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Advanced Treatment Strategies for Spent Caustic Wastewater: A Comprehensive Study

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Abstract

Spent caustic is a highly alkaline and toxic wastewater stream generated in petroleum refining and petrochemical industries, primarily from LPG, naphtha, and ethylene treating units, containing high concentrations of sulphides, mercaptans, and phenolic compounds. Conventional treatment methods such as steam stripping, wet air oxidation, and neutralization suffer from limitations including high energy consumption and incomplete pollutant removal. Advanced oxidation processes (AOPs), particularly hydrogen peroxide (H_2O_2)-based systems, have gained attention due to their ability to generate hydroxyl radicals capable of degrading refractory organic compounds. These methods demonstrate improved efficiency and environmental performance compared to conventional techniques.

Keywords: *Spent caustic, wastewater treatment, hydrogen peroxide, advanced oxidation process, petrochemical effluent, COD removal, sulphide oxidation*

1. Introduction

The petroleum and petrochemical industries generate various hazardous waste streams, among which spent caustic is one of the most challenging due to its extreme alkalinity and complex chemical composition. It is typically produced during the removal of acidic contaminants such as hydrogen sulphide (H_2S), carbon dioxide (CO_2), and mercaptans from hydrocarbon streams using sodium hydroxide solutions.

Spent caustic wastewater is characterized by high COD, toxicity, and resistance to biological degradation (Wang et al., 2016). Improper disposal can lead to severe environmental pollution, including water contamination and air pollution due to volatile sulphur compounds (Khan et al., 2020). Traditional treatment methods have been implemented for decades, but increasing environmental regulations and sustainability goals have driven the need for more efficient and cleaner technologies. Advanced oxidation processes, especially those based on hydrogen peroxide, have emerged as potential alternatives due to their strong oxidative capability and ability to mineralize complex organic pollutants.

The objective of this review is to compare conventional treatment technologies with H_2O_2-based advanced oxidation methods and evaluate their suitability for industrial-scale spent caustic management. Advanced oxidation processes, especially hydrogen peroxide-based systems, have emerged as promising alternatives due to their strong oxidative capability (Oturan & Aaron, 2014).

2. Formation and Characteristics of Spent Caustic

The formation pathway of spent caustic in refinery and petrochemical operations involves the treatment of hydrocarbon streams such as LPG, naphtha, and ethylene feedstocks using sodium hydroxide solution. During caustic washing, acidic contaminants including hydrogen sulphide, mercaptans, and phenolic compounds are chemically absorbed and converted into sodium-based salts. As these reaction products accumulate, the caustic solution becomes saturated and is eventually discharged as spent caustic. This resulting wastewater is characterized by high alkalinity and the presence of toxic sulphur species, making its treatment particularly challenging and often requiring advanced or specialized treatment methods.

Spent caustic is generated during caustic washing processes in petroleum refineries and petrochemical plants, where sodium hydroxide reacts with acidic contaminants such as hydrogen sulphide, carbon dioxide, and mercaptans, forming sodium sulphide and sodium mercaptides (Alnaizy & Akgerman, 2000; Stringfellow & Dobbs, 2000). The wastewater exhibits extremely high pH values, typically in the range of 12–14, along with very high chemical oxygen demand (COD), which can vary from 10,000 mg/L to more than 150,000 mg/L (Wang et al., 2016; Diya'uddeen et al., 2011; Ebrahimi et al., 2020). These characteristics indicate a heavy load of both organic and inorganic pollutants, making treatment processes complex and demanding. In addition to its high alkalinity, spent caustic contains significant concentrations of phenolic compounds, sulphides, and various oxygenated hydrocarbons, all of which contribute to its toxicity and environmental impact (Busca et al., 2008; Santos et al., 2013). The presence of reduced sulphur compounds such as Na_2S and NaHS leads to the generation of hydrogen sulphide gas, which is highly toxic, corrosive, and hazardous (Mishra et al., 2018; Speight, 2014). From a treatment perspective, the high alkalinity inhibits microbial growth, making biological treatment ineffective unless pre-treatment methods are applied (Wang et al., 2016; Abdelwahab et al., 2009). Furthermore, the variability in composition depending on refinery operations adds complexity to process design and optimization, requiring flexible and efficient treatment strategies.

