere appreciation also goes to the **technical and administrative staff of The Chemical Department and Analytical Laboratory,** and specifically to **Dr Maria João Afonso** for her assistance and for providing the resources and facilities necessary to complete this study successfully.

A special word of thanks goes to **my family** — to my parents, for their unconditional love, endless patience, and unwavering belief in me; to my brothers and sister, for their encouragement and understanding; and to all my loved ones, who have supported me in every possible way. Without their constant support and sacrifices, this achievement would not have been possible.

Finally, I would like to express my gratitude to everyone who, in one way or another, contributed to the completion of this work. To all of you, I owe my deepest thanks.

ABSTRACT

Water pollution caused by surfactant-containing industrial effluents has become an important environmental concern due to the extensive use of detergents in domestic and industrial applications. Among these pollutants, sodium dodecyl sulfate (SDS) is one of the most widely used anionic surfactants and is frequently detected in wastewater because of its low biodegradability and adverse effects on aquatic ecosystems. Consequently, the development of efficient and sustainable treatment technologies for surfactant removal is of increasing importance.

This study investigated the removal of SDS from synthetic industrial wastewater using a combined treatment consisting of Moringa oleifera seed-assisted coagulation followed by the Photo Fenton oxidation process. The coagulation stage was evaluated by studying the effects of coagulant dosage, initial surfactant concentration, and pH on SDS removal. Subsequently, the Photo Fenton process was optimized by evaluating the influence of pH, hydrogen peroxide dosage, ferrous ion concentration, and UV irradiation using Response Surface Methodology (RSM).

The coagulation process achieved a maximum SDS removal efficiency of 55.6% under the optimum operating conditions. The subsequent Photo Fenton treatment significantly improved the removal efficiency, reaching 96% SDS removal. Process optimization using Response Surface Methodology predicted a maximum removal efficiency of 99.4% under the optimum conditions of pH 3, 1 mL of H_2O_2, 270 mg of $FeSO_4 \cdot 7H_2O$, and a flow rate (Q) of 84 mL min^{-1}.

The results demonstrate that combining Moringa oleifera-assisted coagulation with the Photo Fenton process is an effective and environmentally sustainable strategy for removing anionic surfactants from industrial wastewater. The integration of a natural coagulant with an advanced oxidation process provides a promising alternative for improving wastewater treatment efficiency while reducing reliance on conventional chemical treatments.

Keywords: Anionic surfactant, coagulation, industrial effluent, Moringa oleifera, Photo-Fenton, sodium dodecyl sulfate.

RESUMO

A poluição da água causada por efluentes industriais contendo surfactantes constitui um importante desafio ambiental devido à utilização generalizada de detergentes em aplicações domésticas e industriais. Entre estes poluentes, o lauril sulfato de sódio (SDS) é um dos surfactantes aniónicos mais utilizados e é frequentemente detetado em águas residuais devido à sua baixa biodegradabilidade e aos seus efeitos adversos nos ecossistemas aquáticos. Neste contexto, o desenvolvimento de tecnologias de tratamento eficientes e sustentáveis para a remoção de surfactantes assume uma importância crescente.

O presente estudo investigou a remoção de SDS de águas residuais industriais sintéticas utilizando um tratamento combinado constituído por coagulação assistida por sementes de Moringa oleifera, seguida de oxidação pelo processo Foto-Fenton. A etapa de coagulação foi avaliada através do estudo da influência da dosagem do coagulante, da concentração inicial de surfactante e do pH na eficiência de remoção do SDS. Posteriormente, o processo Foto-Fenton foi otimizado avaliando-se o efeito do pH, da dosagem de peróxido de hidrogénio, da concentração de ferro e do caudal, recorrendo à Metodologia de Superfície de Resposta (Response Surface Methodology – RSM).

O processo de coagulação permitiu alcançar uma eficiência máxima de remoção de SDS de 55,6% nas condições ótimas de operação. A aplicação subsequente do processo Foto-Fenton aumentou significativamente a eficiência de remoção, atingindo 96% de remoção de SDS. A otimização do processo através da Metodologia de Superfície de Resposta previu uma eficiência máxima de remoção de 99,4%, nas condições ótimas de pH 3, 1 mL de H_2O_2, 270 mg de $FeSO_4 \cdot 7H_2O$ e caudal (Q) de 84 mL min^{-1}.

Os resultados demonstram que a combinação da coagulação assistida por *Moringa oleifera* com o processo Foto-Fenton constitui uma estratégia eficaz e ambientalmente sustentável para a remoção de surfactantes aniónicos de águas residuais industriais. A integração de um coagulante natural com um processo de oxidação avançada representa uma alternativa promissora para melhorar a eficiência do tratamento de águas residuais, reduzindo simultaneamente a dependência de tratamentos químicos convencionais.

PALAVRAS-CHAVE: Coagulação; efluente industrial; Foto-Fenton; lauril sulfato de sódio; Moringa oleifera; surfactante aniónico.

TABLE OF CONTENTS

INDEX OF TABLES

INDEX OF FIGURES

INDEX OF ABBREVIATIONS

AOP: Advanced Oxidative Processes.

BOD: Biological Oxygen Demand.

COD: Chemical Oxygen Demand.

MBAS: Methylene Blue-Anionic Surfactant.

MO: Moringa Oleifera.

PF: Photo-Fenton.

RSM: Response Surface Methodology.

SDBS: Sodium Dodecylbenzene Sulfonate.

SDS: Sodium Dodecyl Sulfate.

TDS: Total Dissolved Solids.

TSS: Total Suspended Solids.

1. INTRODUCTION

The continuity of life on Earth is closely linked to the availability of water and the preservation of its quality, a vital natural resource. Access to clean, safe water is a fundamental human right, and the global water crisis is impacting many people's lives **(Sufiani et al., 2023).** The need for fresh water has increased due to environmental degradation, urbanisation, industrialisation, and the rapid growth of the human population, all of which seriously impair water quality **(Luo et al., 2023).**

Drinking water is obtained from two main natural sources: surface water and groundwater. Surface water refers to water present in rivers, lakes, streams, and reservoirs, whereas groundwater is accessed through wells, boreholes, and similar extraction systems. These resources are essential for a wide range of applications, including domestic use, agriculture, and industrial activities. Despite their importance, both surface and groundwater are increasingly exposed to contamination. Pollutants originating from agricultural runoff, industrial discharges, and domestic waste contribute significantly to the deterioration of water quality. The continuous release of wastewater into natural water bodies further accelerates this degradation. Wastewater, generated by residential, commercial, industrial, and agricultural sectors, contains various dissolved and suspended pollutants. It is estimated that hundreds of trillions of cubic meters of wastewater are produced globally each year, highlighting the scale of this environmental challenge.

Pathogens, suspended solids, microplastics, radioactive materials, and other organic and inorganic components are examples of water contaminants. Heavy metals and dyes are leading causes of water quality decline **(Algarni & Al-Mohaimeed, 2022).**

Among the various contaminants found in industrial wastewater, surfactants have emerged as a significant environmental concern due to their widespread use in household and industrial detergents, textile manufacturing, cosmetics, pharmaceutical products, and car wash facilities. Surfactants are amphiphilic compounds that reduce the surface tension between liquids and solids, making them indispensable in cleaning and industrial processes. However, their extensive use has resulted in increasing concentrations in aquatic environments, where they can persist and adversely affect water quality, aquatic organisms, and wastewater treatment systems. Anionic surfactants, particularly sodium dodecyl sulfate

(SDS), are among the most commonly detected compounds because of their high production and widespread application.

A water or wastewater treatment plant employs several unique methods to remove contaminants that could harm human health, including chemical substances, microorganisms, and suspended particles. Water and wastewater treatment technologies are generally classified into two main categories: conventional and advanced (non-conventional) processes. Conventional treatment methods include coagulation, flocculation, sedimentation, filtration, adsorption, and fluoridation, which are widely applied for the removal of suspended solids and other contaminants. Advanced treatment technologies, such as membrane filtration, ozonation, ultraviolet (UV) irradiation, and biological activated carbon processes, are employed to remove persistent pollutants and improve effluent quality **(Pakharuddin et al., 2021)**. These processes are widely used in the treatment of both drinking water and industrial wastewater, as shown in Figure 1.

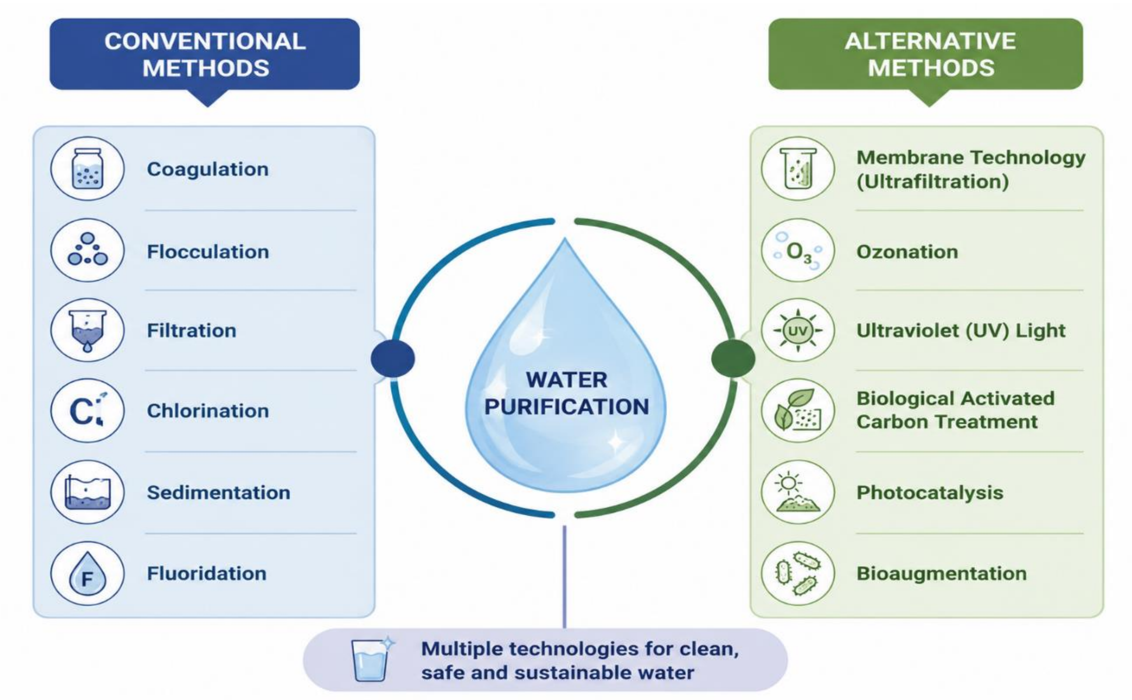

Figure 1. Methods available for the treatment of water **(Kumar et al., 2024)**.

