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ORIGINAL PAPER

Feasibility of Fenton-based oxidation for reducing organic content, toxicity, and carbon footprint of automotive industry wastewater

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Abstract

Automotive industry wastewater, particularly from the cataphoresis process, presents a challenge due to its high chemical oxygen demand and heavy metal content. Biological treatment alone is often insufficient, requiring pretreatment to enhance biodegradability. Fenton oxidation effectively targets toxic compounds, reducing inhibition of biological process. This study evaluates the feasibility of Fenton, Fenton-based, and photo-Fenton oxidation for pretreating automotive industry wastewater, aiming to optimize chemical oxygen demand removal and minimize sludge formation. Experimental studies using Response Surface Methodology revealed that Fenton and Fenton-based oxidations achieved similar chemical oxygen demand removal efficiencies, although the Fenton-based process with ferric iron produced more sludge. Photo-Fenton oxidation did not provide any significant benefit. Inhibition tests showed Fenton pretreatment reduced sludge inhibition from 44 to as low as 9% under optimal conditions. The optimal operating conditions for classical Fenton oxidation were determined as a ferrous iron concentration of 0.58 g L^{-1}, a hydrogen peroxide to chemical oxygen demand molar ratio of 0.58 mol mol^{-1}, and a reaction time of 30 min, resulting in a 49.58% chemical oxygen demand removal with minimal sludge formation and activated sludge inhibition. Compared to the coagulation-flocculation process, Fenton oxidation demonstrated the potential to reduce the carbon footprint by 6.6–16.6%, based on carbon dioxide emissions from chemical consumption. Therefore, classical Fenton oxidation as a pretreatment process can enhance biological treatment efficiency and lower the carbon footprint of automotive industry wastewater treatment.

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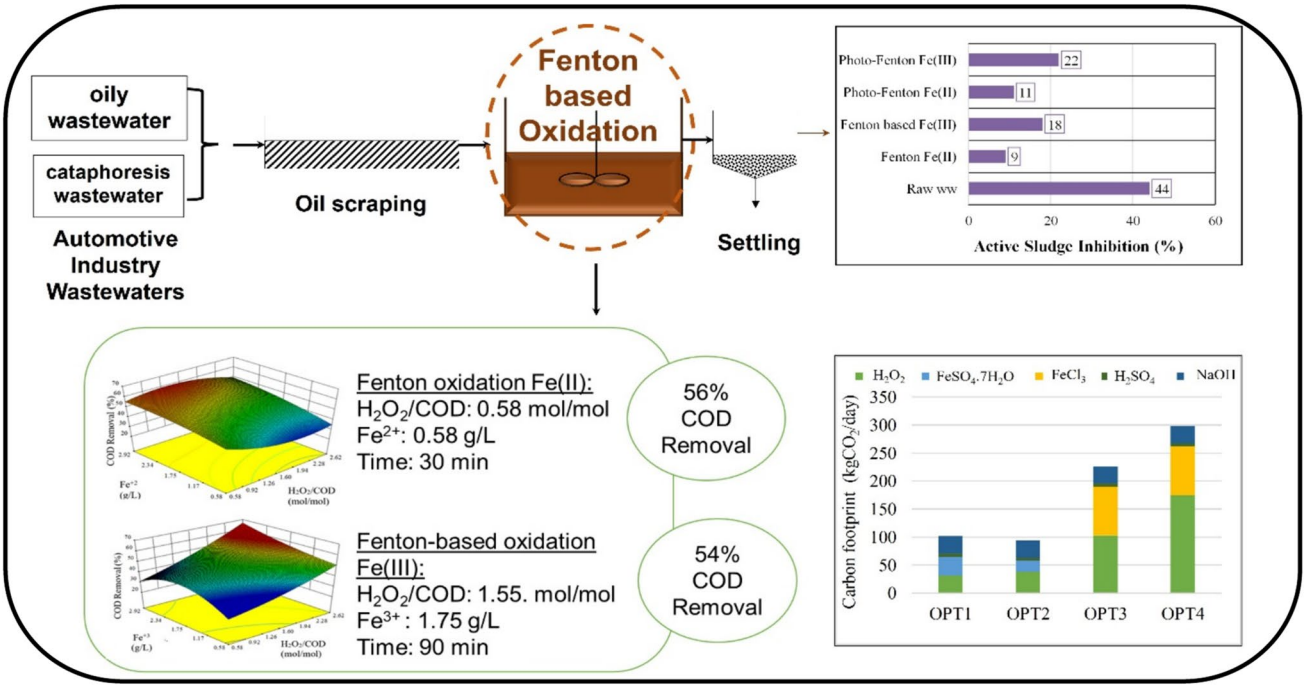
Graphical abstract



Keywords Active sludge inhibition · Automotive industry wastewater · Carbon footprint · Fenton oxidation · Fenton-based oxidation · Photo-Fenton · Toxicity

Introduction

Since the late nineteenth century, when its industrial significance began to rise, the automotive industry has been a key sector driving the steady growth of both developed and developing economies. It also plays a pivotal role in accelerating technological advancements and fostering the expansion of numerous other industries (Traub-Merz 2017). Automotive production processes can be categorized into four main stages: pressing, welding, cataphoresis, and assembly. Among these, the cataphoresis process is the largest contributor to wastewater generation (Rivera and Reyes-Carrillo 2014; Radojevic et al. 2019). In an automotive plant producing 400,000 vehicles per year, an average of 11.4 kg of chemical oxygen demand (COD) per m^3 is discharged, with the cataphoresis departments producing 410,000 m^3 of wastewater annually (Bajaj and Winter 2013). This wastewater is characterized by high concentrations of COD and suspended solids (SS), along with significant levels of heavy metals such as zinc (Zn), nickel (Ni), lead (Pb), copper (Cu), chromium (Cr), and cadmium (Cd) (El-Gohary et al. 1988; Wahaab 2000). Heavy metals are highly toxic to the environment. Therefore, their concentrations in wastewater must be kept within regulated limits during treatment processes. The primary risks posed by heavy metals are their ability to accumulate in the environment over time without breaking down, due to their inorganic nature, and their potential to form even more toxic compounds when combined with other metals (Abu Bakar and Halim 2013; Priya et al. 2024). If the concentrations of heavy metals in treated wastewater discharged into the environment are not reduced to acceptable levels, they can lead to the contamination of freshwater and marine ecosystems by leaching into soil and water sources (Li et al. 2022). In addition to environmental harm, some heavy metals exhibit carcinogenic effects. The cases of Minamata disease caused by mercury (Hg) and itai-itai disease caused by cadmium (Cd) in Japan during the last century are well-known examples of how industrial heavy metal pollution can severely impact human health (Li et al. 2022).

Given these risks, the heavy metals present in automotive industry wastewater (AIW) pose a significant threat to environmental safety. However, biological wastewater treatment processes, known for their cost-effectiveness, are not

suitable for treating such wastewater due to the toxicity of heavy metals. Coagulation-flocculation, electrocoagulation, and adsorption are the primary techniques investigated for removing contaminants from AIW (Abu Bakar and Halim 2013; Priya and Jeyanthi 2019; Veit et al. 2020; Akpomie and Dawodu 2015). In a study by Abu Bakar and Halim (2013) as a result of applying coagulation-flocculation to remove COD from AIW, the highest COD removal efficiency of 70% was obtained by using polyaluminum chloride and polyacrylamide as coagulant aids. Priya and Jeyanthi (2019) achieved a 95.1% COD removal efficiency through the electrocoagulation of AIW. Another study obtained a 92.6% COD removal efficiency by applying adsorption after coagulation-flocculation to car wash wastewater (Veit et al. 2020). Despite the high COD removal efficiencies achieved through chemical treatments, these methods have drawbacks such as high chemical costs and the generation of excessive chemical sludge (Akpomie and Dawodu 2015).

The most appropriate way to mitigate these disadvantages is to combine chemical processes with biological treatments. In addition, although high COD removal efficiencies are achieved with chemical treatment processes, additional treatment is required due to the high COD content of AIW. Biological treatment is the most economical method that can be used for this purpose. Therefore, applying chemical treatment as a pretreatment to reduce toxic substances in AIW and then biological treatment to remove the remaining COD can be considered as an economical approach. Along with this approach, the feasibility of treating AIW treated with physicochemical methods together with domestic wastewater in the activated sludge process was investigated in a recent study (Penas et al. 2024). In the study, the ratio of AIW added to domestic wastewater was gradually increased. As a result of the study, it was reported that there was no decrease in treatment efficiency even if physiochemically treated AIW was added at a ratio of 1:1.

Coagulation-flocculation is commonly used in AIW treatment, but advanced oxidation processes (AOPs), mainly Fenton oxidation, are gaining attraction for treating industrial wastewater containing non-biodegradable and toxic organic substances (Benitez et al. 2007). In AOPs, oxidizing radicals, such as hydroxyl radicals (OH•), react rapidly with pollutants, irrespective of whether they are organic or inorganic, thereby achieving complete degradation. Classical Fenton oxidation, using iron (Fe^{2+}) and hydrogen peroxide (H_2O_2), is known for its simplicity and high efficiency in breaking down complex pollutants, including phenolic compounds (Nieto et al. 2010). The efficiency of this process depends on the H_2O_2/COD and Fe/H_2O_2 ratios and pH levels (Bressan et al. 2004). Studies have explored using ferric ion (Fe^{3+}) as a catalyst to reduce chemical costs, resulting in a slower reaction rate but similar removal efficiency to Fenton oxidation (Nieto et al. 2010; Carlos et al. 2024) The oxidation process including the application of Fe^{3+} as catalyst is called as Fenton-based oxidation. Various enhancements, including electro-, photo-, and sono-assisted Fenton oxidations, have been applied to improve the degradation performance of inorganic and recalcitrant organic compounds. A review of the literature reveals a limited number of studies on the treatment of AIW using Fenton oxidation. To expand this understanding, studies involving Fenton oxidation in automotive, metal coating, and car washing wastewaters were also examined. In most of these studies, pH and reaction time were studied along with H_2O_2 and Fe^{2+} concentrations as the main factors affecting the Fenton oxidation efficiency.