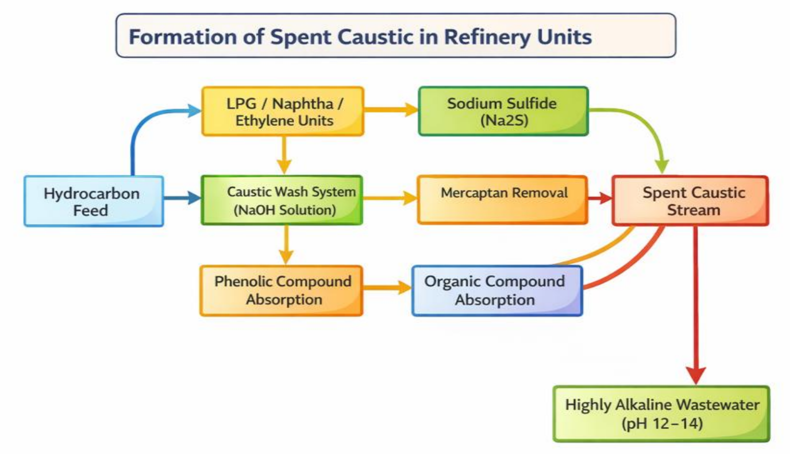

Fig:1Formation of spent caustic

Figure 1 illustrates the formation pathway of spent caustic in refinery and petrochemical operations. Hydrocarbon streams such as LPG, naphtha, and ethylene feed undergo caustic washing using sodium hydroxide solution. During this process, acidic contaminants including hydrogen sulfide, mercaptans, and phenolic compounds are chemically absorbed and converted into sodium-based salts. The accumulation of these reaction products leads to the generation of spent caustic, which is characterized by extremely high alkalinity and toxic sulfur species. This complex mixture makes downstream treatment challenging and necessitates advanced oxidation or specialized treatment processes.

3. Conventional treatment methods

Conventional treatment methods for spent caustic wastewater primarily focus on neutralization, biological degradation, and physical-chemical separation. These methods are widely used in refineries and petrochemical industries due to their simplicity and established operational frameworks. However, their effectiveness is often limited by the high toxicity, chemical oxygen demand (COD), and presence of refractory compounds such as phenols and sulphides.