Conventional wastewater treatment technologies are often insufficient for the complete removal of surfactants because of their relatively low biodegradability and the complexity of industrial effluents. Consequently, increasing attention has been directed toward sustainable treatment technologies that combine environmentally friendly materials with advanced oxidation processes. Natural coagulants, such as *Moringa oleifera* seed extracts, have demonstrated considerable potential for reducing pollutant loads while minimising sludge production and chemical consumption. Furthermore, the Photo Fenton process is recognised as an efficient advanced oxidation technology capable of generating highly reactive hydroxyl radicals that degrade persistent organic pollutants. The combination of natural coagulation with Photo Fenton oxidation therefore represents a promising and sustainable strategy for treating surfactant-containing industrial wastewater.

In this combined approach, coagulation acts as a pre-treatment step that removes suspended matter and part of the surfactant load, while the subsequent Photo Fenton process oxidises the remaining dissolved organic pollutants. This sequential treatment can improve overall removal efficiency while reducing chemical consumption and operational costs.

In this context, the present study investigates the removal of sodium dodecyl sulfate (SDS) from synthetic industrial wastewater using a combined treatment consisting of coagulation with *Moringa oleifera* seed extract followed by Photo Fenton oxidation. The study evaluates the influence of operational parameters on surfactant removal efficiency and chemical oxygen demand (COD) reduction, contributing to the development of sustainable and efficient wastewater treatment technologies.

2. OBJECTIVES

2.1 General objective

Examine how well coagulation (green coagulant) and photo Fenton processes degrade sodium dodecyl sulfate, a common anionic surfactant found in homes and businesses.

2.2 Specific objective

1. Review of analytical methods to be used.
2. Research and preparation of a green coagulant using Moringa oleifera seed.
3. Pre-treatment of synthetic effluent using different dosages of Moringa coagulant
4. Experimental trials by photo Fenton process (temperature, pH, H_2O_2, Fe^{2+}, UV intensity).

3. STATE OF THE ART

3.1 Chemical Structures and Classifications of Detergents

Surfactants such as soaps and detergents contain molecules with two main parts: a hydrophobic (water-repelling) hydrocarbon chain and a hydrophilic (water-attracting) head group. The hydrophobic part is usually a long alkyl chain derived from fatty acids or similar compounds. In contrast, the hydrophilic part may consist of polar or ionic functional groups that interact with water. This dual structure allows the molecules to position themselves at interfaces between water and oily or solid substances. As a result, the hydrophobic portion attaches to grease or dirt, while the hydrophilic portion remains in water, enabling soil removal during washing **(Khalfallah, 2023).**

Surfactants are commonly classified into four main groups based on the electrical charge of their hydrophilic head in aqueous solution. **Anionic surfactants** carry a negative charge when dissolved in water and include soaps and many widely used synthetic detergents. **Cationic surfactants** possess a positively charged head group in solution. **Non-ionic surfactants** do not form ions in water and therefore remain electrically neutral. **Amphoteric (or ampholytic) surfactants** contain both positive and negative functional groups and may behave as either anionic or cationic, depending on the pH of the solution **(Khalfallah, 2023).**

3.1.1 Anionic Surfactants

Among synthetic detergents, anionic surfactants are the most widely used due to their strong cleaning power. These detergents usually consist of molecules with a long hydrophobic hydrocarbon chain and a negatively charged hydrophilic group, such as a sulfonate. This structure allows the molecules to interact with both water and oily substances, enabling dirt to be removed during washing. A common example is linear alkylbenzene sulfonate, which is widely used in household and industrial detergents and is produced through sulfonation reactions during manufacturing **(Al Ghatta, Contreras Aravenas, & Wu, 2022).**

3.1.1.1 Sodium Dodecyl Sulfate (SDS)

Because of their advantageous physicochemical properties, such as their ability to reduce the medium's surface tension and solubilise water-insoluble substances, surfactants, known as surface-active agents, are widely used across various scientific and technological fields. Sodium dodecyl sulfate (SDS) is a common anionic surfactant used in many industrial sectors, as well as commercial detergents, soaps, shampoos, and shower gels. However, its waste is disposed of directly into surface water bodies or sewage treatment plants after use, resulting in significant long-term ecological impacts and health issues for people. Thus, to preserve water purity, this surfactant must be removed from the environment. **(da Cunha et al., 2024).**

3.1.1.2 Sodium Dodecylbenzene Sulfonate (SDBS)

The most widely used anionic surfactant in homes and other industries is sodium dodecylbenzene sulfonate (SDBS), which is also used as a detergent. However, because industrial and household wastes are not properly disposed of, SDBS may end up in various water bodies due to its widespread production and use. SDBS residues in water seriously harm ecology and human health. In this regard, it is desirable to efficiently remove SDBS from various environmental fluids **(Yu et al., 2024).**

3.2 The Environmental Impact of Wastewater from Detergent Industries

The environmental impact of wastewater from detergent and cleaning industries is largely determined by its high chemical content rather than its quantity. Wastewater from industrial and household detergent use is a major contributor to numerous environmental issues **(Pandey & Gopal, 2010).** Wastewater from detergent manufacturing is typically rich in organic matter, including surfactants and their degradation products, which can contribute to high chemical oxygen demand (COD) and pose environmental challenges **(Sarmah & Khan, 2020).** Measured BOD_5 concentrations (250–6,300 mg L^{-1}) and COD levels (2,400–26,400 mg L^{-1}) reveal a low BOD_5/COD ratio, highlighting the limited biodegradability of this type of wastewater. Furthermore, high levels of sulfates, ammonia, and methylene blue active substances (MBAS), ranging up to 16,900 mg L^{-1}, were also observed. pH was another crucial factor, varying widely (2.7–11.6). The properties of wastewater from several detergent industrial units were published **by Cavalli et al. (1993).** The findings demonstrated that wastewater had a high COD concentration.

Depending on the type of carbon-to-carbon bond they contain, distinct classes of organic molecules exert different influences on effluent treatment. Even when dual bonds are present, aromatic compounds exhibit high resistance to reaction with other components. Furthermore, many ring compounds, both aromatic and non-aromatic, exhibit remarkable resistance to biological degradation. Because different synthetic detergents have distinct structures, they also exhibit varying degrees of resistance and behaviours to sewage treatment processes. **(Eckenfelder, 1989).**

Domestic and industrial wastewater discharge introduces varying concentrations of detergents into soils and aquatic environments. These detergents affect wastewater treatment processes and the plants and animals in natural ecosystems. Detergents can have various consequences, including reducing natural water quality, altering soil and water pH, causing eutrophication, decreasing light transmission, and increasing salinity in water sources, due to their low biodegradability, foaming, toxicity, and high particle adsorption. They significantly affect both the cost of treatment and the effectiveness of biological treatment procedures. High detergent concentrations in wastewater can reduce gas production in anaerobic systems and the efficiency of aerobic treatment systems. Since detergent is essential to human existence, its manufacture and use cannot be stopped. Therefore, several strategies should be employed to lessen their impact on biological treatment processes, the environment, and human health **(Mousavi & Khodadoost, 2019).** Figure 2 shows some effects and the distribution of detergents in the environment.

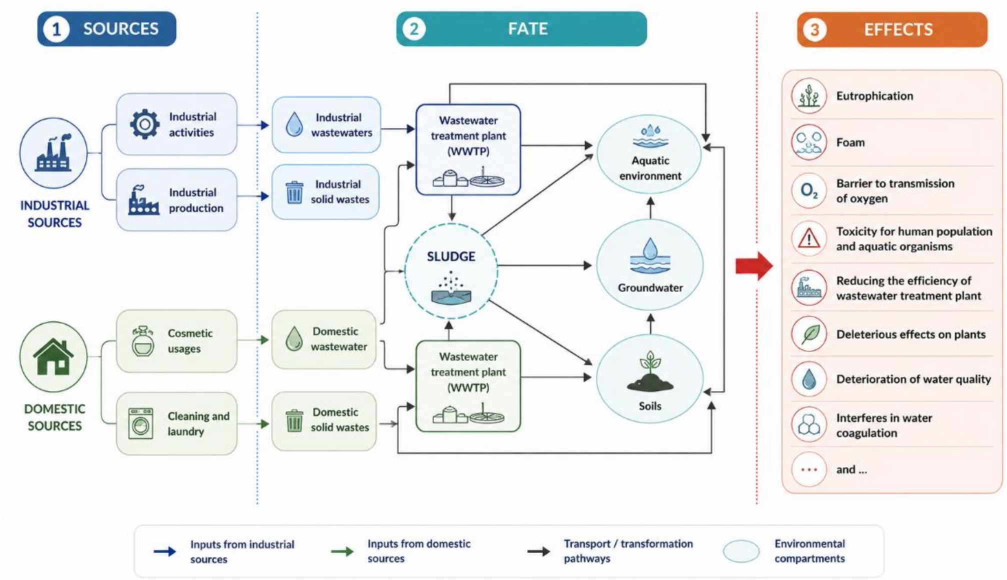

Figure 2. Distribution and effects of detergents in the environment

(Mousavi & Khodadoost, 2019).

3.2.1 Carwash Wastewater

Wastewater from vehicle washes is among the most contaminated and most impurity-rich. The reasons included sand and particles, oil and grease, detergent, phosphates, surfactants, and hydrofluoric acid. **(Mandac et al., 2014)**.

The direct discharge of car wash wastewater containing heavy metals into the sewer system may negatively impact the efficacy of sewage treatment processes or, at a minimum, impose an additional burden on the sewage treatment facility **(Al-Gheethi et al., 2013)**.

The water used for car washes is unregulated in terms of quality. Consequently, coagulation and flocculation techniques, which are effective for turbidity control and cost-effective, may be utilised to treat and repurpose wastewater from high-turbidity vehicle washes **(Firdaus, 2013)**.