In a study conducted by Budak Ozlu (2016), the optimal conditions were determined to remove copper, zinc, iron, nickel and chromium from wastewaters of metal coating industry. The optimum H_2O_2/COD and Fe/H_2O_2 ratios for the highest removal efficiency of each heavy metal were determined differently. Sahinkaya (2017) identified optimal conditions for the classical Fenton oxidation of enamel coating wastewaters as pH 3, a reaction time of 60 min, 200 mg/L of Fe^{2+}, and 200 mg/L of H_2O_2, resulting in 82% COD removal. Tony and Bedri (2014) determined that a pH of 3.5 and an H_2O_2/Fe^{2+} molar ratio of 13.71 were optimal for COD removal in wastewater from a car washing facility, achieving a COD removal efficiency of 92% by photo-Fenton oxidation. In another study by Yilmaz (2008), Fenton oxidation was applied to wastewater from chrome plating baths in the metal plating industry. The optimal operating conditions for achieving high COD removal were determined to be a COD/H_2O_2 ratio of 1.12, an H_2O_2/Fe^{2+} ratio of 0.66, and a pH of 3.5, resulting in a 60% COD removal efficiency. Magnago et al. (2018) applied both Fenton and photo-Fenton oxidations to car wash wastewater containing various residues such as gasoline, oil, and grease. For the photo-Fenton oxidation, two black fluorescent lamps of 40 W were used. In oxidation experiments conducted at a pH of 3 for both processes, the Fenton oxidation achieved an 84% COD removal efficiency, while the photo-Fenton oxidation achieved a 93% COD removal efficiency. Although the efficiency of Fenton oxidation is typically assessed in terms of COD or heavy metal removal, the success of subsequent biological treatment relies on the absence of toxic effects on microorganisms. However, no studies have been identified in the literature that evaluate the biodegradability or potential toxic effects on microorganisms following Fenton oxidation of AIW.

Today, in the effort to slow down global warming and climate change, selecting wastewater treatment processes that produce low carbon dioxide emissions has become as important as process efficiency and cost, similar to other sectors. The carbon dioxide equivalent (CO_2e) value of the greenhouse gases emitted by a process or product over a specific period is defined as its carbon footprint (CF). Combining CF

calculations with technical and economic factors to evaluate the sustainability of treatment processes has become a critical issue. In a study assessing the CF of Fenton oxidation, it was found that approximately 66% of the total CF of the process is attributable to chemical consumption, while the impact of infrastructure and transportation is negligible (Salazar et al. 2019).

This study aims to assess the applicability of the Fenton-based oxidations for the treatment of AIW prior to biological treatment. The objective is to identify the optimal operating conditions for Fenton-based oxidation to maximize the removal efficiency of contaminants. To achieve this, the study employs an experimental design using the Response Surface Methodology (RSM) and Central Composite Design (CCD) to test different iron and hydrogen peroxide concentrations, along with varying reaction times. As Fenton oxidation is intended as a pretreatment before biological processes, the study evaluates the impact of different operating conditions (iron concentration, hydrogen peroxide concentration, and reaction time) on removal efficiency, with a focus on toxicity reduction. Activated sludge inhibition tests were performed on Fenton-treated AIW under these varying conditions to assess toxicity removal efficiency. Additionally, COD measurements were conducted after Fenton oxidation to determine the most effective operating conditions for both COD and toxicity removal while minimizing sludge formation. In the final stage of the study, the chemical-based carbon footprint was calculated for the chemical consumption determined for Fenton-based oxidation processes, as well as for the chemical consumption in the coagulation-flocculation process used for AIW treatment at the facility where the wastewater was sourced. The impact of Fenton-based oxidation on reducing the carbon footprint was then evaluated. The study was conducted at Akdeniz University in Antalya, Türkiye, between September 2023 and May 2024.

Materials and methods

Wastewater characterization

Wastewater samples were collected from a mass production automotive facility, where the cataphoresis process generates the highest COD concentration, reaching 56,200 mg L^{-1}. Wastewater from all production stages is stored in an equalization tank without prior treatment. The wastewater used in the experiments was obtained from the equalization tank and stored at + 4 °C in the laboratory during experiments. Prior to Fenton oxidation experiments, the oil and grease layer accumulated on the wastewater was removed. After removing the surface oil and grease layer, the COD concentration of the wastewater was measured to serve as a basis for the experimental calculations. The analysis revealed a COD concentration of 1314.83 ± 32.05 mg L^{-1}, which decreased to 1137.96 ± 110.53 mg L^{-1} after settling. The COD concentration was measured according to standard methods (APHA 2012).

Experimental design

The literature review identified key factors, such as pH, reaction time, and Fe and H_2O_2 concentrations, as critical to the efficiency of the Fenton oxidation. Optimizing these parameters individually is both time-consuming and costly. To address this, the experimental studies were designed using the Response Surface Methodology (RSM) and Central Composite Design (CCD), based on insights from the initial literature review. The RSM is a combination of mathematical and statistical techniques widely used in engineering research for process design, analysis, modeling, and optimization (Arslan-Alaton et al. 2010). The RSM establishes a numerical relationship between the selected independent variables and the process output, developing a model with a high regression coefficient to describe the process response (Myers et al. 2016). This model allows for the estimation of optimal values for the process variables to achieve high or desired efficiency. The main advantage of RSM over other statistical design methods is that it minimizes the number of experiments required to evaluate multiple parameters and their ranges. However, its major limitation is the inability to determine interaction effects between the independent variables. The CCD is the most commonly used design type for determining the functions in RSM (Myers et al. 2016). As a more efficient alternative to factorial designs in terms of the number of experiments, CCD aims to achieve the same purpose as RSM but with fewer experiments, making it both time- and cost-effective. What sets CCD apart from other design methods is the use of axial points, which are the highest or lowest levels of a factor (Jensen 1995). The center point represents the average level of all values. Axial points vary based on the desired design characteristics and the number of factors.

In this study, the Fenton oxidation experiments were optimized using the RSM and CCD methods. The primary goal was to achieve high COD removal from AIW while minimizing sludge formation. To accomplish this, three key variables were selected: H_2O_2 /COD ratio, Fe concentration, and reaction time. A review of similar studies in the literature (Table 1) indicates that a pH of 3 and 3.5 are optimal for maximizing COD removal efficiency. Therefore, in order to determine the pH that should be applied to AIW, preliminary experiments were carried out at the highest selected H_2O_2 and Fe^{2+} doses at pH 3 and 3.5. As a result of the preliminary experiments, it was determined that higher COD removal efficiencies could be obtained when Fenton

Table 1 Fenton oxidation efficiency in removing COD

Wastewater type	pH	COD (mg L^{-1})	H_2O_2/COD (mol mol^{-1})	H_2O_2/Fe (mol mol^{-1})	Time (min)	COD Removal (%)	References
Metal plating	3	300	0.471	1.64	25	53[a)]	Budak Ozlu (2016)
Enamel coating	3	590	0.399	2.74	60	82	Sahinkaya (2017)
Car wash facility	3.5	82	4.64	13.71	–	92	Tony and Bedri (2014)
Metal plating	3.5	168	1.12	0.66	60	60	Yilmaz (2008)
Car wash facility	3	201	0.053	0.16	60	84	Magnago et al. (2018)
Car repair facility	3	950	1.88	0.78	120	76	Bogacki and Al-Hazmi (2017)
	9	933	1.92	4.46	15	45	
Car wash facility	3	5022	0.042	3.7	45	90	Cüce and Temel (2021)
	3	567	0.166	2.19	45	98	
Metal plating	3.5	613	0.768	2.74	60	39	Yemen (2019)

[a]Total organic carbon removal efficiency

oxidation was applied at pH 3. Consequently, a pH of 3 was maintained throughout the Fenton oxidation experiments.

In accordance with the previous studies, the reaction times were adjusted to a minimum of 30 min and a maximum of 90 min. Studies using Fenton oxidation (Table 1) indicate that suitable H_2O_2/COD molar ratios fall between 0.31 and 1.88 mol mol^{-1}. Since the Fenton oxidation in this study is intended as a pretreatment step before biological treatment, the H_2O_2/COD molar ratios were extended, with the highest ratio set at 2.62 and the lowest at 0.58. Similarly, the selection of low and high levels of iron concentration was based on the H_2O_2/Fe molar ratios used in previous studies with Fenton and Fenton-based oxidations. The most suitable H_2O_2/Fe molar ratios generally range from 0.155 to 4.45 mol mol^{-1} (Table 1). Since defining two variables based on one parameter (H_2O_2) would complicate the calculations, it was decided to treat Fe concentration as a variable, rather than the H_2O_2/Fe molar ratio. The H_2O_2/Fe ratio would then be calculated based on the optimized Fe concentration and presented in the results. Accordingly, the Fe concentration was selected to range between 0.58 and 2.92 g L^{-1}, corresponding to an H_2O_2/Fe molar ratio of 1–5 mol mol^{-1}. Once the variables for process optimization were identified, their minimum and maximum levels (supplementary Table S1) were input into the Design Expert® statistical software (Stat Ease, USA) to create the experimental design. All experiments were performed in duplicates at the process conditions proposed by RSM.