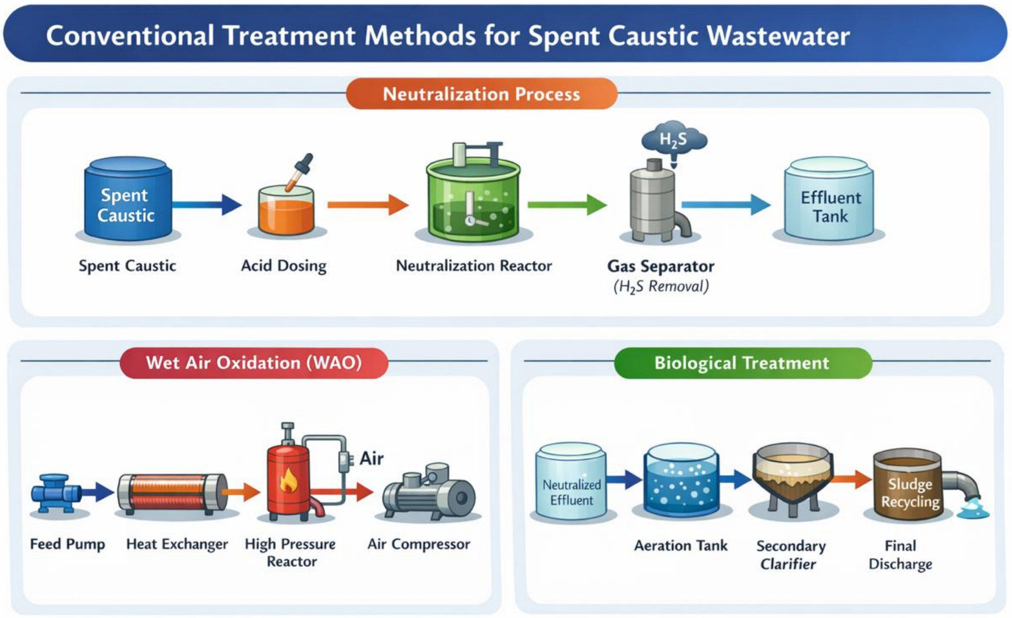

Fig: 2 Conventional Treatment methods for Spent Caustic Wastewater

3.1 Neutralization

Neutralization is the first and most essential step in the treatment of spent caustic streams. The highly alkaline wastewater, with a pH ranging from 10 to 14, is treated with acids such as sulfuric acid (H_2SO_4) or hydrochloric acid (HCl) to bring the pH down to a neutral range of 6–8 (Khan et al., 2020; Diya'uddeen et al., 2011). This process serves multiple purposes: it reduces the overall alkalinity of the wastewater, converts sulphides (S^{2-}) into hydrogen sulphide (H_2S) gas, and prepares the effluent for downstream treatment processes (Stringfellow & Dobbs, 2000). However, the release of H_2S gas introduces safety and environmental concerns due to its toxicity and strong Odor, necessitating proper gas handling and scrubbing systems (Mishra et al., 2018). A typical neutralization process involves a spent caustic storage tank, an acid dosing unit, a neutralization reactor, a gas separator for H_2S removal, and an effluent tank to collect the treated wastewater.

3.2 Wet Air Oxidation (WAO)

Wet Air Oxidation (WAO) is a high-temperature (150–320°C) and high-pressure (5–20 MPa) treatment process designed to oxidize both organic and inorganic pollutants in spent caustic wastewater (Debellefontaine et al., 1996; Gogate & Pandit, 2004). During this process, air or oxygen is injected into the wastewater, oxidizing organic compounds into carbon dioxide (CO_2) and water (H_2O), while sulphides are converted into sulphates (Diya'uddeen et al., 2011). WAO is highly effective in reducing chemical oxygen demand (COD) and toxicity, making it suitable for pretreatment or standalone treatment of strong industrial effluents (Khan et al., 2020). However, the process has several drawbacks, including high capital and operating costs, energy-intensive operation, and the requirement for corrosion-resistant materials to withstand the harsh operating conditions (Gogate & Pandit, 2004). A typical WAO system consists of a feed pump, heat exchanger, high-pressure reactor, air compressor, and separator, ultimately producing treated effluent with significantly reduced pollutant load.

3.3 Biological Treatment

Biological treatment relies on microorganisms to degrade organic pollutants and is widely used due to its cost-effectiveness (Mishra et al., 2018; Wang et al., 2016). Common biological treatment systems include the activated sludge process, aerated lagoons, and sequencing batch reactors (SBR). Despite their advantages, biological methods face challenges when applied to spent caustic wastewater. The high toxicity of the effluent can inhibit microbial growth, while compounds such as sulphides and phenols are difficult to biodegrade (Busca et al., 2008; Ebrahimi et al., 2020), often necessitating dilution or pre-treatment to improve process efficiency. Nevertheless, biological systems are frequently employed as secondary treatment following neutralization or oxidation to remove residual biodegradable organics (Khan et al., 2020). A typical biological treatment sequence involves neutralized effluent entering an aeration tank, followed by a secondary clarifier, with sludge recycled back to maintain microbial activity, and the final treated effluent discharged safely.