Car wash effluents typically contain a variety of **physicochemical pollutants** including **total dissolved solids (TDS)**, **total suspended solids (TSS)**, **biochemical oxygen demand (BOD)**, **chemical oxygen demand (COD)**, **oil and grease**, **surfactants**, and trace **metal ions** such as zinc and lead, reflecting contaminants introduced by vehicle cleaning chemicals, surface abrasion, and lubricant residues **(Dadebo et al., 2022).** These Parameters are summarised in Table 1, giving an idea about the characterisation of carwash wastewater

Table 1. The characteristics of carwash wastewater **(Awad et al.,2023).**

Parameters	Unit	Range
pH	----	6.3–8.7
Turbidity	NTU	7.7–1,400
Total Suspended Solids	mg L^{-1}	60–2,458
Total Dissolved Solids	mg L^{-1}	120–7,920
Chemical Oxygen Demand	mg L^{-1}	59–1,810
Biochemical oxygen demand	mg L^{-1}	10.5–650
Anionic surfactant	mg L^{-1}	0.7–51

3.3 Challenges and Solutions in Treating Surfactants

Biological mechanisms are the primary means of treating surfactants. However, this treatment method may pose challenges due to its poor biodegradability. Adsorption and other physical-chemical treatment techniques are also employed. However, they require additional chemical additives, which increase sludge generation. Advanced oxidative processes (AOPs) are an extra-effective method of eliminating harmful pollutants from the environment. Strong oxidising species are produced during AOPs, a series of chemical processes that completely mineralise organic molecules through non-selective reactions. **(da Cunha et al., 2024).**

Coagulation and flocculation play a key role in the treatment of wastewater. Conventional treatment typically relies on chemical agents such as ferric sulphate, ferrous sulphate, ferric chloride, and ferric chloride sulphate as coagulants and flocculants. Recently, increasing attention has been given to natural alternatives. Unlike synthetic chemicals, these materials are considered more environmentally friendly, as they can minimize the formation of toxic by-products, including carcinogenic compounds, while also being cost-effective. Therefore, the use of natural coagulants represents a promising approach to reduce chemical consumption and enhance water quality for safe reuse **(Mohamed et al., 2014a).**

3.3.1 Advanced Oxidation Process

The breakdown of persistent pollutants that are not eliminated by biological processes may be possible with advanced oxidation processes (AOPs). The production of extremely reactive $HO^{\bullet}$ radicals, which can oxidise a wide range of organic molecules, is linked to the high efficiency of AOPs. Complete mineralisation to water, CO_2, and mineral compounds may eventually be achieved. The AOPs most widely explored include UV/H_2O_2, photocatalysis, and the photo Fenton process (PF) **(Esteban García et al., 2021)**.

By producing short-lived free radicals like hydroperoxide ($\boldsymbol{HO_2^{\cdot}}$) Moreover, hydroxyl radical (·OH) and PF technology quickly and non-selectively oxidise organic and inorganic pollutants in wastewater, converting them into carbon dioxide, water, or biodegradable components. It enhances the effluent's biodegradability, reduces its toxicity, and improves the effectiveness of subsequent treatments **(San Juan-Garisado et al., 2024)**.

PF increases the process's efficiency by combining the Fenton process's activity with ultraviolet (UV) light exposure to promote iron regeneration and (·OH) production. PF is the breakdown of (H_2O_2) when the reducing agent ferrous ion (Fe^{2+}) is present. Fenton-Like reactions occur in an acidic medium to yield (˙OH) and ($HO_2^{\cdot}$) with reduced oxidative power. According Equations 1-4, the reaction is autocatalytic due to the oxidation of (Fe^{2+}) to the ferric ion (Fe^{3+}) **(San Juan-Garisado et al., 2024).**

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^{-} + \cdot OH \quad (1)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\cdot} + H^{+} \quad (2)$$

$$Fe^{2+} + HO_2^{\cdot} \rightarrow Fe^{3+} + HO_2^{-} \quad (3)$$

$$Fe^{3+} + HO_2^{\cdot} \rightarrow Fe^{2+} + O_2 + H^+ \quad (4)$$

UV radiation causes charge transfer on Fe^{3+} complexes, leading to their dissociation into Fe^{2+} and ·OH; in this way, the reduced iron Fe^{2+} reacts again with H_2O_2 to produce more ·OH, which can increase process efficiency and reduce sludge production.

Compared the use of Fenton reagents (Fe^{2+} or Fe^{3+} with H_2O_2 in the presence or absence of solar radiation), photo-catalysis (TiO_2 with solar irradiation), and photo-degradation using solar sensitiser (pyrylium salt) to the degradation of two commercial anionic surfactants, such as sodium dodecyl sulfate and dodecylbenzenesulfonate. Their additional research revealed that the photo Fenton process employing solar radiation (0.1 mM Fe^{2+} or Fe^{3+} and 1 mM H_2O_2) achieved a higher surfactant degradation rate than the solar-TiO2 treatment. They also showed that adding the solar sensitiser did not effectively degrade the surfactants **(Amat et al., 2004).**

The photo Fenton process performs better at pH 3.0 when the hydroxy-(Fe^{3+}) complexes are more soluble, and $Fe(OH)^{2+}$ is more photoactive, based on **(Amat et al., 2004)**.

Studies suggest that photo Fenton oxidation is more effective than the conventional Fenton process. The use of solar energy reduces costs but may slow pollutant degradation. Acidic conditions (around pH 3) are favourable, likely because carbonate and bicarbonate ions are converted into carbonic acid, which is less reactive with hydroxyl radicals.

The photo Fenton technique was used by **Malakootian et al. (2016)** to remove sodium dodecyl sulphate from soft drink effluent and synthetic solutions. In 30 minutes, they removed his surfactant from the sample with 71% effectiveness.

3.3.2 Natural coagulant

Green coagulants, sometimes known as natural coagulants, are less harmful to both people and the environment. Plant-based coagulants, for example, are less toxic, biodegradable, non-corrosive, and generate less sludge. More sustainable wastewater treatment is facilitated by applied research on natural coagulants **(Balbinoti et al., 2024).**

Investigating the use of natural coagulants in wastewater treatment has become a viable alternative due to their benefits, including affordability, ubiquity, and the absence of non-biodegradable chemicals. According to Gonçalves et al. (2024), Moringa oleifera is a popular natural coagulant for water treatment due to its water-soluble cationic proteins and its ability to aggregate and precipitate through charge destabilisation. These proteins can be extracted using saline, ethanol, or distilled water, all of which have proven effective for cleaning industrial effluent.

In a previous study **Mohamed et al. (2014b)** investigated the efficiency of Moringa oleifera as a natural coagulant compared with synthetic common coagulants for treating car wash wastewater. The study indicated that M. oleifera contains coagulating substances capable of removing turbidity, chemical oxygen demand (COD), Biochemical oxygen demand (BOD), and Total suspended solids (TSS). Figure 3 illustrates the coagulation mechanism for MO.

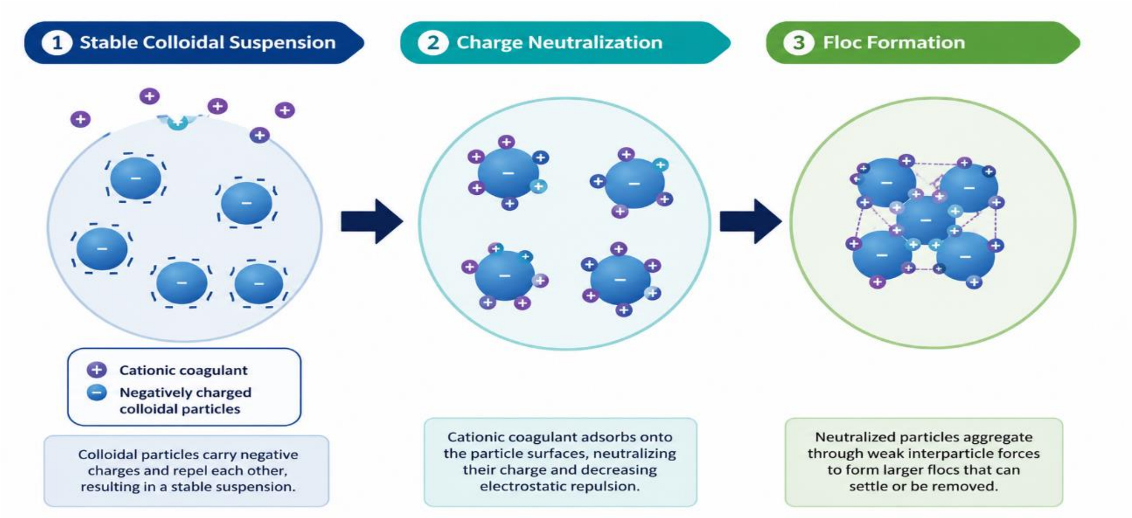

Figure 3. MO seeds cationic protein mechanism of coagulation/flocculation **(Yamaguchi et al.,2021).**

3.3.2.1 Preparation of natural coagulant Moringa oleifera

After being dried in the oven for 48 hours at 40 °C, the seeds of Moringa oleifera were ground in a processor using a 1 M sodium chloride (NaCl) solution at a 5% (v/v) ratio. The mixture was shaken for 30 minutes to extract the active substance from Moringa oleifera. Afterwards, the seed remnants were removed from the coagulant by vacuum filtration of the extract. The finished dish was kept in the fridge for up to seven days.
(Gonçalves et al., 2024).

3.4 Determination of anionic surfactants

With the rapid proliferation of anionic surfactants in home and commercial applications, it is increasingly crucial to identify them as Methylene Blue active substances (MBAS) in water, wastewater, and sludge samples. Sodium dodecyl sulphate (SDS), an anionic surfactant of the alkyl sulphate class, functions as the standard anionic surfactant in our modified MBAS methodology. The improved approach has reduced the chloroform requirement, eliminated the need for costly glassware, and decreased the sample size compared to the conventional procedure. The experimental calibration curves confirmed the theoretical relationship between the novel methodology and the conventional method. The R^2 values of the linear calibration curves varied from 0.994 to 0.999. The improved approach is as effective as the conventional procedure for extracting anionic surfactant molecules from samples, as demonstrated by statistical analysis of MBAS recoveries from standard additions and spiked samples **(Vega-Crespo et al., 2021)**.

3.5 Methodology

This research was conducted in the Laboratory of Chemical Processes at the Polytechnic Institute of Bragança.

3.5.1 Determination of pH for Water Quality Assessment

The pH is a logarithmic scale used to measure a solution's acidity, neutrality, or alkalinity. The pH measuring instrument to be utilised is the HANNA Edge model, which provides immediate results.