Fenton oxidation experiments

After completing the experimental design using RSM and CCD, Fenton oxidation experiments were initiated. Ferrous sulfate heptahydrate ($FeSO_4.7H_2O$) was used as the Fe^{2+} source, and ferric chloride ($FeCl_3$) was used as the Fe^{3+} source in the Fenton-based oxidations. For each experiment, 250 mL of AIW was placed in a beaker, and predetermined amounts of H_2O_2 and, Fe^{2+} or Fe^{3+} solutions were added. First, H_2O_2 were added to the 250 mL of wastewater and the samples were stirred continuously. After adding Fe^{2+} or Fe^{3+}, the pH of the samples was adjusted to 3 ± 0.1 using 6 M sulfuric acid (H_2SO_4) to initiate the Fenton reaction. The reactions were carried out for the times determined according to experimental plan recommended by the Design Expert® program. At the end of the reaction, the pH of the wastewater was raised to 10 ± 0.1 by adding 1 M or 6 M sodium hydroxide (NaOH) to stop the oxidation reaction. The treated wastewater was then transferred to 250 mL measuring cylinders and allowed to settle for 1 h. After settling, the sludge volumes were measured and recorded, while the liquid phases were separated and stored at + 4 °C for further analysis.

Photo-Fenton experiments

A 30-W UV fluorescent lamp (Led Advance brand) with a wavelength of 253.7 nm was used for the photo-Fenton experiments. Detailed information about the UV lamp is provided in Table S2. In these experiments, the optimal conditions established from the optimization of Fenton-based oxidation aimed at minimizing sludge formation while maximizing COD removal, were applied. The objective of the photo-Fenton experiments was to evaluate the potential for further improving COD removal and reducing sludge formation compared to the Fenton oxidation alone. The photo-Fenton experiments followed the same procedure as the Fenton oxidation experiments, with the addition of UV light exposure during the reaction. After each experiment, the treated AIW was allowed to settle for 1 h, as in previous tests. The sludge volumes were then measured and recorded,

and the liquid phases were stored at + 4 °C for subsequent COD analysis.

Activated sludge inhibition tests

Since different toxicity levels were determined for different target microorganisms in the toxicity tests applied after the application of Fenton-based oxidations, it was suggested that the toxicity test to be applied should be selected according to the nature of the microorganisms in the receiving environment to which the wastewater will be discharged (Kumar et al. 2020). In line with this finding, the activated sludge inhibition test was selected to evaluate the effectiveness of Fenton-based oxidants in reducing the toxic effects of AIW on mixed microbial culture. Unlike toxicity tests conducted with specific microorganisms, this test directly assesses the response of the microorganisms responsible for biological treatment to toxic substances, providing a more relevant measure for wastewater treatment processes. The purpose of the activated sludge inhibition test is to determine the concentrations that do not exhibit inhibitory effects for use in biodegradation tests and to quickly identify substances that could negatively impact aerobic biological treatment plants. In this study, to evaluate the effectiveness of Fenton-based oxidations in eliminating the toxic effects of AIW, both raw wastewater and wastewater treated under optimal conditions with the Fenton-based oxidation were used in activated sludge inhibition tests (ISO 2007).

To perform the tests, activated sludge was obtained as inoculum from a municipal wastewater treatment plant. The activated sludge was gradually fed synthetic wastewater with increasing COD concentrations on a weekly basis until it was fully acclimated in the fill-and-drawn reactor. The synthetic wastewater solution was prepared with the following components: 32 g L^{-1} peptone, 22 g L^{-1} meat extract, 6.0 g L^{-1} urea, 1.4 g L^{-1} sodium chloride, 0.8 g L^{-1} calcium chloride dihydrate, 0.4 g L^{-1} magnesium sulfate heptahydrate, and 5.6 g L^{-1} anhydrous potassium monohydrogen phosphate (ISO 2007). The acclimation process was monitored by periodically taking samples from the reactor and conducting suspended solids (SS) and volatile suspended solids (VSS) analyses. The SS and VSS concentrations were measured according to standard methods (APHA 2012). During the inhibition tests, an aeration system was set up to provide parallel and equal airflow to test bottles. The calculated amount of activated sludge and water was added to the bottles, aerators were placed inside, and the sludge was aerated for 10 min. Subsequently, different wastewater samples, including raw and Fenton-treated AIW with the same COD concentration, were added to each bottle to begin the inhibition tests. The same concentration of microorganisms was exposed to synthetic wastewater as a control in all inhibition tests. For calculation of percent inhibition, the decrease in dissolved oxygen concentrations was measured at different times in each sample. Oxygen consumption rates were calculated from the linear part of the dissolved oxygen consumption graphs using Eq. (1):

$$R = \frac{\left(DO_1 - DO_2\right)}{\Delta t} \tag{1}$$

The oxygen consumption rate expressed by Eq. (1) represents oxygen consumption rate (R) as $mgO_2\ L^{-1}\ h^{-1}$, the dissolved oxygen concentration at the start of the selected linear phase (DO_1) as mg $O_2\ L^{-1}$, at the end of the selected linear phase (DO_2) as mg $O_2\ L^{-1}$ and time interval between measurements of DO_1 and DO_2 (Δt) as a second.

After the calculation of oxygen consumption rates of aerobic microorganisms, the inhibition percentages for raw and pretreated AIW were calculated by comparing with the respiration rate measured in control sample using Eq. (2):

$$I = \frac{\left(R_0 - R_W\right)}{R_0} \times 100 \tag{2}$$

The percent inhibition (I) expressed by Eq. (2) represents the oxygen consumption rate calculated for the control sample (R_0) and the oxygen consumption rate calculated for the raw and pretreated AIW (R_W).

Chemical based carbon footprint calculation

At the automotive industry factory where the wastewater was sourced, approximately 280 trucks, 60 vans, 124 minibuses, 33 buses, and 1 armored defense vehicle are assembled per month. The average daily wastewater generated during vehicle production is 40 $m^3\ day^{-1}$. The quantities of anionic polyelectrolyte (polyacrylamide, PAM), $FeCl_3$, H_2SO_4, and hydrochloric acid (HCl) consumed for the treatment of 40 $m^3\ day^{-1}$ of wastewater in the coagulation-flocculation process prior to biological treatment were determined. Similarly, after optimizing the Fenton-based oxidations, the quantities of chemicals (H_2O_2, $FeSO_4{\cdot}7H_2O$, $FeCl_3$, H_2SO_4, NaOH) required at the operating conditions yielding the highest efficiency were calculated to determine the chemical usage needed to treat 40 m^3 of wastewater. The CF assessment was based solely on the chemicals consumed, excluding energy consumption during the processes. Emission factors provided in Table 2 were used to calculate the chemical-based CFs. For 40 m^3 of wastewater, the chemical usage was multiplied by the emission factor to calculate CO_2e emissions for each chemical, and the daily chemical-based CF for each process was determined.

Table 2 Emission factor used for carbon footprint calculations

Chemical substance	Emission factor (EF) ($kgCO_2e\ kg^{-1}$)	References
Anionic polyelectrolyte (polyacrylamide, PAM)	1.50	T/CAEPI 49 (2022), Sun et al. (2024)
Ferric chloride ($FeCl_3$)	0.43	Hilbert et al. (2022)
Ferrous sulfate ($FeSO_4$)	0.167	EPA (2016)
Hydrogen peroxide, 50% (H_2O_2)	1.19	
Sulfuric acid (H_2SO_4)	0.2175	Edwards et al (2017)
Sodium hydroxide (NaOH)	0.5297	
Hydrochloric acid (HCl)	1.06	

Results and discussion

Performance of Fenton and Fenton-based Oxidations on COD removal and sludge formation

Fenton oxidation

Fenton oxidation experiments were conducted according to experimental plan created using RSM and CCD to determine the optimal operating parameters for the removal of automotive industry wastewater (AIW) using the classical Fenton oxidation. The COD removal efficiency increases with higher Fe^{2+} concentrations in the Fenton oxidation (Fig. 1a). However, when the Fe^{2+} concentration is kept constant, increasing the H_2O_2/COD molar ratio, and consequently the H_2O_2 concentration, leads to a reduction in COD removal efficiency. The highest COD removal efficiency, 59.93%, was achieved with a Fe^{2+} concentration of 2.92 g L^{-1}, an H_2O_2/COD molar ratio of 0.58 mol mol^{-1}, and a reaction time of 90 min. In contrast, the lowest COD removal efficiency, 31.36%, was observed with a Fe^{2+} concentration of 0.58 g L^{-1}, an H_2O_2/COD molar ratio of 2.62 mol mol^{-1}, and a reaction time of 30 min.