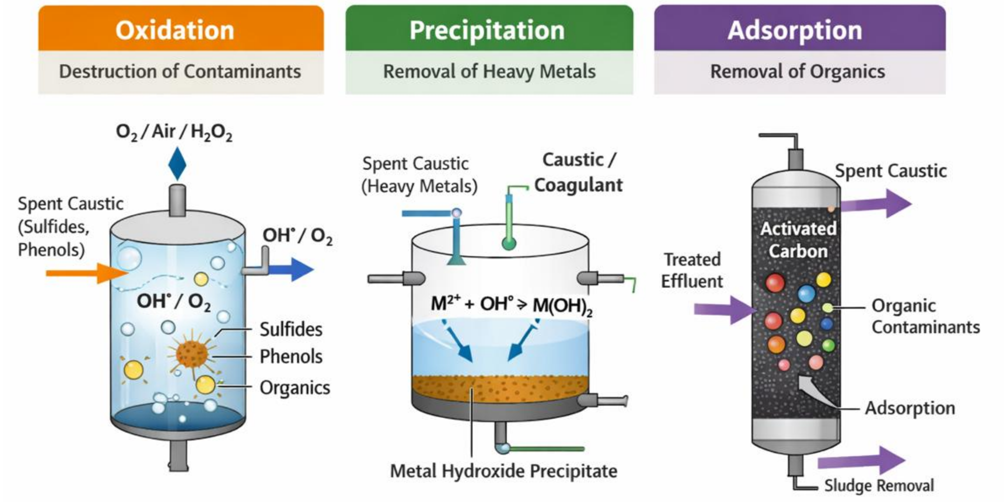

Fig: 3 Mechanism for spent caustic wastewater treatments in conventional treatment

Figure 3 shows steps represent conventional treatment methods for spent caustic wastewater. The processes shown—oxidation, precipitation, and adsorption—are widely used traditional techniques in industrial wastewater treatment. Oxidation (using air, oxygen, or chemicals like H_2O_2) is a standard method for breaking down sulphides and phenols; precipitation is a classic approach for removing heavy metals by converting them into insoluble hydroxides; and adsorption using activated carbon is a well-established polishing step to remove remaining organic contaminants. These methods are considered conventional because they are mature, commonly applied, and do not involve more advanced technologies like advanced oxidation processes (AOPs), electrochemical treatment, or membrane systems.

However, while effective, conventional methods may have limitations such as incomplete removal of refractory organics, higher sludge generation, and longer treatment times—this is why modern research often compares them with advanced methods like H_2O_2-based AOPs or electrocoagulation.

3.4 Limitations of Conventional Methods

Conventional treatment methods, while widely adopted in the industry, have several notable limitations. They often fail to achieve complete removal of refractory compounds, leaving persistent pollutants in the effluent (Gogate & Pandit, 2004; Diya'uddeen et al., 2011). High sludge generation and the release of odorous sulfides further complicate their operation and disposal (Khan et al., 2020). Processes such as wet air oxidation (WAO) can be operationally complex, requiring high temperature, high pressure, and corrosion-resistant materials (Debellefontaine et al., 1996). Additionally, meeting stringent environmental discharge standards can be challenging with conventional systems alone (Wang et al., 2016). These drawbacks have motivated the development and adoption of advanced oxidation processes (AOPs), which offer higher treatment efficiency and will be discussed in detail in the following chapter (Oturan & Aaron, 2014).