3.5.2 Evaluation of Turbidity as an Indicator of Suspended Particles

Turbidity measures the clarity of a liquid and reflects the amount of suspended particles present. This parameter was measured using a nephelometric turbidity meter. The turbidity meter measures light scattering caused by suspended particles in the sample, and results are expressed in Nephelometric Turbidity Unit (NTU)

3.5.3 Determination of Chemical Oxygen Demand (COD)

Using the Standard Method 5220D, the samples will be digested at 150 degrees Celsius for 2 hours in the HANNA HI 839800 COD digester. The samples will be analysed with a UV spectrophotometer (Jasco 530).

3.5.4 Determination of Biochemical Oxygen Demand (BOD_5)

Biochemical Oxygen Demand (BOD) indicates the amount of oxygen required for the biochemical decomposition of organic matter in water. This parameter will be determined using the standard method (5210B). The samples will be incubated in BOD bottles at 20°C for 5 days in a dark, controlled environment to avoid interference from photosynthesis. After the incubation period, the final DO will be measured, and the BOD will be calculated as the difference between the final and initial DO.

3.5.5 Determination and Classification of Total Solids in Water Samples

A solid is a form of matter distinguished by its rigidity and its ability to maintain a definite shape. It may also be defined by its equilibrium relationship with the liquid phase, particularly during phase changes such as melting. Accordingly, any material that retains these characteristics, even after undergoing processes like drying or calcination, can be classified as a solid. **(Sampaio, 2017).** Table 2 outlines the different classifications of solid types.

Table 2: Classifications of types of solids **(Sampaio, 2017).**

TYPE	CLASSIFICATION
Total solids	All the matter that remains in the container after the total drying of a given mass at 100 °C
Fixed solids	Total matter remaining in the vessel after a given mass has been calcined at about 1000 °C.
Volatile solids	All matter that is volatilized after calcination
Solids in Suspension	All matter that, after filtration and drying, remains retained in the membrane
Fixed Suspension Solids	All matter that, after filtration, drying, and calcination, is retained in the membrane
Volatile Suspension Solids	Any material that values after calcination in the muffle furnace (subtraction between the two previous classifications)
Dissolved Solids	All matter that is not retained after filtration and remains after complete drying of the sample
Setteable solids	All substances present in a liter of the sample that are settled by gravity.

4. EXPERIMENTAL

All experimental procedures were performed in the Chemical Processes Laboratory of the School of Technology and Management at the Polytechnic Institute of Bragança.

This study conducted two experiments: Coagulation and Photo Fenton oxidation processes. The removal of Sodium Dodecyl Sulfate and the reduction of organic load (COD).

This section presents the standard calibration curves employed and details the optimisation of operational parameters for the coagulation–flocculation and Foto-Fenton processes to enhance treatment efficiency.

4.1 Materials and methods:

4.1.1 Equipment

A variety of laboratory glassware and equipment necessary for the experiments are employed in this study:

Glass Rod; Magnetic stirrer (Hanna HI 180); pH meter (Hanna EDGE); Test Tube; COD Reactor (Hanna HI 839800); Spectrophotometer (Jasco V-530). UV photoreactor (UV Lamp, 14 W)

4.1.2 Determination of chemical oxygen demand (COD)

Chemical oxygen demand (COD) is an important indicator in water quality assessment, as it measures the amount of oxygen required to oxidize substances present in a sample, particularly organic matter. In this study, the closed reflux technique described in the Standard Methods for the Examination of Water and Wastewater (APHA et al., 2017; Method 5220) was applied. COD values within the range of 0–1000 mg O_2 L^{-1} were determined using a JASCO V-530 spectrophotometer at a wavelength of 600 nm.

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}, as shown in Figure 4.

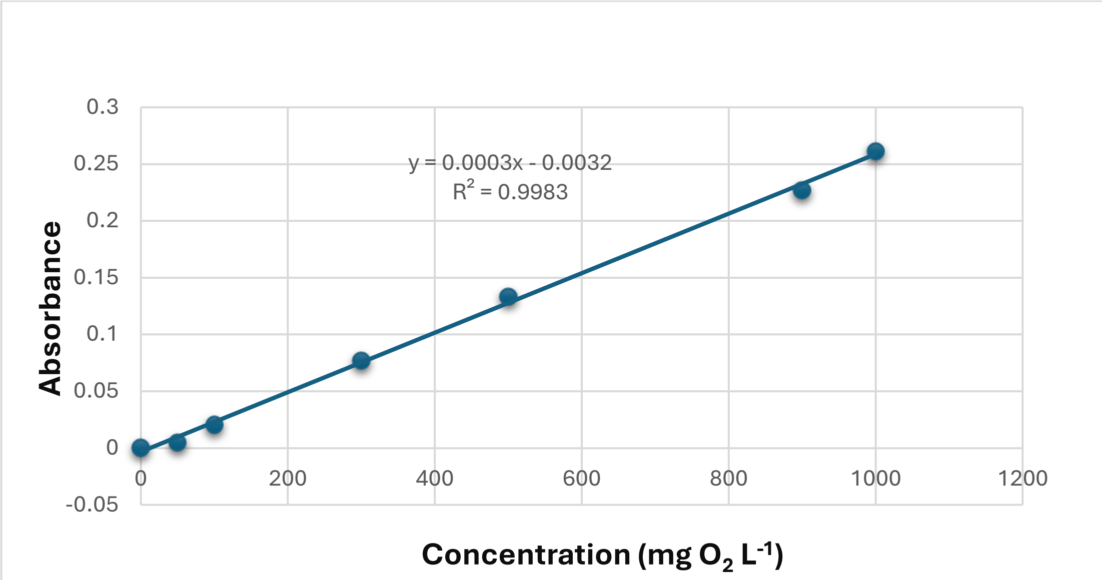

Figure 4. Calibration curve for COD determination using standard solutions.

With an R^2 value of 0.9983, the calibration curve demonstrates a strong linear correlation, confirming the validity of the Equation (5) for COD determination within the range of 0 – 1000 mg O_2 L^{-1}.

$$COD, mg\ O_2\ L^{-1} = \frac{Abs + 0.0032}{0.0003} \quad (5)$$

The Chemical Oxygen Demand (COD) removal efficiency was calculated using Equation (6), which quantifies the reduction in contaminant concentration after treatment:

$$\text{Removal efficiency (\%)}\ \frac{[inicial\ COD\ concentration\ (\text{mg}\ O_2L^{-1}) - final\ COD\ concentration\ (\text{mg}\ O_2\ L^{-1})]*100}{inicial\ COD\ concentration\ (\text{mg}\ O_2L^{-1})} \quad (6)$$

4.1.3 Surfactant analysis

A technique based on the methylene blue-anionic surfactant association was employed to analyse surfactant concentration **(Tôei & Fujii, 1977)**.

A separating funnel was filled with 5 mL of the cleared sample. After adding 25 mL of trichloromethane and 25 mL of the methylene blue solution, the funnel was violently shaken. After removing the organic fraction, 50 mL of cleaning solution was added to another separating funnel. After another shake of the funnel, the organic fraction was transferred to a 25 mL flask. It was filled with trichloromethane, and the concentration of methylene blue was measured using visible spectrophotometry at 625 nm. A zero was created with pure trichloromethane.

Reagents were prepared as follows: Cleaning solution: 43.5 g of NaH2PO4 was taken and diluted to 500 mL with distilled water. 6.6 mL of H_2SO_4, 98%, w/w were added and dilution was raised up to 1L. Methylene blue solution: 30 mg of methylene blue was added to 1 L of cleaning solution.

A calibration curve was constructed using this method, as shown in Figure 5:

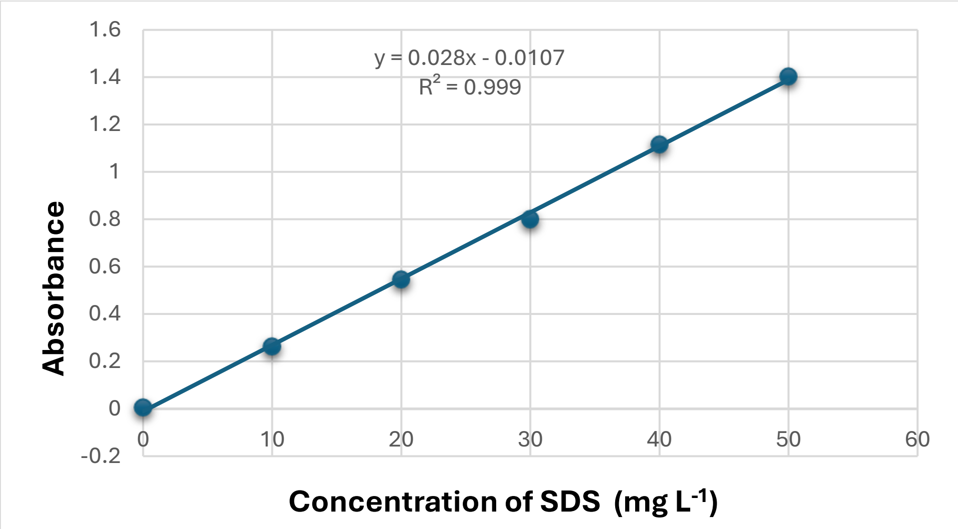

Figure 5. Calibration curve for SDS determination using the MBAS method.

The R^2 value of 0.999 indicates that, over the range 10 to 50 mg of SDS, Equation (7) is valid for determining the amount of SDS.

$$SDS, mg\ L^{-1} = \frac{Abs+0{,}0107}{0.028} \quad (7)$$

The Sodium Dodecyl Sulfate (SDS) removal efficiency was calculated using Equation (8), which quantifies the reduction in contaminant concentration after treatment:

$$\text{Removal efficiency (\%)} = \frac{inicial\ SDS\ concentration\ (\text{mg}\ L^{-1}) - final\ SDS\ concentration\ (\text{mg}\ L^{-1})}{inicial\ SDS\ concentration\ (\text{mg}\ L^{-1})} * 100 \quad (8)$$

4.1.4 Extraction of Moringa

Moringa oleifera seeds were triturated in a processor using a sodium chloride solution (NaCl, 1 M) at a 5% mass/volume ratio after being oven-dried for 48 hours at 40 ºC. To extract the active ingredient from Moringa oleifera, the mixture was mechanically agitated for 30 minutes. The seed remnants were subsequently separated from the coagulant by vacuum-filtering the extract, as shown in Figure 6.