A major drawback of Fenton oxidation is the generation of chemical sludge. The sludge volumes produced after each experiment were measured and are given in Fig. 1b. Under the conditions that achieved the highest COD removal efficiency, approximately 150 mL of sludge was produced. This suggests that, despite the high COD removal efficiency, the final treated wastewater volume would be reduced to around 100 mL. As expected, the most influential parameter on sludge volume is the Fe^{2+} concentration. While the H_2O_2/COD molar ratio and reaction time do not significantly impact sludge volume, increasing the Fe^{2+} concentration leads to a substantial rise in sludge production. The lowest sludge volume, approximately 28 mL, was observed in the experiment with a Fe^{2+} concentration of 0.58 g L^{-1}, an H_2O_2/COD molar ratio of 2.62 mol mol^{-1}, and a reaction time of 90 min. However, under these conditions, the COD removal efficiency was 35.05%

Fenton-based oxidation

In these experiments, Fe^{3+} was used as a catalyst instead of Fe^{2+}. The COD removal efficiency increases as the Fe^{3+} concentration in the Fenton-based oxidation is raised from 0.58 to 1.75 g L^{-1} (Fig. 2a). However, further increasing the Fe^{3+} concentration from 1.75 to 2.92 g L^{-1} results in a decrease in COD removal efficiency. The highest COD removal efficiency, 58.83%, was achieved with a Fe^{3+} concentration of 1.75 g L^{-1}, an H_2O_2/COD molar ratio of 2.62 mol mol^{-1}, and a reaction time of 60 min. The lowest COD removal efficiency, 36.57%, was observed under the same conditions (0.58 g L^{-1} Fe^{3+}, H_2O_2/COD molar ratio of 2.62 mol mol^{-1}, 30 min) as those that produced the lowest COD removal efficiency in the classical Fenton oxidation.

The chemical sludge volumes resulting from the Fenton-based oxidation are presented in Fig. 2b. Approximately 112 mL of chemical sludge was produced under the conditions that achieved the highest COD removal efficiency with Fenton-based oxidation. Overall, while using Fe^{3+} in Fenton oxidation led to less sludge formation, there was no significant difference in the COD removal efficiencies between the classical Fenton and Fenton-based oxidations.

Modeling

Modeling of Fenton oxidation

The COD removal efficiencies (Fig. 1a) and chemical sludge volumes (Fig. 1b) were input into the Design Expert software for statistical analysis. The analysis revealed that COD removal could be effectively modeled using a cubic (third-order) model with a high regression coefficient (R^2) of 0.9781, while sludge volume was best modeled with a quadratic (second-order) model, yielding an R^2 of 0.8255. According to the model for COD removal, 97.81% of the total variables and results could be explained by the proposed model. The adjusted regression coefficient (adj-R^2) was 0.9453, and the predicted regression coefficient (pred-R^2) was 0.8175. The close alignment of adj-R^2 and pred-R^2 with the R^2 value indicates high model reliability, showing that no additional terms are needed. For sludge volume, the adj-R^2 and pred-R^2 values were 0.7450 and 0.5817, respectively, and the program confirmed that these values were consistent with the R^2 value. The comparison between the observed (experimental) and theoretical results, calculated using the third-order model for COD removal and the second-order model for sludge volume, is shown in Fig. S1. The actual equation of the third-order model for COD removal,

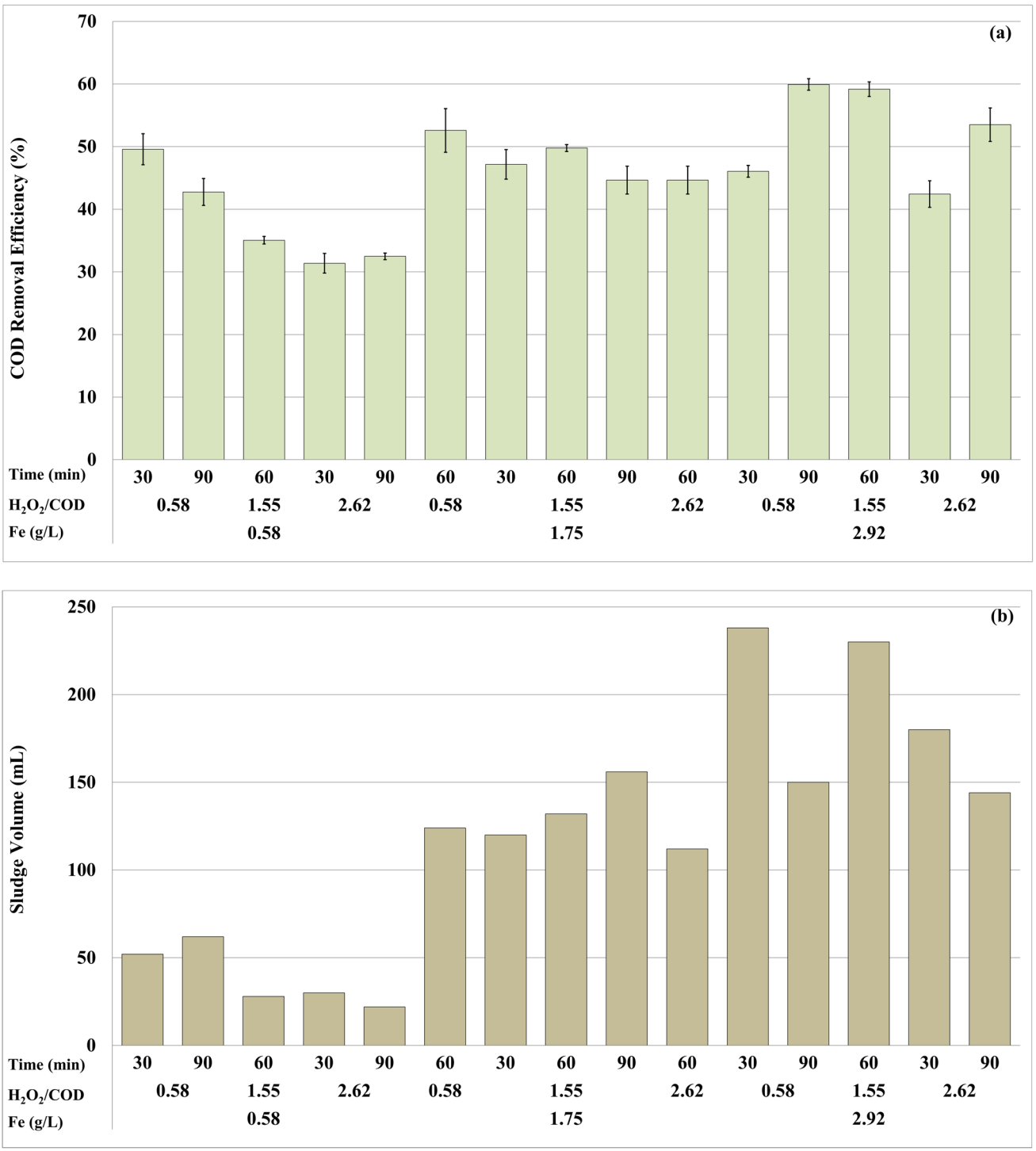
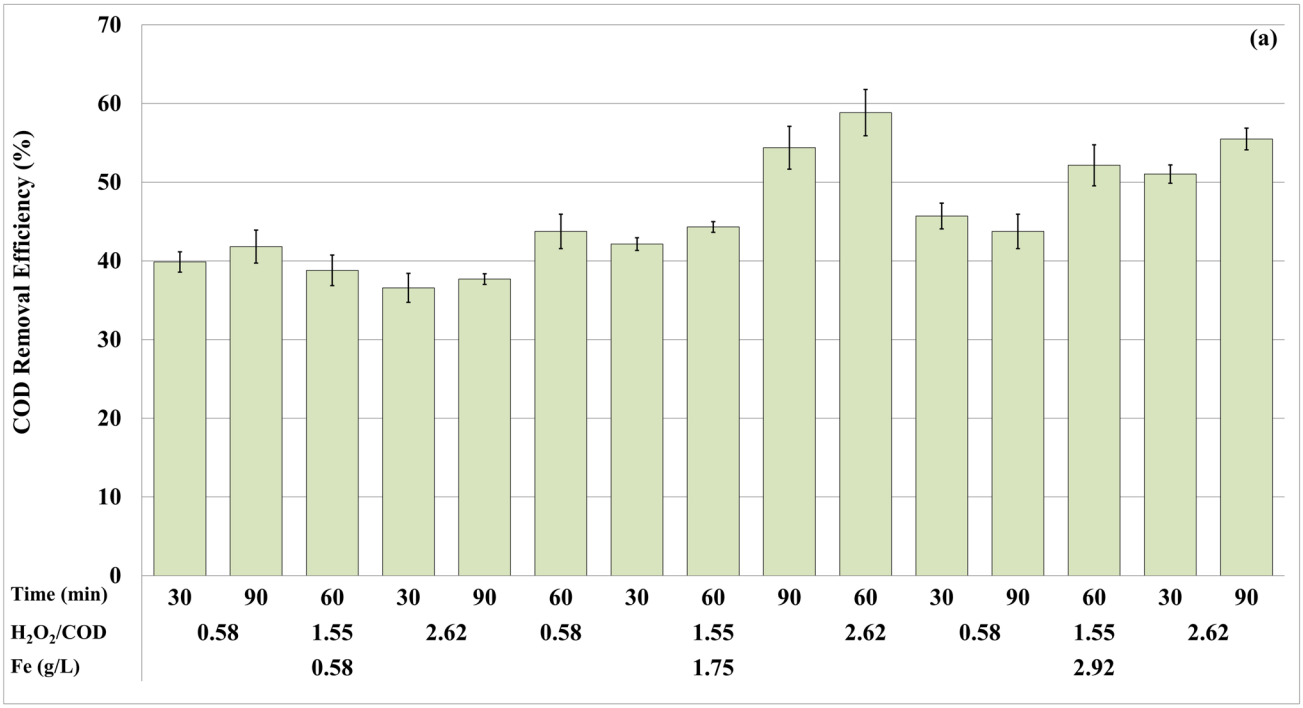


Fig. 1 **a** The COD removal efficiencies and **b** chemical sludge volumes obtained in Fenton oxidation