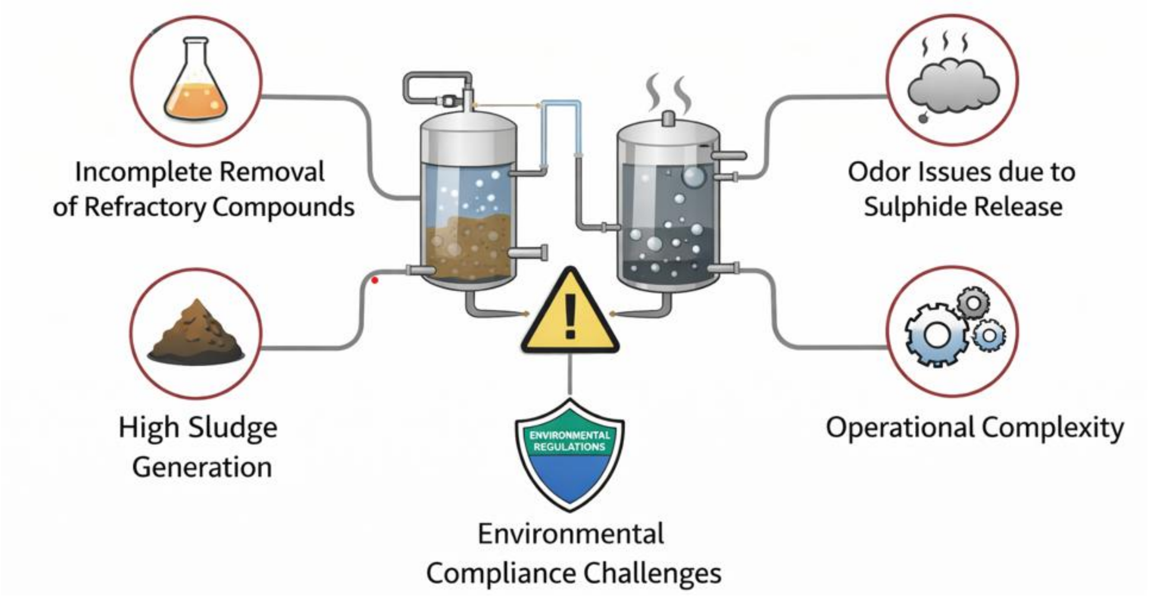

Fig: 4 Limitations in conventional methods

4. Advanced Oxidation Processes (H_2O_2-Based Treatment)

4.1 Introduction to AOPs

Advanced Oxidation Processes (AOPs) represent a class of highly efficient treatment technologies designed for the degradation of recalcitrant and toxic organic pollutants present in industrial wastewater (Oturan & Aaron, 2014; Brillas et al., 2009). In the context of spent caustic streams generated from petroleum refining and petrochemical industries, conventional treatment methods often fail to achieve adequate removal of high-strength contaminants such as phenols, sulfides, mercaptans, and other non-biodegradable organics (Diya'uddeen et al., 2011; Khan et al., 2020). AOPs overcome these limitations by generating highly reactive species, primarily hydroxyl radicals (•OH), which possess a very high oxidation potential (2.8 V) and are capable of non-selectively oxidizing a wide range of pollutants (Gogate & Pandit, 2004). Hydrogen peroxide (H_2O_2)-based AOPs are particularly attractive due to their operational simplicity, environmental compatibility, and ability to achieve deep oxidation of contaminants (Brillas et al., 2009). These processes either utilize H_2O_2 alone or in combination with catalysts, ultraviolet (UV) radiation, or other oxidants to enhance radical generation.

4.2 Fundamental Chemistry

The effectiveness of advanced oxidation processes (AOPs) is governed by the in-situ generation of hydroxyl radicals (•OH), which are highly reactive and powerful oxidizing agents (Oturan & Aaron, 2014). These radicals react rapidly with organic compounds through mechanisms such as hydrogen abstraction, electron transfer, and electrophilic addition (Brillas et al., 2009). The general oxidation mechanism can be represented as:

$$\mathrm{RH} + \cdot\mathrm{OH} \rightarrow \mathrm{R}\cdot + \mathrm{H_2O}$$
$$\mathrm{R}\cdot + \mathrm{O_2} \rightarrow \mathrm{ROO}\cdot \rightarrow \text{intermediates} \rightarrow \mathrm{CO_2} + \mathrm{H_2O}$$

Through these reactions, complex organic molecules are broken down into smaller intermediates and ultimately mineralized into carbon dioxide (CO_2), water (H_2O), and inorganic ions (Gogate & Pandit, 2004). The non-selective nature of •OH radicals make AOPs highly effective for treating complex wastewater matrices such as spent caustic.

Hydrogen peroxide (H_2O_2) is a strong oxidizing agent capable of directly oxidizing certain pollutants (Khan et al., 2020). However, its effectiveness is significantly enhanced when it decomposes to form hydroxyl radicals:

$$H_2O_2 \rightarrow 2 \cdot OH$$

In standalone oxidation, sulfides are converted into sulfates:

$$\mathrm{S^{2-}} + 4\mathrm{H_2O_2} \rightarrow \mathrm{SO_4^{2-}} + 4\mathrm{H_2O}$$

Phenolic compounds undergo partial oxidation:

$$\mathrm{C_6H_5OH} + \cdot\mathrm{OH} \rightarrow \text{intermediates} \rightarrow \mathrm{CO_2} + \mathrm{H_2O}$$

However, standalone H_2O_2 oxidation is relatively slow and requires high dosages, making it less economical for large-scale applications (Gogate & Pandit, 2004).