Figure 6. Extraction of Moringa

4.1.5 Photo Fenton Process

Heptahydrate iron sulphate ($FeSO_4.7H_2O$) and hydrogen peroxide were the main chemicals utilised. Sulphuric acid (H_2SO_4) 1 M and sodium hydroxide (NaOH) 6 M were used to maintain the pH required for the Fenton reaction (between 2.5 and 3.5) at the beginning of the response and to neutralise it (pH between 10 and 12) to complete the process.

The photo Fenton process is an advanced oxidation process that uses the hydroxyl radical to disinfect and decontaminate water. These experiments employing the process were conducted as follows.

1. A solution of sodium dodecyl sulfate (SDS) was prepared at a concentration of 50 mg L^{-1} (250 ml). To this solution, moringa powder was added at a concentration of 700 mg L^{-1}. The mixture was then shaken for 1 hour at 40 rpm to ensure proper mixing and interaction. After shaking, the solution was left undisturbed for at least 1 hour to allow sedimentation or stabilisation. **(Figure 7.)**

2. The pH of the samples was adjusted to the desired range between 2.5 and 3.5 using H_2SO_4 (1M) and NaOH (6M)

3. Added the desired amount of hydrogen peroxide and iron sulfate, mixing the solution for up to 5 min with fast stirring.

4. The sample was taken for the UV photo reactor (UV Lamp 14 W) for 1 hour, as shown in **Figure 8**.

5. Subsequently, the pH of the sample was adjusted again between 9 and 11 to stop the reaction.

6. The sample was allowed to stabilise for at least 12 h (**Figure 9.**)

7. The sample volume for the removal analysis was obtained from the supernatant of the sample, with due care not to mix the two phases of the sample.

Figure 7 is a photo of our samples after the shaking of MO and SDS.

Figure 7. Mixing SDS with Moringa powder.

The Photo Fenton process is shown in Figure 8.

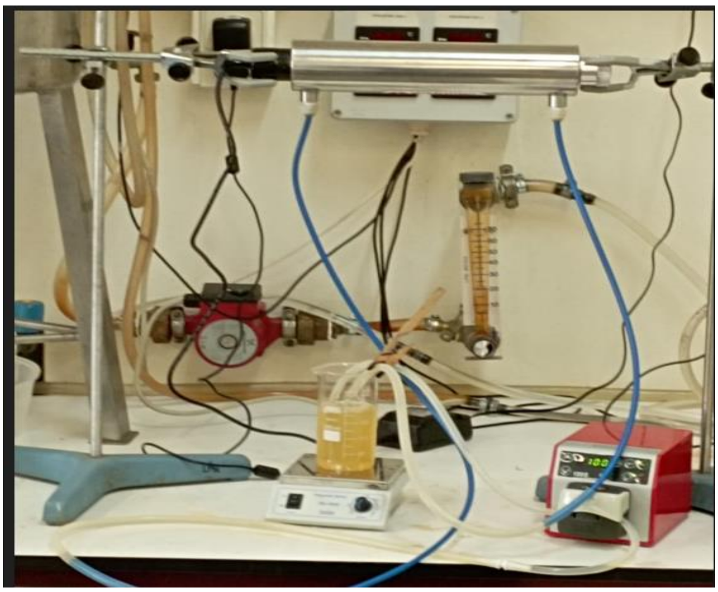

Figure 8. Photo Fenton Process.

Figure 9 shows a photo of the samples after 12 h of stabilisation.

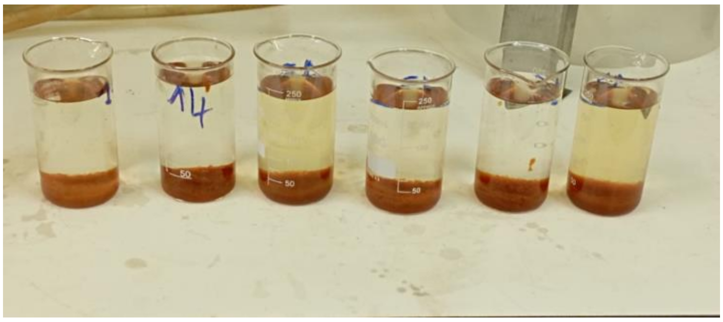

Figure 9. Final Solution after 12 h.

4.1.5.1 Parameters Influencing the Process

Numerous factors affect the effectiveness of Fenton and photo Fenton procedures for remediating wastewater containing surfactants. These methods break down the organic constituents in wastewater.

I Influence of pH on the Photo Fenton Process

The Photo Fenton reaction is highly pH-dependent and uses hydrogen peroxide (H_2O_2) and ferrous ions (Fe^{2+}) to produce highly reactive oxidising species. Iron speciation, the production of hydroxyl radicals, and overall oxidation efficiency are all strongly impacted by this parameter.

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)**.

II Temperature and reaction time

The present study used a reaction time of 60 min for the Fenton oxidation process, conducted at ambient temperature. This choice is supported by findings in the literature indicating that a 60-minute duration is generally sufficient to achieve substantial pollutant removal.

III H_2O_2: COD Ratio

The H_2O_2:COD ratio is a key parameter in evaluating the oxidation capacity and efficiency of the Photo Fenton process. In this experiment, 1 mL of 30% w/w hydrogen peroxide (approximately 333 mg of H_2O_2) was added to a 250 mL solution containing 280 mg of

COD. This results in a H_2O_2:COD mass ratio of approximately **1.19:1**, meaning that slightly more oxidant was supplied than the amount of organic matter present. This near-stoichiometric ratio provided sufficient hydroxyl radicals to achieve effective degradation without excessive oxidant use. The results showed good treatment efficiency, indicating that this ratio supports a favourable balance between organic load and available oxidising agent under the applied Photo Fenton conditions.

IV 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, 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 $Fe^{3.+}$ (Deng & Englehardt, 2006).

The optimal molar ratio of H_2O_2 to Fe^{2+} depends strongly on the specific physicochemical characteristics of the process.

In this study, the effect of the H_2O_2:Fe^{2+} ratio on the performance of the Photo Fenton process was evaluated by using 1 mL of hydrogen peroxide (30% w/w) and 180 mg of ferrous sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$) in 250 mL of solution. This combination yielded a favourable degradation result, indicating that the selected ratio was effective for generating hydroxyl radicals without excessive scavenging. The amount of $FeSO_4 \cdot 7H_2O$ corresponds to approximately 36 mg of Fe^{2+}, and the 1 mL of 30% H_2O_2 provides about 333 mg of hydrogen peroxide. Therefore, the mass ratio of H_2O_2 to Fe^{2+} in this setup is approximately 9.25:1. This ratio ensured efficient catalytic cycling of iron under UV irradiation while minimising side reactions or excess sludge generation. The outcome suggests that this proportion provides a balanced condition for maximising radical production and COD degradation in the photo-assisted Fenton reaction.

4.1.6 Response Surface Methodology

Response Surface Methodology (RSM) was employed to systematically evaluate the effects of different H_2O_2-to-Fe^{+2} molar ratios on treatment performance. By creating predictive models that account for interactions among factors, this statistical method enables the identification of optimal process conditions, thereby improving treatment effectiveness and experimental reproducibility.

Minitab® version 21.4.1 (64-bit) was used for the statistical analysis, experimental modelling, and graphical outputs for multivariate interpretation. An experimental design was created to investigate the relationships among four crucial process variables: pH, ferrous ion concentration, hydrogen peroxide concentration, and flow rate Q, all of which are part of the Response Surface Methodology (RSM). All this data is summarised in Table 3.

Table 3. Levels of factor variation for experimental design.

Level	H_2O_2(30% w/v)	$FeSO_4.7H_2O$	Ph	Flow Q
	Amount (ml)	Amount (g)		(ml/min)
+1	1.5	0.27	3.5	128
0	1.0	0.18	3.0	84
- 1	0.5	0.09	2.5	40

Note: The concentrations of H_2O_2 and Fe^{2+} were established based on the COD concentration measured after the coagulation-flocculation pretreatment.

The Box-Behnken design enables a systematic assessment of the combined impact of the selected operating parameters on the performance of the photo Fenton process. This method makes it easier to identify important linear, quadratic, and interaction effects, enabling a more thorough understanding of the process behaviour. Additionally, the architecture enables the creation of a trustworthy second-order polynomial model to forecast SDS removal efficiency in the experimental domain under investigation. Because it reduces experimental effort, ensures experimental robustness, and offers insight into the relative influence of each variable and its interactions, such modelling is crucial for process optimisation.

Twenty 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 four central replicates were included to evaluate model reliability and estimate experimental error, as shown in Table 4.

Table 4. Experimental matrix based on the Box–Behnken Design.

Run	Level	Factor			
	----	H_2O_2	Fe^{2+}	pH	Q
1	--00	0.5	0.090	3	84
2	+-00	1.5	0.090	3	84
3	-+00	0.5	0.270	3	84
4	++00	1.5	0.270	3	84
5	0--0	1	0.090	2.5	84
6	0+-0	1	0.270	2.5	84
7	0-+0	1	0.090	3.5	84
8	0++0	1	0.270	3.5	84
9	00--	1	0.180	2.5	40
10	00+-	1	0.180	3.5	40
11	00-+	1	0.180	2.5	128
12	00++	1	0.180	3.5	128
13	-00-	0.5	0.180	3	40
14	+00-	1.5	0.180	3	40
15	-00+	0.5	0.180	3	128
16	+00+	1	0.180	3	128
17	0000	1	0.180	3	84
18	0000	1	0.180	3	84
19	0000	1	0.180	3	84
20	0000	1	0.180	3	84

This method ensured the selection of optimal conditions for maximum pollution removal by enabling a systematic assessment of the effects of various variables. The success of the photo Fenton reaction depends on several variables, including pH, ferrous ion concentration, flow rate, and hydrogen peroxide dosage. Statistical research shed light on these relationships.