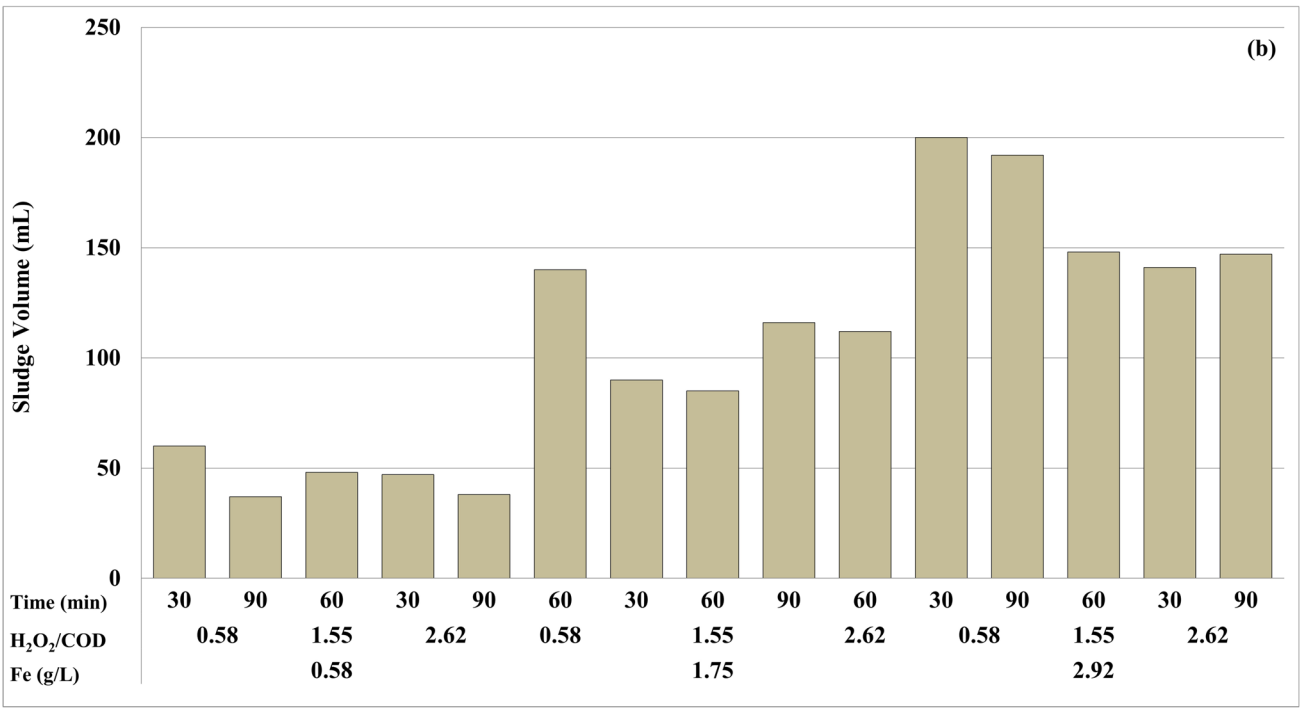


Fig. 2 **a** The COD removal efficiencies and **b** chemical sludge volumes obtained in Fenton-based oxidation

as suggested by the Design Expert program, is presented in Eq. (3).

$$\begin{aligned}&\textit{COD removal efficiency}\\&= +31{,}46635 - (2{,}60830 \times A)\\&\quad + (0{,}76342 \times B) + (0{,}11896 \times C)\\&\quad + (2{,}60482 \times A \times B) + (0{,}15559 \times A \times C)\\&\quad - \left(1{,}19052 \times A^2\right) + \left(1{,}58575 \times B^2\right)\\&\quad + (0{,}050708 \times A \times B \times C) - \left(0{,}90757 \times A \times B^2\right)\\&\quad - \left(1{,}67534 \times 10^{-3} \times A \times C^2\right) - \left(0{,}026959 \times B^2 \times C\right)\end{aligned} \tag{3}$$

where A stands for H_2O_2/COD molar ratio (mol mol^{-1}), B is the Fe^{2+} concentration (g L^{-1}) and C refers to the reaction time (min).

The impact of the model and the selected independent variables on the process response, COD concentration, was evaluated using ANOVA test. The ANOVA results for the developed model to predict COD removal through the Fenton oxidation are provided in Table S3. The p-value (< 0.0001) obtained for the model indicates it is statistically significant at a 99.9999% confidence level. Parameters with p-values less than 0.05 are statistically significant and influential on the process. The main effects of the independent variables, H_2O_2/COD molar ratio (A) and Fe^{2+} concentration (B), in the cubic model for COD removal were statistically significant due to their low p-values. However, the p-value for reaction time (C) was 0.4767, indicating that reaction time does not have a significant direct effect on the Fenton oxidation. Additionally, second-order interactions, such as the interaction between H_2O_2/COD ratio and Fe^{2+} concentration (AB), Fe^{2+} concentration and reaction time (BC), and the squared effect of reaction time (C^2), were statistically significant ($p < 0.05$). Third-order interaction effects, including the combined effect of H_2O_2/COD ratio, Fe^{2+} concentration, and reaction time (ABC), and the squared effect of H_2O_2/COD ratio with Fe^{2+} concentration (A^2B), were also found to be statistically significant model terms. The response surface plots illustrating the effects of process variables on COD concentration are presented in Fig. 3. According to H_2O_2/COD-Fe^{+2} response surface plot (Fig. 3a), showing the influence of H_2O_2/COD molar ratio and Fe^{2+} concentration on COD removal efficiency at a fixed reaction time of 60 min, COD removal efficiency decreases as the H_2O_2/COD ratio increases at fixed Fe^{2+} concentrations. To achieve high COD removal efficiency with a reaction time of 60 min, Fenton oxidation should be performed with a low H_2O_2/COD ratio and a high Fe^{2+} concentration.

At a fixed Fe^{2+} concentration of 1.82 g L^{-1}, the response surface graph showing the effect of H_2O_2/COD molar ratio and reaction time is provided in Fig. 3b. This plot indicates that, at a fixed Fe^{2+} concentration, changes in H_2O_2/COD molar ratio and time have a limited effect on COD removal efficiency. To achieve high COD removal efficiency with a fixed Fe^{2+} concentration of 1.82 g L^{-1}, a reaction time of 40–65 min and an H_2O_2/COD molar ratio of 0.58–0.6 mol mol^{-1} are recommended. Increasing the H_2O_2/COD molar ratio leads to a decrease in COD removal efficiency. With an H_2O_2/COD molar ratio of 1.75 mol mol^{-1}, the response surface graph in Fig. 3c highlights the effect of Fe^{2+} concentration and reaction time. This plot shows that increasing both Fe^{2+} concentration and reaction time leads to improved COD removal efficiency. COD removal rates of up to 60% can be achieved with a reaction time of 70–90 min and a Fe^{2+} concentration of around 2.92 g L^{-1}.

Modeling of Fenton-based oxidation

The analysis determined that COD removal could be modeled using a cubic (third-order) model with a high regression coefficient (R^2) of 0.9702, while sludge volume was best modeled with a cubic model and an R^2 of 0.9999. According to the COD removal model, 97.02% of the variables and results were explained by the proposed model, with a corrected regression coefficient (adj-R^2) of 0.9291 and a predicted regression coefficient (pred-R^2) of 0.8064, indicating strong alignment with the R^2 value. The closeness of adj-R^2 to R^2 confirms that no additional terms are needed for the model. For sludge volume, adj-R^2 and pred-R^2 values were 0.9999 and 0.9566, respectively, further confirming the model's high reliability. The comparison of observed (experimental) results against the theoretical results calculated using the cubic model for COD removal and the cubic model for sludge volume is shown in Fig. S2. The actual equation of the third-order model for COD removal, as suggested by the Design Expert program, is presented in Eq. (4).

$$\begin{aligned}&\textit{CODremovalefficiency}\\&= +31{,}46635 - (2{,}60830 \times A) + (0{,}76342 \times B)\\&\quad + (0{,}11896 \times C) + (2{,}60482 \times A \times B)\\&\quad + (0{,}15559 \times A \times C) - \left(1{,}19052 \times A^2\right)\\&\quad + \left(1{,}58575 \times B^2\right) + (0{,}050708 \times A \times B \times C)\\&\quad - \left(0{,}90757 \times A \times B^2\right) - \left(1{,}67534 \times 10^{-3} \times A \times C^2\right)\\&\quad - \left(0{,}026959 \times B^2 \times C\right)\end{aligned} \tag{4}$$

where A stands for H_2O_2/COD molar ratio (mol mol^{-1}), B is the Fe^{3+} concentration (g L^{-1}) and C refers to the reaction time (min).