The Fenton process is one of the most widely applied AOPs for high-strength wastewater treatment (Oturan & Aaron, 2014; Neyens & Baeyens, 2003). It involves the catalytic decomposition of hydrogen peroxide by ferrous ions:

$$\mathrm{Fe^{2+}} + \mathrm{H_2O_2} \rightarrow \mathrm{Fe^{3+}} + \cdot\mathrm{OH} + \mathrm{OH^-}$$

The generated hydroxyl radicals degrade organic pollutants:

$$\text{Organic pollutants} + \cdot\mathrm{OH} \rightarrow \mathrm{CO_2} + \mathrm{H_2O}$$

Ferric ions can be partially reduced back to ferrous ions:

$$\mathrm{Fe^{3+}} + \mathrm{H_2O_2} \rightarrow \mathrm{Fe^{2+}} + \mathrm{HO_2}\cdot + \mathrm{H^+}$$

These reactions effectively degrade phenolic and sulfur-containing compounds, reducing chemical oxygen demand (COD) and toxicity (Busca et al., 2008; Diya'uddeen et al., 2011). However, the process requires acidic conditions (pH 2.5–3.5) and produces ferric hydroxide sludge:

$$\mathrm{Fe^{3+}} + 3\mathrm{OH^-} \rightarrow \mathrm{Fe(OH)_3} \downarrow$$

The UV/H_2O_2 process enhances hydroxyl radical production through photolysis:

$$\mathrm{H_2O_2} + h\nu \rightarrow 2 \cdot \mathrm{OH}$$

This significantly improves oxidation efficiency compared to standalone hydrogen peroxide treatment (Brillas et al., 2009; Oturan & Aaron, 2014). However, the efficiency depends on water clarity, as turbidity and suspended solids can hinder UV penetration (Gogate & Pandit, 2004).

The peroxone process (O_3/H_2O_2) further enhances hydroxyl radical generation through synergistic reactions:

$$\mathrm{H_2O_2} + \mathrm{O_3} \rightarrow \cdot\mathrm{OH} + \mathrm{O_2} + \mathrm{HO_2}$$
$$\mathrm{O_3} + \mathrm{OH^-} \rightarrow \mathrm{O_2} + \cdot\mathrm{OH}$$

These reactions significantly improve oxidation efficiency, enabling the degradation of refractory compounds and near-complete mineralization (Beltrán, 2004; Brillas et al., 2009). However, this process involves higher operational costs and increased system complexity.

The efficiency of AOPs is influenced by several operational parameters, including pH, hydrogen peroxide dosage, catalyst concentration, and temperature (Neyens & Baeyens, 2003; Gogate & Pandit, 2004). Maintaining optimal conditions is essential, as excess hydrogen peroxide can act as a hydroxyl radical scavenger:

$$\cdot\mathrm{OH} + \mathrm{H_2O_2} \rightarrow \mathrm{HO_2}\cdot + \mathrm{H_2O}$$

This reduces the overall oxidation efficiency (Brillas et al., 2009).

AOPs offer several advantages, including high removal efficiency for COD and the ability to degrade non-biodegradable and toxic compounds (Oturan & Aaron, 2014; Khan et al., 2020). These processes produce environmentally benign end products such as CO_2 and H_2O, minimizing secondary pollution. Additionally, AOPs exhibit rapid reaction kinetics, enhancing treatment efficiency (Brillas et al., 2009).

Despite their effectiveness, AOPs have limitations. They are associated with high operational costs and require precise control of process parameters (Gogate & Pandit, 2004). Certain processes, such as the Fenton reaction, generate sludge requiring proper disposal, while UV-based systems involve significant energy consumption (Neyens & Baeyens, 2003).

AOPs are widely applied in petroleum refineries and petrochemical industries as pre-treatment, post-treatment, or standalone systems (Khan et al., 2020; Wang et al., 2016). These processes improve wastewater biodegradability and help meet stringent environmental discharge standards (Diya'uddeen et al., 2011).

5. Comparative analysis – Conventional methods vs Advanced Oxidation Processes

5.1 Introduction

The treatment of spent caustic wastewater presents significant challenges due to its high alkalinity, elevated chemical oxygen demand (COD), and the presence of toxic and refractory compounds such as phenols, sulfides, and mercaptans. Over the years, both conventional treatment methods and advanced oxidation processes (AOPs) have been employed to address these challenges. This chapter provides a comprehensive comparative analysis of these two approaches based on key performance indicators such as treatment efficiency, cost, operational complexity, environmental impact, and suitability for industrial applications.