5. RESULTS AND DISCUSSION

5.1 Coagulation Treatment Using Moringa Oleifera

5.1.1 Determination of The Optimal Coagulant Dose

Different concentrations of Moringa were tested to find the most effective dose that would yield the desired result; this allowed for comparison and evaluation of the effects of each dosage, ultimately assisting in the establishment of the optimal amount of Moringa to be added to 100 mL of SDS solution with a concentration of 50 mg L^{-1}. The solution was mixed at 40 rpm for 1 h; many studies report that this period is sufficient for kinetic stabilisation. The effect of varying Moringa concentrations is presented in Figure 10

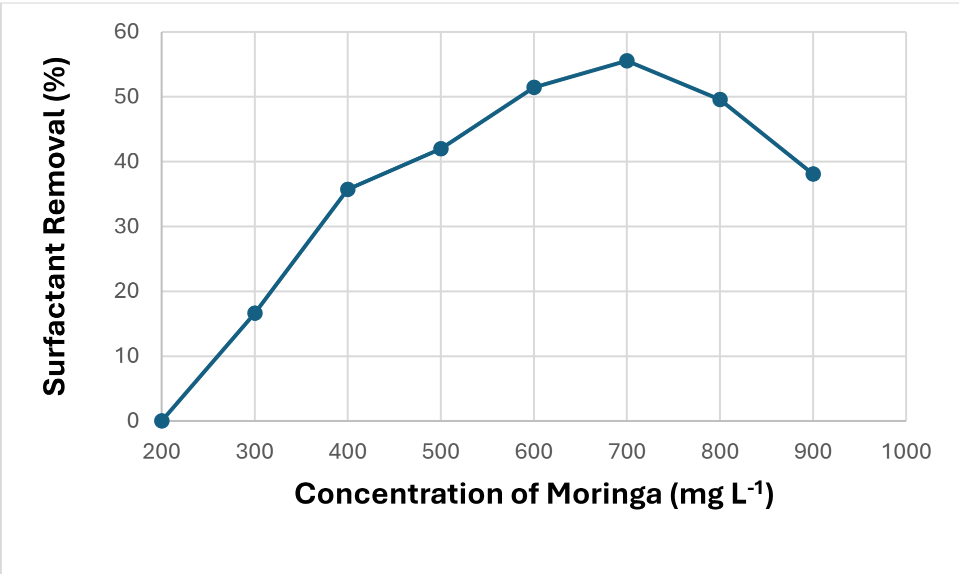

Figure 10. Determination of the optimal dose

Figure 10 illustrates the effect of coagulant dosage on surfactant removal efficiency. A solution containing an initial surfactant concentration of 50 mg L^{-1} was treated with progressively increasing amounts of Moringa oleifera. The highest removal efficiency (55.55%) was observed at a dosage of 700 mg L^{-1}. An increase in removal was noted up to this concentration; however, beyond 700 mg L^{-1}, the efficiency declined. Complete elimination of the residual surfactant could not be achieved using M. oleifera seed extract. This limitation may be attributed to the existence of an equilibrium surfactant concentration, which is difficult to remove **(Beltrán-Heredia & Sánchez-Martín, 2009).**

5.1.2 Effect Of Initial Surfactant Concentration on Removal Efficiency

The initial surfactant dosage ranged from 30 to 80 mg L^{-1}. To assess the impact of raising the initial surfactant dosage, a fixed dosage of 700 mg L^{-1} of M. oleifera seed extract was used. The findings are displayed in Fig 11.

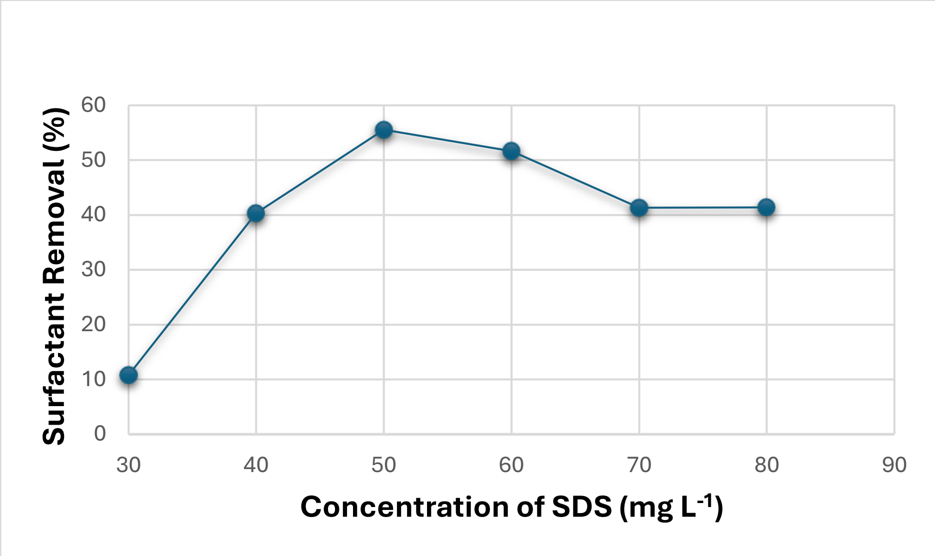

Figure 11. Fixed dose of MO (700 mg L^{-1})

Removal efficiency (%) versus initial surfactant concentration (mg L^{-1}) is shown there. At concentrations up to 50 mg L^{-1}, this proportion usually peaks before declining. M. oleifera poses treatment-ability limitations. It is known that increasing the total amount of surfactant (and particularly anionic surfactant) may lead to a denaturation of proteins **(Beltrán-Heredia & Sánchez-Martín, 2009)**.

5.1.3 Influence of pH on the Coagulation Performance

The pH was adjusted from 4 to 7 to assess the effect on surfactant elimination. Figure 12 displays a set of experimental findings.

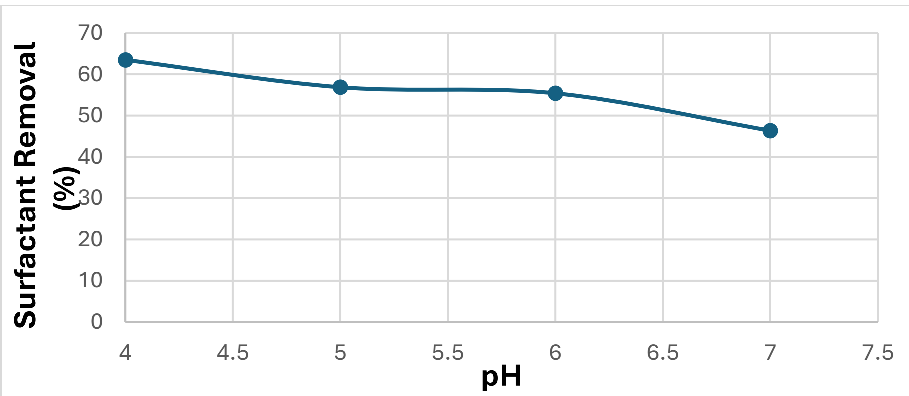

Figure 12. pH Influence on the coagulation Performance.

As can be seen, a fixed dose of 700 mg L^{-1} of M. oleifera seed extract, combined with a 50 mg L^{-1} surfactant dose, tends to lose its effectiveness as pH rises. Lowering pH should not significantly reduce the surfactant's anionic character, but M. oleifera's proteinic nature renders this extract cationic, and its cationic form would be more abundant at acidic pH **(Kwaambwa & Maikokera, 2007)**. There is increased electrostatic interaction between the cationic proteins of M. oleifera and the active sites of negatively charged surfactants. Furthermore, connections to hydrophobic chains would be strengthened **(Ayranci & Duman, 2007)**.

5.2 Photo Fenton

The Photo Fenton treatment experiments were systematically designed to investigate the influence of key operational parameters on the degradation of sodium dodecyl sulfate (SDS) and to generate a robust dataset for subsequent modelling and optimisation. Hydrogen peroxide concentration and ferrous ion dosage were selected as the primary inputs governing hydroxyl radical generation. At the same time, pH was considered due to its critical role in controlling iron speciation and reaction kinetics. In addition, the flow rate was varied to assess its effect on contact time and mass transfer within the reactor system. The SDS removal efficiency was used as the response variable, as it provides a direct, quantitative measure of treatment performance. The experimental results obtained from this design form the basis for statistical evaluation, response surface analysis, and identification of optimal Photo Fenton operating conditions.

Table 5 details the experimental matrix employed in the Photo Fenton treatment phase, listing the independent process variables (H_2O_2 concentration, Fe^{2+} dosage, pH and flow Q), along with the response variable (Y), defined as the experimentally determined SDS removal efficiency (%).

Table5. Experimental matrix employed in the Photo Fenton treatment phase.

Run	Level	Factor				Removal %
	----	H_2O_2	Fe^{2+}	pH	Q	
1	--00	0.5	0.090	3.0	84	90
2	+-00	1.5	0.090	3.0	84	93
3	-+00	0.5	0.270	3.0	84	94
4	++00	1.5	0.270	3.0	84	95
5	0--0	1.0	0.090	2.5	84	94
6	0+-0	1.0	0.270	2.5	84	96
7	0-+0	1.0	0.090	3.5	84	96
8	0++0	1.0	0.270	3.5	84	96
9	00--	1.0	0.180	2.5	40	87
10	00+-	1.0	0.180	3.5	40	93
11	00-+	1.0	0.180	2.5	128	94
12	00++	1.0	0.180	3.5	128	91
13	-00-	0.5	0.180	3.0	40	92
14	+00-	1.5	0.180	3.0	40	94
15	-00+	0.5	0.180	3.0	128	95
16	+00+	1.0	0.180	3.0	128	96
17	0000	1.0	0.180	3.0	84	97
18	0000	1.0	0.180	3.0	84	97
19	0000	1.0	0.180	3.0	84	97
20	0000	1.0	0.180	3.0	84	97

5.2.1 ANOVA Analysis

a) Model Summary

The goodness-of-fit statistics for the developed model are summarised below.

S	R-sq	R-sq(adj)	R-sq(pred)
1.75085	83.89%	56.27%	*

The statistical analysis showed that although the model explained a significant proportion of the response's variation (R^2 = 83.89%), the adjusted R^2 was much lower (56.27%), indicating that the inclusion of several factors did not significantly increase the model's explanatory power.

b) Analysis of Variance

Table 6 summarizes the analysis of variance results for the investigated factors.

Table6. ANOVA results showing the effects of factors on the response variable.