The impact of the model and selected independent variables on COD concentration as the process response was evaluated using ANOVA test. The ANOVA results for the developed model to predict COD removal through the Fenton oxidation are provided in Table S4. The p-value

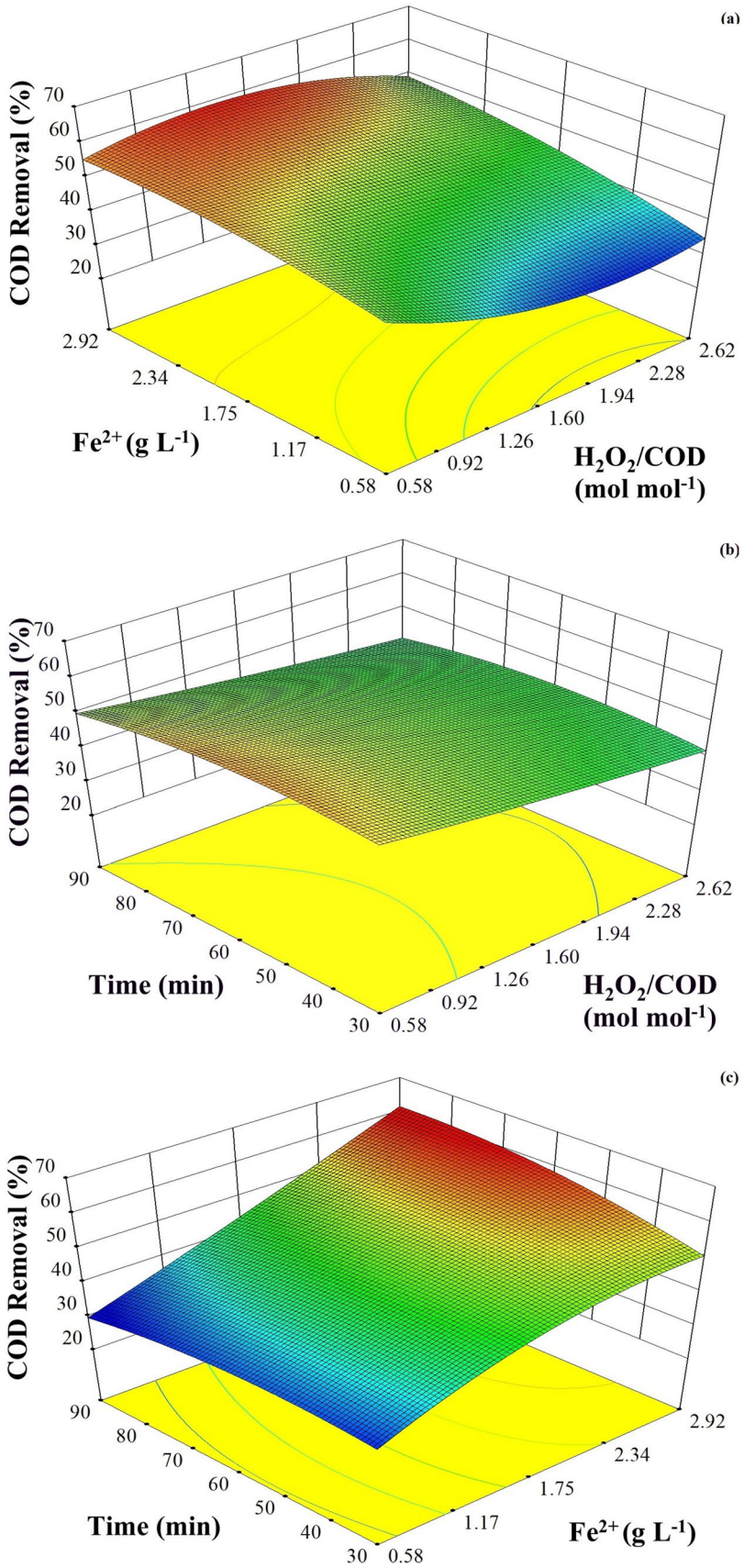


Fig. 3 Response surface (RS) plots showing the effects of process variables on COD removal by Fenton oxidation: **a** H_2O_2/COD-Fe^{+2} RS; **b** H_2O_2/COD-Time RS; **c** Fe^{+2}-Time RS

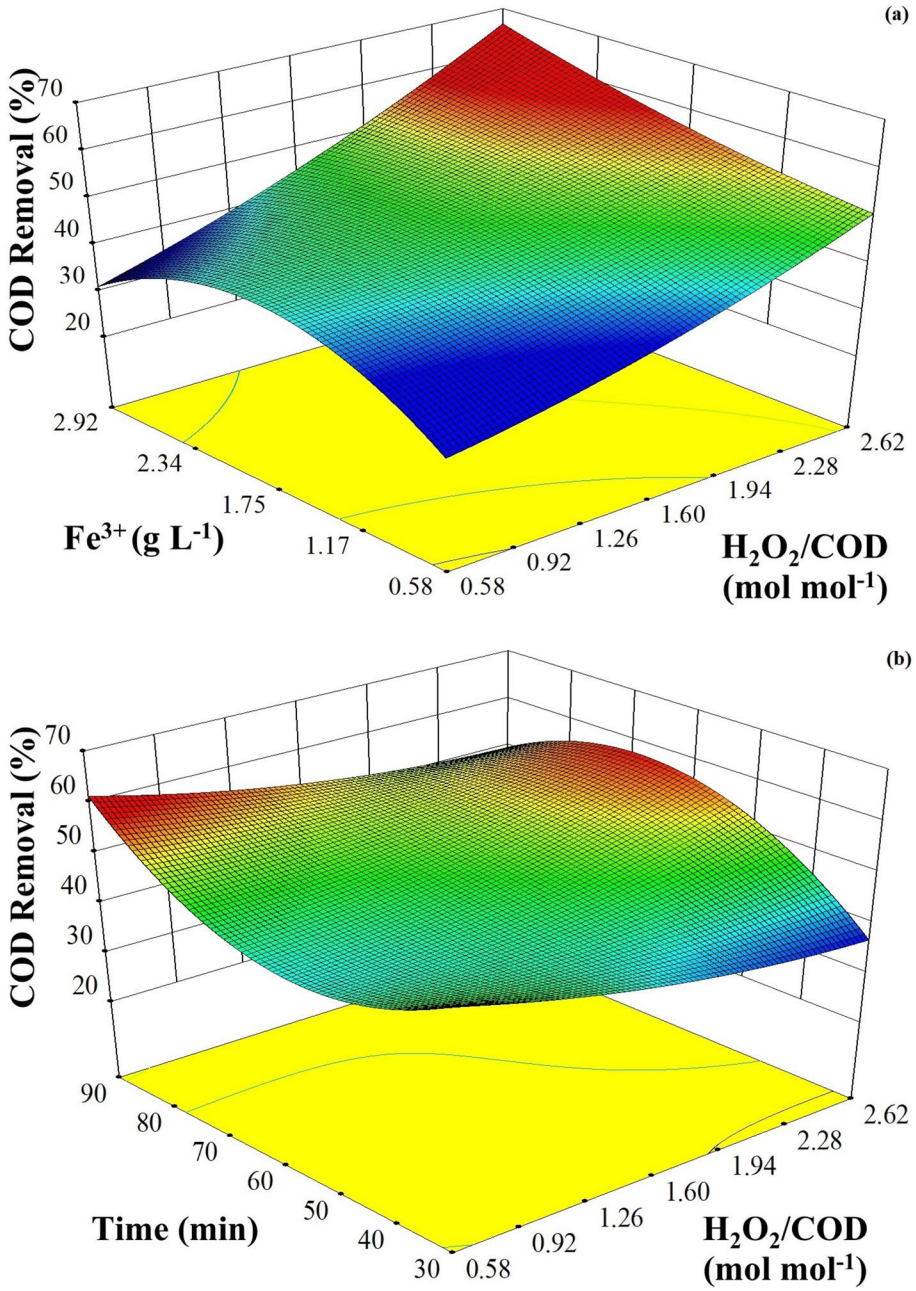


Fig. 4 Response surface (RS) plots showing the effects of process variables on COD removal by Fenton-based oxidation: **a** H_2O_2/COD-Fe^{+3} RS; **b** H_2O_2/COD-Time RS

(< 0.0001) obtained from the ANOVA test for the recommended optimal values indicates that the model is significant at a 99.9999% confidence level. Parameters with p-values less than 0.05 were considered statistically significant and impactful on the process. The main effects of the independent variables (H_2O_2/COD molar ratio (A), Fe^{3+} concentration (B), and reaction time (C)) in the cubic model for COD removal were statistically significant due to their low p-values. Additionally, the second-order interaction between H_2O_2/COD molar ratio and Fe^{3+} concentration (AB), as well as the squared effects of H_2O_2/COD molar ratio (A^2) and Fe^{3+} concentration (B^2), were also statistically significant ($p < 0.05$). Among the third-order interaction effects, the interaction between H_2O_2/COD molar ratio and the squared effect of Fe^{3+} concentration (AB^2), the interaction between H_2O_2/COD molar ratio and the squared effect of reaction time (AC^2), and the interaction between Fe^{3+} concentration and the squared effect of reaction time (B^2C) were found to be statistically significant. Response surface plots illustrating the effects of the process variables on COD concentration are shown in Fig. 4.

At a fixed reaction time of 60 min, the response surface plot illustrating the effect of the H_2O_2/COD molar ratio and Fe^{3+} concentration on COD removal efficiency is shown in

Fig. 4a. Unlike in Fenton oxidation, increasing the H_2O_2/COD molar ratio, in addition to Fe^{3+} concentration. According to Fig. 4a, to achieve high COD removal efficiency with the Fenton-based oxidation at a fixed 60-min reaction time, the highest Fe^{3+} concentration and H_2O_2/COD molar ratio should be applied. With an H_2O_2/COD molar ratio of 1.82 mol mol^{-1}, the response surface graph illustrating the effect of the H_2O_2/COD molar ratio and reaction time is shown in Fig. 4b. This plot reveals that increasing the reaction time at a fixed Fe^{3+} concentration improves COD removal efficiency. However, a long reaction time at a high H_2O_2/COD molar ratio negatively impacts COD removal efficiency. For optimal COD removal at a fixed Fe^{3+} concentration of 1.82 g L^{-1}, either a reaction time of 55–80 min with an H_2O_2/COD molar ratio of 2.6 mol mol^{-1}, or a reaction time of 85–90 min with an H_2O_2/COD molar ratio of 0.58–1.26 mol mol^{-1}, should be applied. According to the developed model for COD removal, the combined effect of Fe^{3+} concentration and reaction time was insignificant, and therefore, the model did not generate graphs illustrating their interaction.