5.2 Treatment Efficiency

One of the most critical parameters in wastewater treatment is the removal efficiency of pollutants, particularly COD and toxic organics. Conventional methods such as neutralization and biological treatment generally achieve moderate COD removal efficiencies, typically in the range of 50–80%. However, they are less effective in degrading refractory compounds due to their complex molecular structure and resistance to biodegradation.In contrast, hydrogen peroxide-based AOPs demonstrate significantly higher treatment efficiency, often achieving COD removal rates of 80–99%. The generation of hydroxyl radicals enables the non-selective oxidation of complex organic molecules, resulting in their breakdown into simpler and less harmful compounds. This makes AOPs particularly suitable for treating high-strength and toxic wastewater streams like spent caustic.

5.3 Removal of Refractory Compounds

Refractory compounds such as phenols, sulfides, and mercaptans are significant contributors to the toxicity and environmental burden of industrial effluents, particularly spent caustic wastewater. These compounds are highly resistant to biodegradation due to their complex chemical structures, making their removal challenging using conventional treatment methods. Biological and physicochemical processes often result in incomplete degradation, leaving residual toxicity in the treated effluent (Manna & Sen, 2023; Mukherjee et al., 2023).

Advanced oxidation processes (AOPs) have emerged as an effective alternative for the degradation of such refractory pollutants. AOPs operate through the in situ generation of highly reactive species, primarily hydroxyl radicals (•OH), which possess strong oxidation potential and non-selective reactivity. These radicals can break down stable organic molecules, including phenolic and sulfur-containing compounds, via oxidation pathways, leading to their transformation into simpler, less toxic intermediates or complete mineralization into CO_2 and H_2O (Manna & Sen, 2023; Silva, 2024). Consequently, AOPs significantly enhance pollutant removal efficiency, reduce toxicity, and enable treated wastewater to meet stringent environmental discharge standards (Mukherjee et al., 2023; Wang et al., 2021).

$$OrganicPollutant + \cdot OH \rightarrow LessToxicIntermediates \rightarrow CO_2 + H_2O + Inorganic$$

5.4 Sludge Generation

Sludge generation is an important consideration in wastewater treatment, as it directly influences disposal costs and environmental sustainability. Conventional treatment methods, particularly biological processes and chemical precipitation, tend to generate large volumes of sludge that require further treatment, handling, and safe disposal (Manna & Sen, 2023; Mukherjee et al., 2023). The management of this excess sludge adds to operational complexity and may contribute to secondary environmental pollution if not properly treated.

In contrast, advanced oxidation processes (AOPs) generally produce minimal sludge because they primarily rely on chemical oxidation mechanisms rather than biomass growth or precipitation reactions (Wang et al., 2021). An exception is the Fenton process, which generates iron-based sludge due to the use of ferrous salts as catalysts. However, even in this case, the amount of sludge produced is typically lower than that generated by conventional treatment methods (Manna & Sen, 2023). Therefore, reduced sludge production is considered a significant advantage of AOPs, as it lowers disposal requirements and minimizes secondary pollution, contributing to more sustainable wastewater treatment practices (Mukherjee et al., 2023).

5.5 Operational Complexity

Conventional wastewater treatment methods are generally simpler to operate, particularly neutralization and biological processes, which rely on well-established and robust mechanisms (Manna & Sen, 2023). However, certain advanced conventional techniques, such as Wet Air Oxidation (WAO), require high temperature and pressure conditions, making them operationally complex and dependent on specialized equipment (Wang et al., 2021).

Advanced oxidation processes (AOPs), on the other hand, require precise control of operating parameters such as pH, hydrogen peroxide dosage, catalyst concentration, and reaction time (Mukherjee et al., 2023). Although this increases operational complexity, recent advancements in automation and process monitoring have significantly improved the feasibility of managing these systems. Overall, AOPs can be considered moderately complex but manageable with proper design and control strategies (Manna & Sen, 2023).

5.6 Cost Analysis

Cost is a critical factor in the selection of wastewater treatment technologies. Conventional treatment methods generally have lower capital and operational costs, making them suitable for large-scale applications (Mukherjee et al., 2023). However, their relatively lower efficiency in removing refractory pollutants may require additional treatment stages, thereby increasing overall costs (Manna & Sen, 2023).