Source	DF	Adj SS	Adj MS	F Value	P Value
H_20_2	2	17.721	8.86060	2.89	0.122
Fe	2	11.643	5.82139	1.90	0.219
pH	2	11.365	5.68260	1.85	0.226
Q	2	11.467	5.73333	1.87	0.223
H_20_2*Fe	4	31.764	7.94097	2.59	0.129
Error	7	21.458	3.06548	*	*
Lack-of	4	21.458	5.36458	*	*
Pure Error	3	0.000	0.00000	*	*
Total	19	133.200	*	*	*

With all p-values above 0.05, the ANOVA findings show that none of the components that were tested, H_2O_2, Fe, pH, and Q, have a statistically significant impact on the response at the 5% level. Fe, pH, and Q all had lower effects, with p-values above 0.20, while H_2O_2 had the largest influence among the individual components ($F = 2.89$, $p = 0.122$), indicating a possible trend worth further research. A minor effect was also observed in the interaction between H_2O_2 and Fe ($F = 2.59$, $p = 0.129$), suggesting that combination effects might be involved but not substantially so in the current experimental setup. Due to the lack of a pure error term, all unexplained variance was attributed to model inadequacies, as indicated by the error term. This suggests that the model does not fully capture the variability in responses, and additional experimental replicates or model refinement may be necessary. Overall, while no factor reached statistical significance, H_2O_2 and its interaction with Fe appear to be the most influential and could become significant with increased sample size or improved experimental design. The factorial plots illustrating the effects of the studied factors on SDS removal efficiency are presented in Figure 13.

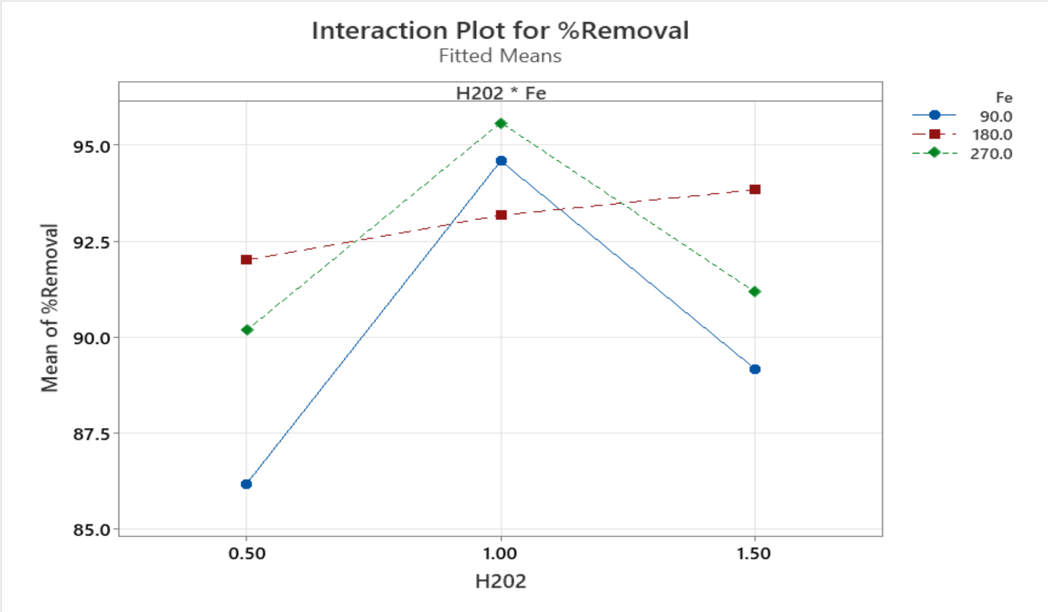

Figure13. Factorial Plots for Removal % of SDS.

5.2.2 Predicted Optimal Conditions for Maximum Removal Efficiency

The predicted optimal conditions for achieving maximum SDS removal efficiency, as determined by the response optimiser, are presented in Figure 14.

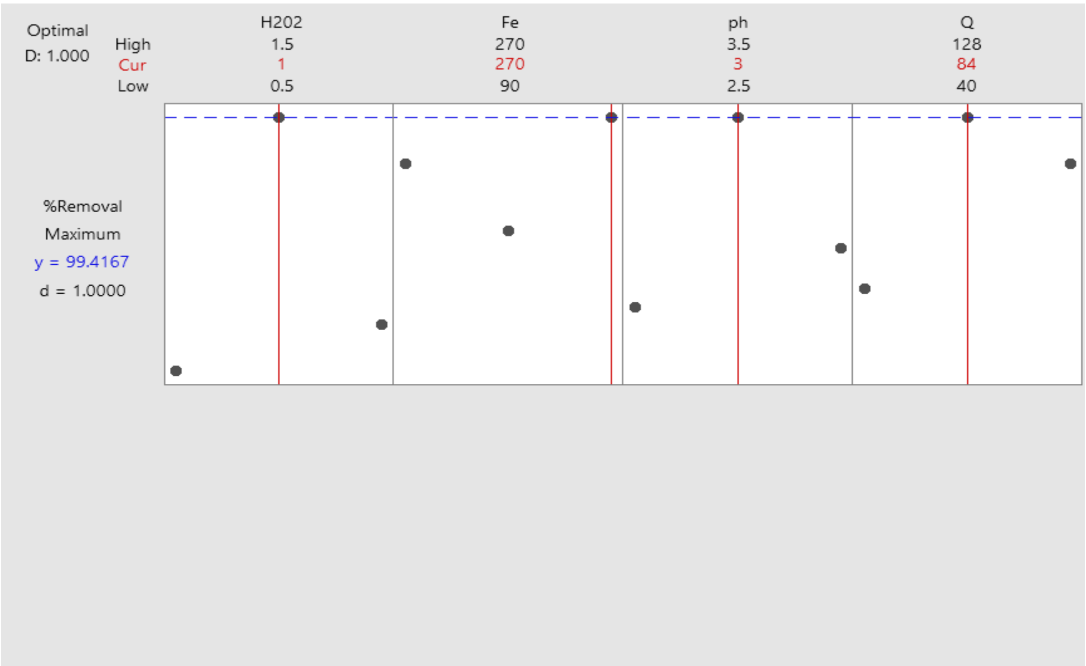

Figure 14. Response optimiser showing predicted optimum conditions for removal (%).

a) Multiple Response Prediction

The predicted optimal factor settings and corresponding response statistics from the multiple-response prediction analysis are presented below.

Variable	Setting
H202	1
Fe	270
ph	3
Q	84

Response	Fit	SE Fit	95% CI	95% PI
Removal %	99.42	2.42	(93.68, 105.15)	(92.35, 106.49)

The optimisation analysis determined the optimal operating conditions for optimising removal efficiency. The response optimiser indicated that H_2O_2 = 1.0 mL, Fe = 270 mg L^{-1}, pH = 3.0, and Q = 84 ml/min were the ideal levels of the input variables. This resulted in a predicted elimination efficiency of 99.42% with a desirability of 1.000. This result was validated by the multiple-response prediction, which had a standard error of 2.42 and a 95% CI of 93.68% to 105.15%. Because of the inherent heterogeneity in the experimental settings, the prediction interval was rather wider (92.35%–106.49%). These findings imply that, with careful balancing of operating parameters, near-complete elimination can be achieved under ideal conditions. The results highlight the importance of using an acidic medium, a high Fe concentration, and a relatively modest oxidant dose to maximise hydroxyl radical formation while avoiding scavenging effects. Although experimental validation is necessary to establish model dependability and practical feasibility, the high desirability value suggests that the discovered operating point is the most efficient within the investigated experimental domain.

5.2.3 Response Surface Methodology

5.2.3.1 Evaluation of Factor Significance

The standardised effects of the investigated factors on removal efficiency are illustrated in Figure 15.

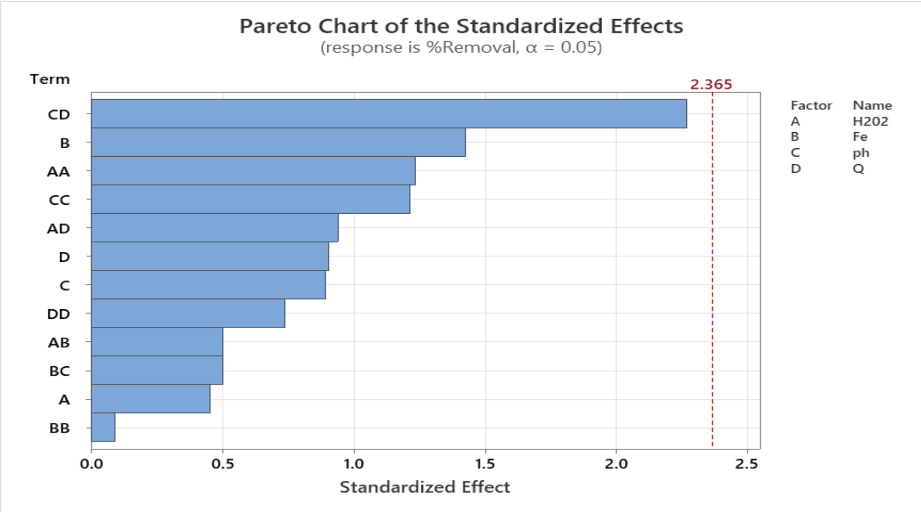

Figure 15. Pareto Chart of Standardised Effects for Removal (%).

The most significant elements influencing the percentage removal (Removal (%)) are identified by the Pareto chart of standardised effects ($\alpha = 0.05$). The interaction between pH (C) and Q (D) (CD), among all the variables investigated, exceeds the significance threshold of 2.365, suggesting that it affects the response in a statistically significant way. This implies that the removal efficiency is strongly influenced by the combined effects of pH and Q. The comparatively strong standardised effect of the Fe concentration (B), which is close to the significance threshold, suggests that it may have a significant, albeit unsubstantiated, impact on Removal (%). The other primary effects and interactions, on the other hand, such as pH, H_2O_2, and their higher-order terms, show lesser standardised effects and are consequently regarded as less important within the range under study. All things considered, these findings emphasise the importance of simultaneously optimising pH and Q to maximise the effectiveness of removal.

The residual diagnostic plots used to assess the adequacy of the regression model are presented in Figure 16.