Optimization

Although the primary goal of Fenton and Fenton-based oxidations is COD removal, minimizing chemical sludge formation is crucial for making these processes advantageous over other treatment methods. Therefore, during process optimization, conditions that maximize COD removal while minimizing chemical sludge production were investigated.

Optimization of Fenton oxidation

Each process variable and response was assigned an importance level (1–5) and an optimization objective. For each parameter, one of five objectives were selected: within range, maximize, minimize, target value, or equalize. Additionally, lower and upper limits were set for each process variable and response. Using these features, the process variables (H_2O_2/COD molar ratio, Fe^{2+} concentration, and reaction time) were optimized based on their weight. While the reaction time limits remained between 30 and 90 min, the lower and upper limits for Fe^{2+} concentration and H_2O_2/COD molar ratio were adjusted based on experimental results. Since increasing Fe^{2+} concentration and decreasing the H_2O_2/COD ratio improved COD removal efficiency, the H_2O_2/COD ratio lower limit was set at 0.45 mol mol^{-1}, and the upper limit for Fe^{2+} concentration was set at 3.5 g L^{-1}.

After defining the objectives and limits for the process variables, adjustments were made to optimize the process responses (COD removal and sludge volume). The COD removal efficiency was given the highest importance level (5), with the optimization goal set to "maximize". For sludge volume, the objective was to "minimize", with a medium importance level (3). Two optimization criteria were applied. The first criterion was to optimize the process variables to achieve the highest possible COD removal efficiency while keeping the sludge volume below half of the wastewater volume. The second criterion aimed to identify conditions that would minimize sludge volume while still achieving 50% COD removal, as Fenton oxidation is intended to serve as a pretreatment before biological treatment.

The low H_2O_2/COD molar ratios (0.47–0.58 mol mol^{-1}) and high Fe^{2+} concentrations (3.09–3.43 g L^{-1}) to achieve

Table 3 Optimization results of Fenton based oxidations

Objective	Independent variables			Process responses			
				COD (%)		Sludge volume (mL)	
	H_2O_2/COD (mol mol^{-1})	Fe (g L^{-1})	Time (min)	Prediction	Observation	Prediction	Observation
Fenton oxidation (Fe^{2+})							
Maximum COD removal with moderate sludge volume	0.47	1.03	45	54.40 (3.54%)[a]	56.38	107.19 (1.11%)[a]	106
Minimum sludge volume with 50% COD removal	0.58	0.58	30	49.60 (0.04%)[a]	49.58	55.33 (6.41%)[a]	52
Fenton-based oxidation (Fe^{3+})							
Maximum COD removal with moderate sludge volume	1.55	1.75	90	53.37 (1.85%)[a]	54.38	115.02 (0.84%)[a]	116
	2.62	1.75	60	56.65 (3.71%)[a]	58.83	112.05 (0.05%)[a]	112

[a]Percentage error in the model

high COD removal efficiency were revealed. However, the experimental results under these suggested conditions did not align with the model's predictions. To improve the model's accuracy, the results from the initial optimization studies were incorporated into the experimental plan, and the optimization was repeated. Then, the predicted COD removal efficiencies and the chemical sludge volumes were consistent with the experimental results (Table 3), confirming the accuracy of the revised model.

Optimization of Fenton-based oxidation

The optimization objectives, lower and upper limit values, and importance levels were defined similarly to those used for classical Fenton oxidation. Since the chemical sludge volumes produced by the Fenton-based oxidation were significantly lower than those generated by the classical Fenton oxidation, the optimization criterion focused on achieving the highest COD removal efficiency while limiting sludge volume to no more than half of the wastewater volume. The optimization process identified two different H_2O_2/COD molar ratios. Since the biodegradability of AIW pretreated with Fenton oxidation will be evaluated after these studies, both conditions with varying H_2O_2/COD molar ratios were considered optimal. The removal efficiencies and sludge volumes from the Fenton-based experiments conducted under the recommended conditions, along with the model-predicted values, are presented in Table 3. The models were validated, with the highest error margins between the experimental and predicted COD removal efficiencies and sludge volumes being 3.71% and 0.84%, respectively.

As shown in Table 3, achieving similar COD removal efficiencies in Fenton and Fenton-based oxidations, higher amounts of chemical reagents should be consumed in the Fenton-based oxidation, resulting in greater chemical sludge formation. In Fenton oxidation, the dominant removal mechanism may be oxidation or coagulation-depending on the selected H_2O_2/Fe^{2+} molar ratios and the Fe species. Additionally, if the Fe^{2+} concentration exceeds the H_2O_2 concentration, coagulation may become the primary mechanism for pollutant removal. It has also been reported that ferric species enhance pollutant removal from wastewater through the coagulation mechanism (Tambosi et al. 2006). Studies comparing the effects of Fenton and Fenton-based oxidations on the treatment of industrial wastewater have produced varied results. Sodium diatrizoate (Velo-Gala et al. 2014), a persistent pollutant found in surface, ground, and wastewater, as well as phenol from olive mill wastewater (Ciggin et al. 2021a), were more efficiently removed by classical Fenton oxidation compared to Fenton-based oxidation using Fe^{3+}. However, similar COD removal efficiencies were observed for cosmetic wastewater (Bautista et al. 2014), landfill leachate treated with lime precipitation (Kilic et al. 2014), and carpet manufacturing effluents (Ciggin et al. 2021b) when comparing classical Fenton and Fenton-based oxidations with Fe^{3+}. On the other hand, Fenton-based oxidation using Fe^{3+} is determined as more efficient for removal of paint industry wastewaters owing to the coagulation mechanism (Carlos et al. 2024). These differing results indicate that the efficiency of Fe^{2+} and Fe^{3+}-based Fenton oxidations depends on the type of wastewater being treated. Therefore, selecting the appropriate Fe species is crucial for optimization of process. This selection will also help determine whether the oxidation or coagulation mechanism is more effective for a given wastewater type.

Photo-Fenton oxidation

To investigate the impact of applying photo-Fenton oxidation on COD removal efficiency and sludge production, photo-Fenton experiments were conducted under UV light after identifying the optimal operating conditions for both processes that maximize COD removal and minimize chemical sludge formation. A total of four optimal conditions were tested, with two selected for each process. The COD removal efficiencies and sludge volumes obtained from photo-Fenton oxidation under UV light, compared to the results from Fenton and Fenton-based oxidation under the same conditions, are presented in Table 4.

The application of photo-Fenton to AIW did not significantly affect the COD removal efficiencies or chemical sludge volumes compared to those obtained with Fenton and Fenton-based oxidations. The Fenton based and photo-Fenton experiments resulted in nearly identical COD removal

Table 4 Comparison of results from classical and Fenton-based oxidation with photo-Fenton oxidation

Experiment	Optimal conditions			Fenton and Fenton-based oxidation		Photo-Fenton oxidation	
	H_2O_2/COD (mol mol^{-1})	Fe (g L^{-1})	Time (min)	COD (%)	Sludge volume (mL)	COD (%)	Sludge volume (mL)
1 (Fe^{2+})	0.47	1.03	45	56.38	106	53.34	120
2 (Fe^{2+})	0.58	0.58	30	49.58	52	48.55	48
3 (Fe^{3+})	1.55	1.75	90	54.38	116	51.54	125
4 (Fe^{3+})	2.62	1.75	60	58.83	112	56.03	104

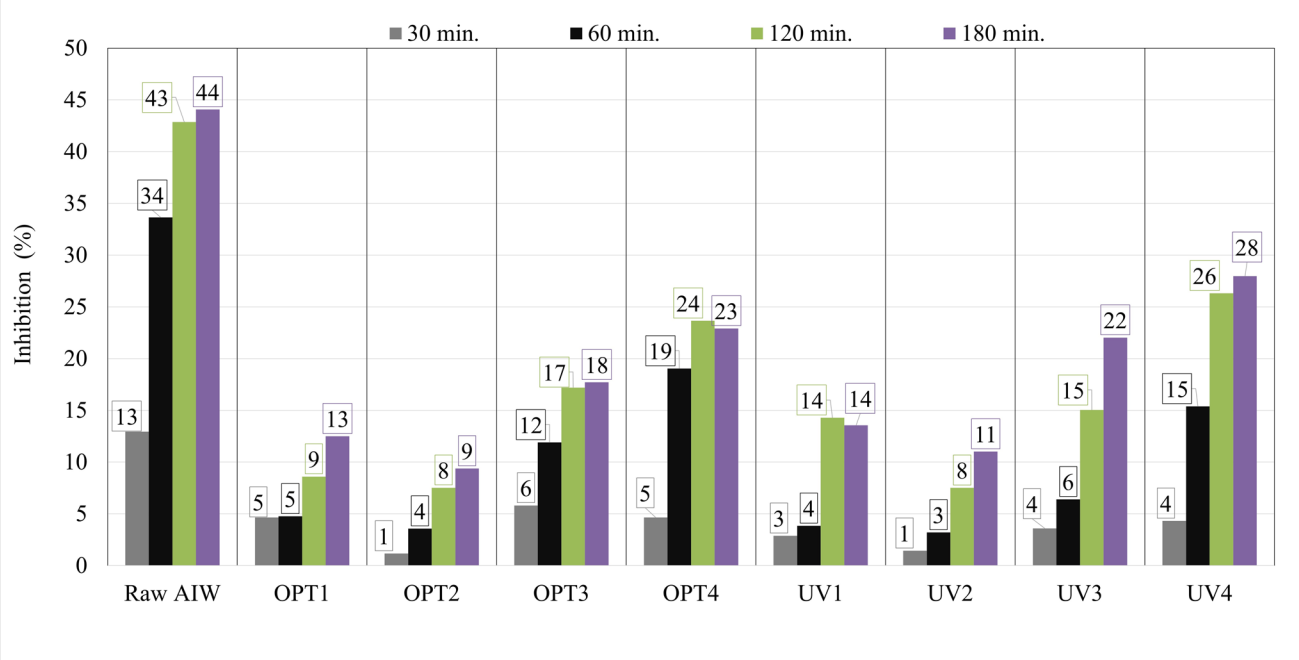


Fig. 5 Result of activated sludge inhibition tests

efficiencies and chemical sludge volumes. In this study, similar to this finding, there is no increase was observed in efficiency with the application of Photo-Fenton to chemical industry wastewater (Metin and Çifçi 2023). In contrast to these findings, in the studies on the removal of nitrophenols (Kavitha and Palanivelu 2005) and car wash wastewaters (Magnago et al. 2018), photo-Fenton oxidation was determined to perform better than the Fenton reaction. In a study by Benitez et al. (2007), it was reported that when photo-Fenton oxidation was used for the oxidation of phenylurea herbicides, removal efficiencies were initially similar to those of Fenton oxidation, but the efficiency of photo-Fenton increased as the reaction time progressed. Based on this finding, it was concluded that longer reaction times than those applied in this study may be necessary to fully assess the efficiency of photo-Fenton oxidation.

Effect of Fenton-based oxidations on the toxicity of AIW

After determination of optimum conditions, the impact of pretreatment with Fenton, Fenton-based, and photo-Fenton oxidations on the toxicity of AIW was examined. In the active sludge inhibition tests, raw AIW and wastewater treated with Fenton-based oxidations under optimal conditions were used at the same concentration. The calculated percentage inhibitions, based on the dissolved oxygen concentrations measured during the activated sludge inhibition tests, are presented in Fig. 5.

Raw AIW causes a 44% inhibition of microorganisms by the 180th minute. When Fenton oxidation is applied under optimal conditions, the inhibition of activated sludge decreases to 13% in the first optimal condition (OPT1) and 9% in the second optimal condition (OPT2). Using the Fenton-based oxidation with Fe^{3+}, 18% and 23% inhibition were observed under the third (OPT3) and fourth (OPT4) optimal conditions, respectively. The application of UV-assisted photo-Fenton oxidation under these four optimal conditions did not affect COD removal or sludge formation, nor did it contribute to reducing the inhibition effects. Inhibition tests indicate that applying Fenton-based oxidations as a pretreatment before biological treatment can lead to high treatment efficiencies. Based on these results, it was concluded that the operating conditions used in the OPT2 experiment, which reduced inhibition to 9% at the 180th minute, are the most suitable for treating AIW with the Fenton oxidation prior to biological treatment. Similar to this study, significant toxicity reduction was achieved by applying Fenton oxidation to textile industry wastewaters (Starling et al. 2017) and pharmaceutical industry wastewaters (Zeng et al. 2015). However, unlike this study, Fenton-based oxidation with Fe^{3+} was reported to be more effective in reducing the toxicity

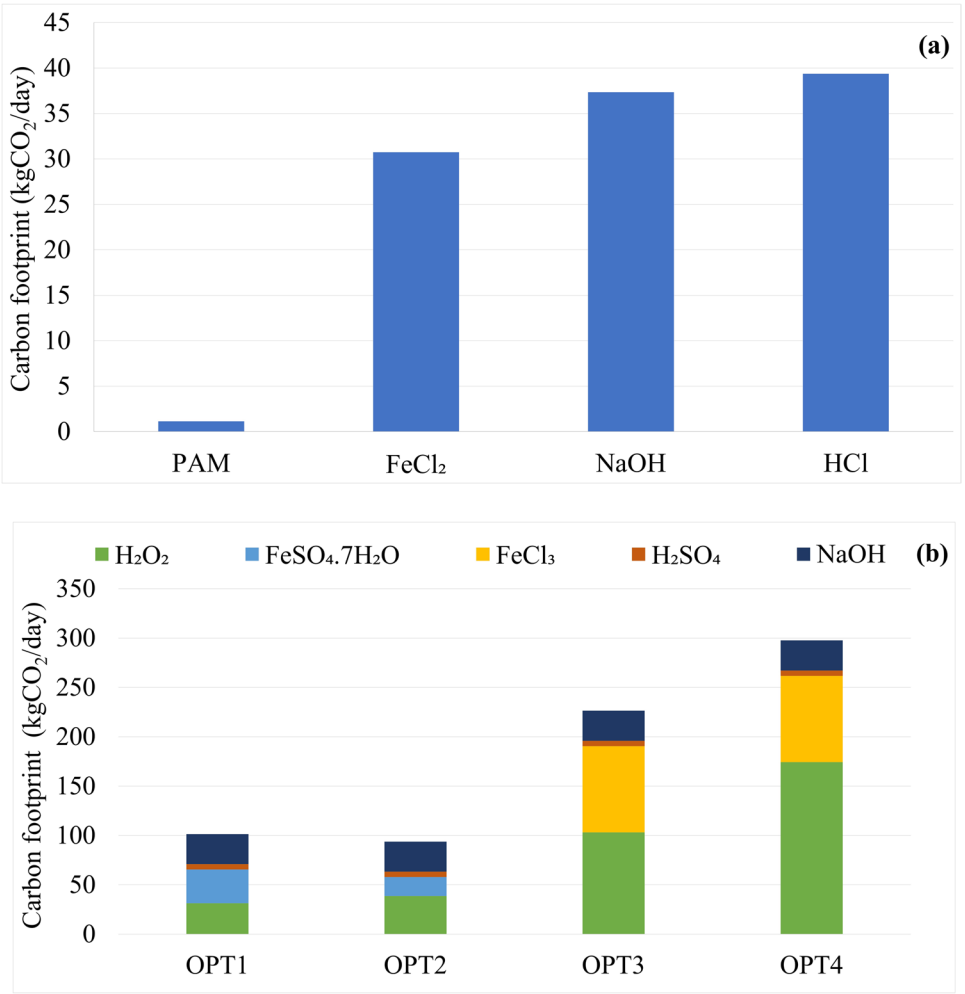


Fig. 6 Chemical based CF's of **a** coagulation-flocculation, **b** Fenton based oxidation

of olive mill wastewater (Ciggin et al. 2021a) and carpet manufacturing effluents (Ciggin et al. 2021b).

Chemical based carbon footprints

The daily chemical-based CF was calculated as 108.58 $kgCO_2e\ day^{-1}$, based on the amount of chemicals used to treat 40 m^3 of AIW per day during the coagulation-flocculation process at the plant. The contribution of each chemical used in coagulation-flocculation to the CF is shown in Fig. 6a, with hydrochloric acid (HCl) identified as the largest contributor. The carbon footprints for Fenton-based oxidation, calculated under the optimum conditions based on the chemical usage required to treat 40 m^3 of AIW, are presented in Fig. 6b.

As expected from the optimization results in Table 3, higher CFs were calculated for Fe^{3+}-based Fenton oxidation, corresponding to increased chemical consumption. The CFs for OPT3 and OPT4 were calculated as 226.43 and 297.62 $kgCO_2e\ day^{-1}$, respectively—more than twice the CF from coagulation-flocculation. In contrast, the CFs for OPT1 and OPT2 were 101.41 and 93.76 $kgCO_2e\ day^{-1}$, respectively, indicating that applying classical Fenton oxidation instead of coagulation-flocculation could reduce the chemical-based CF by 6.6–16.6%. When analyzing the chemicals contributing to the CF from Fenton oxidation, it was found that H_2O_2 had the largest impact, followed by NaOH, similar to the findings of Salazar et al. (2019).

Conclusion

Automotive industry wastewater poses significant challenges for treatment due to its high concentrations of heavy metals and chemical oxygen demand. Biological processes, though economical, are often inadequate. Fenton oxidation, as a pretreatment, offers a promising solution by effectively oxidizing toxic substances while minimizing chemical usage and sludge production. This study aimed to evaluate the feasibility of Fenton oxidation

as a pretreatment process to enhance the biodegradability of automotive industry wastewater.

Optimal operating conditions were determined using response surface methodology for three Fenton-based processes: classical Fenton oxidation with ferrous iron, Fenton-based oxidation with ferric iron, and photo-Fenton oxidation. Classical Fenton oxidation was found to be more efficient than Fenton-based oxidation with ferric iron. Photo-Fenton tests revealed that ultraviolet light did not significantly enhance process performance. Activated sludge inhibition tests showed that inhibition rates in untreated wastewater, initially 44%, were reduced to 9% with classical Fenton oxidation and 18% with Fenton-based oxidation. These findings indicate that Fenton-based oxidation as a pretreatment process significantly improves biological treatment efficiency. Classical Fenton oxidation emerged as the most effective solution for pretreating automotive industry wastewater.

A comparison of chemical-based carbon footprints revealed that Fenton oxidation could reduce the carbon footprint by 6.6–16.6% compared to coagulation-flocculation processes. Among the chemicals used, H_2O_2 contributed the most to the carbon footprint, followed by NaOH. To better evaluate the environmental benefits, further studies should include detailed carbon footprint analyses, incorporating energy efficiency considerations for all processes.

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Declarations

Conflict of interests The authors declare no competing interests.

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