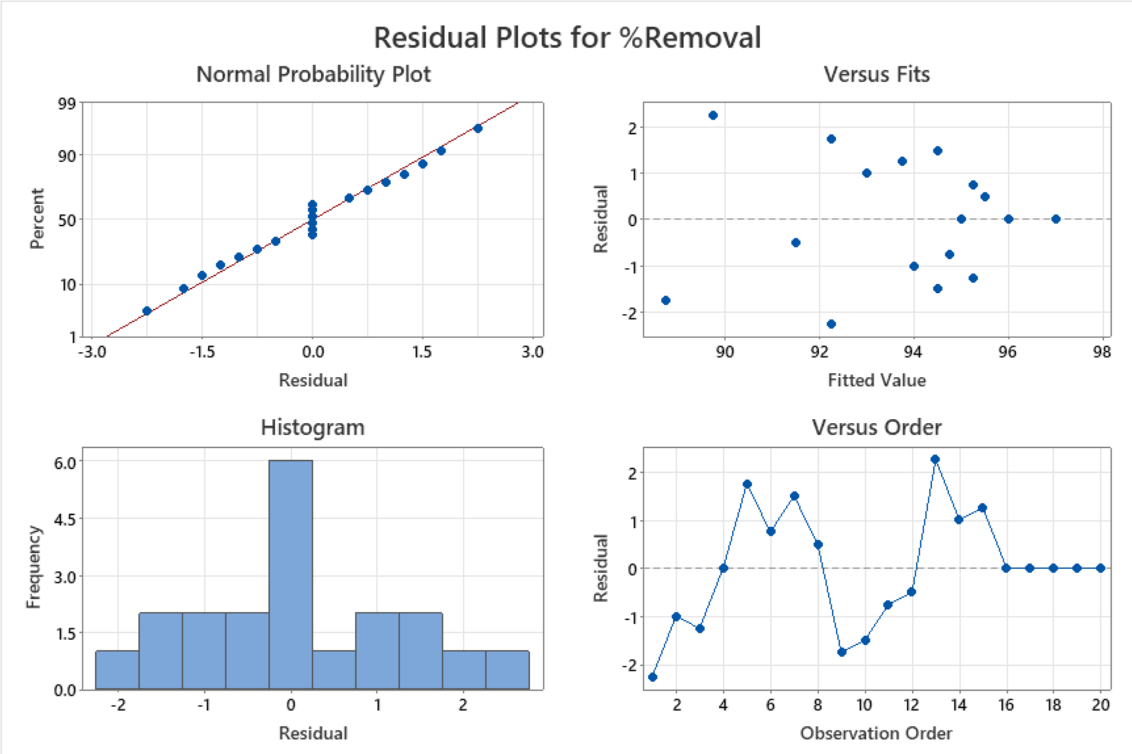

Figure 16. Residual Plots for Removal (%).

The regression model's sufficiency was evaluated using residual plots of Removal (%). The assumption of normalcy is reasonably satisfied, as evidenced by the residuals' strong adherence to a straight line in the Normal Probability Plot. This conclusion is supported by the residuals histogram, which is roughly symmetric and centred around zero. The points in the Residuals vs Fitted Values plot appear haphazardly dispersed and lack discernible structure, indicating that the residuals' variance is approximately constant and that the model has accurately captured the data's systematic variation.

The lack of a clear trend or systematic pattern in the Residuals vs Order plot suggests that the residuals are independent and that there are neither time-related nor order-related effects. All things considered, these diagnostic plots indicate no significant deviations from the model's assumptions and that the regression model fits the data adequately.

5.2.3.2 Effect of Interaction Between H2O2, Fe, pH, and Q on Removal (%)

The plot (Figure 17) shows how H_2O_2, Fe, pH, and Q interact to affect the percentage removal (Removal (%)).

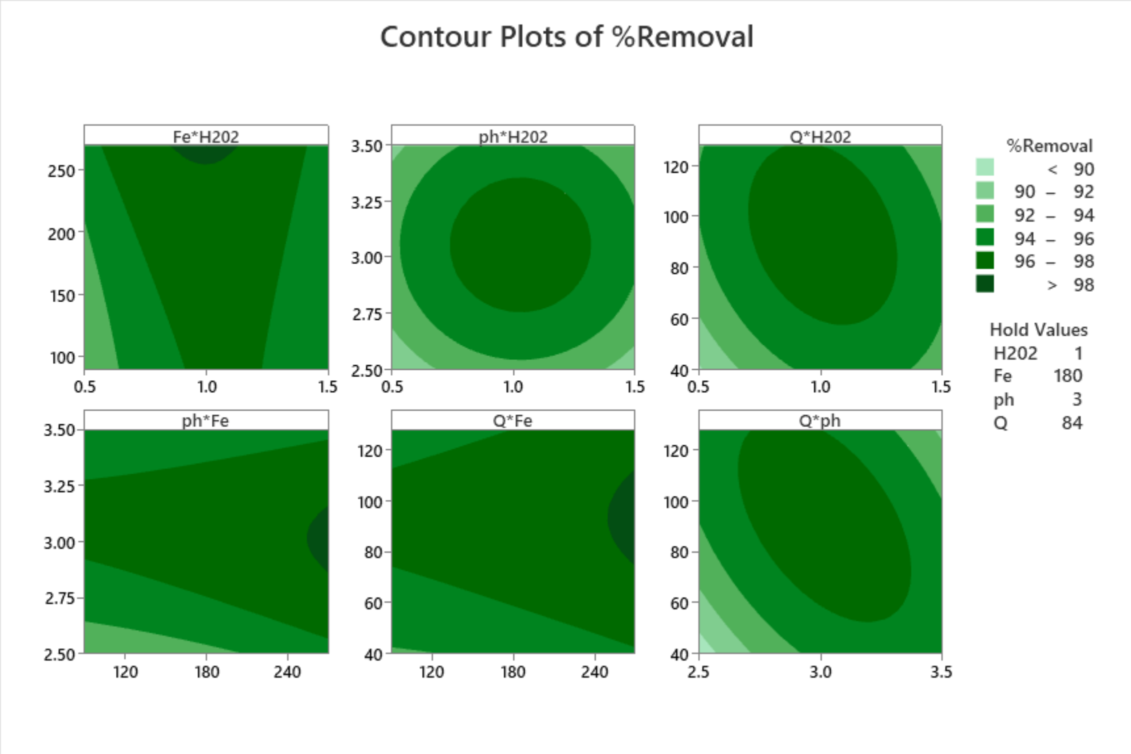

Figure 17. Effect of interaction between H_2O_2, Fe, pH, and Q on Removal (%).

A substantial synergistic effect between these two parameters is indicated by the plot of Fe × H_2O_2, which reveals that better removal efficiencies are obtained at moderate levels of H_2O_2 (about 1.0) and higher Fe concentrations (over 200 mg L^{-1}). According to the pH × H_2O_2 interaction, the highest removal percentage occurs at intermediate pH values (around 3.0) and intermediate H_2O_2 levels, indicating that both excessively basic and acidic environments reduce effectiveness. In a similar vein, the Q × H_2O_2 figure confirms that balanced operating conditions are necessary for best performance, showing that Removal % increases as both Q and H_2O_2 reach moderate levels.

Other relationships between pH, Q, and Fe are also important. Fe functions well as a catalyst in acidic environments, as evidenced by the pH × Fe plot, which demonstrates that removal effectiveness increases at high Fe concentrations and moderately acidic pH levels. Decreased returns at larger reagent dosages are implied by the Q × Fe interaction, which shows that increasing both Fe and Q increases Removal (%) up to an ideal point before stabilising. Last but not least, the Q × pH plot indicates that the greatest removal occurs at moderate Q and pH values, suggesting that very acidic conditions and excessive flow may reduce removal effectiveness.

All things considered, these contour plots demonstrate that the ideal pH (around 3.0), high Fe dosage, and moderate H_2O_2 levels provide the best conditions for achieving maximal Removal (%). The findings support the Pareto analysis and show that the most important interactions in the process are between pH and Q, and between Fe and H_2O_2.

6. CONCLUSION

An effective treatment strategy for wastewater polluted with anionic surfactants was achieved by combining plant-based coagulation using Moringa oleifera with the photo Fenton oxidation process. The experimental results confirmed that Moringa oleifera acts as a sustainable and efficient natural coagulant, achieving up to 55.55% removal of sodium dodecyl sulfate (SDS). This preliminary step significantly reduced the organic and surfactant load, thereby improving the performance of the subsequent advanced oxidation treatment.

When applied under optimised conditions, the Photo Fenton process achieved a remarkable 99.42% removal efficiency. The optimal operating parameters were determined to be a hydrogen peroxide dosage of 1.0 mL, an Fe^{2+} concentration of 270 $mg \cdot L^{-1}$, a pH of 3.0, and a flow rate (Q) of 84 $mL \cdot min^{-1}$. The Response Surface Methodology (RSM) and statistical analyses revealed that the interactions between pH and Q, and between Fe and H_2O_2, had the most significant effects on removal performance. These findings highlight that maintaining an acidic pH and an appropriate balance between oxidant and catalyst concentrations are crucial for maximising hydroxyl radical generation and enhancing degradation efficiency.

An assessment of residual behavior through normal probability plots, along with residuals plotted against fitted values and run order, confirmed the suitability and stability of the proposed regression model. The model exhibited a good fit, with residuals randomly distributed around zero and no major deviations from normality or homoscedasticity, indicating that the regression assumptions were satisfactorily met. The contour plots further illustrated the synergistic interactions among process variables, confirming that moderate H_2O_2 levels, high Fe dosage, and controlled pH and Q values lead to the highest removal efficiencies.

Overall, this research highlights the synergistic advantage of integrating natural coagulation with advanced oxidation processes. The Moringa pretreatment reduces turbidity and organic content, enhancing Photo Fenton efficiency while lowering reagent consumption and sludge generation. This integrated system represents a promising, eco-friendly, and cost-effective hybrid treatment technology suitable for wastewater streams containing surfactants, such as those from the car wash and detergent industries.

6.1 Recommendations for Further Work

To enhance the favourable results of this study, the following recommendations are proposed:

1. **Scale-Up Studies:**
   Conduct pilot-scale experiments to evaluate the performance of the Moringa–Photo Fenton hybrid system under continuous flow conditions and real industrial effluent loads.
2. **Economic and Environmental Assessment:**
   Perform a detailed cost-benefit and life-cycle analysis to assess the economic feasibility and environmental sustainability of the proposed treatment approach compared with conventional methods.
3. **Optimisation of Moringa Dosage and Preparation:**
   Investigate the effect of Moringa seed concentration, extraction method, and storage stability on coagulation efficiency and by-product formation.
4. **Reusability and Sludge Management:**
   Evaluate the potential for reusing the Moringa-based sludge as fertiliser or bioresource and assess its environmental safety through toxicity and biodegradability tests.
5. **Integration with Other Advanced Treatments:**
   Explore coupling the Moringa–Photo Fenton system with membrane filtration or photocatalytic processes to achieve further purification and resource recovery.

6.2 Final Statement

In conclusion, the integration of biobased natural coagulants and advanced oxidation processes offers a viable and sustainable alternative for treating surfactant-laden wastewater. The developed process achieves high pollutant removal efficiency while supporting the circular economy and green chemistry principles, marking a significant step toward sustainable environmental management and water reuse applications.

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