AOPs, particularly those involving ultraviolet (UV) radiation or ozone, tend to have higher operational costs due to energy consumption and chemical usage (Wang et al., 2021). The Fenton process is considered one of the more cost-effective AOPs; however, it still incurs costs related to chemical reagents and sludge management (Manna & Sen, 2023). Despite these higher costs, the superior treatment efficiency of AOPs often justifies their application, especially in cases where strict environmental regulations must be met (Mukherjee et al., 2023).

5.7 Environmental Impact

Environmental considerations play a crucial role in evaluating wastewater treatment technologies. Conventional methods may lead to secondary pollution issues, including sludge generation and the emission of odorous gases such as hydrogen sulfide (H_2S) (Manna & Sen, 2023). Furthermore, incomplete degradation of refractory compounds can pose long-term environmental risks (Mukherjee et al., 2023). In contrast, AOPs are generally more environmentally sustainable, as they convert pollutants into less harmful end products such as carbon dioxide and water through oxidative degradation (Wang et al., 2021). The reduced sludge production and minimal formation of toxic by-products further enhance their environmental performance. However, the relatively high energy consumption associated with some AOPs must be considered when evaluating their overall sustainability (Mukherjee et al., 2023).

5.8 Space Requirement and Scalability

Conventional treatment systems, particularly biological processes, often require large land areas for installation, which can be a limitation in space-constrained industrial settings (Manna & Sen, 2023). In contrast, AOP systems are typically more compact and can be integrated into existing treatment facilities with relative ease (Wang et al., 2021). Regarding scalability, conventional methods are well-established and widely implemented across various industries. AOPs are increasingly being adopted at industrial scales, with ongoing technological advancements improving their efficiency, feasibility, and cost-effectiveness (Mukherjee et al., 2023). This makes AOPs a promising alternative for future wastewater treatment applications.

5.9 Hybrid Treatment Approach

Given the advantages and limitations of both conventional treatment methods and advanced oxidation processes (AOPs), hybrid treatment approaches are increasingly recognized as the most effective solution for complex wastewater streams. In such systems, conventional methods are typically employed as primary or secondary stages to remove bulk pollutants, followed by AOPs as a polishing step to eliminate residual refractory compounds (Mukherjee et al., 2023; Manna & Sen, 2023; Hubner et al., 2024).

This integrated approach offers several important benefits. The combination of conventional and advanced processes significantly improves overall treatment efficiency and enables effective degradation of persistent pollutants (Ahmed et al., 2025). Hybrid systems also reduce operational costs compared to standalone AOP systems by distributing treatment loads efficiently (Mousset et al., 2021). Furthermore, they enhance compliance with stringent environmental discharge standards by producing high-quality effluents with reduced toxicity (Alazaiza et al., 2026). Recent studies also highlight that hybrid AOP systems, including electrochemical and photocatalytic combinations, are particularly effective for the removal of emerging contaminants and micropollutants (Jieun et al., 2020).

Thus, hybrid treatment strategies provide a balanced, efficient, and sustainable solution for treating complex industrial wastewater such as spent caustic streams.

5.10 Overall Evaluation

The comparative analysis indicates that conventional treatment methods are economical and widely implemented but have limitations in treating highly toxic and refractory pollutants (Manna & Sen, 2023; Mukherjee et al., 2023). In contrast, advanced oxidation processes, particularly those based on hydroxyl radical generation, demonstrate superior performance in removing persistent organic pollutants and improving effluent quality (Hubner et al., 2024; Ahmed et al., 2025).

Recent studies confirm that AOPs can achieve removal efficiencies exceeding 90% for micropollutants, making them highly effective for advanced wastewater treatment applications (Mukul et al., 2026). However, their application is often associated with higher energy and chemical costs, which must be considered in large-scale implementation (Zhou et al., 2025). The selection of appropriate treatment technology ultimately depends on wastewater characteristics, regulatory requirements, available infrastructure, and economic feasibility (Mousset et al., 2021). In many practical scenarios, hybrid systems combining conventional and AOP-based processes provide the most effective and sustainable solution, balancing cost and treatment performance (Alazaiza et al., 2026; Hubner et al., 2024).

The comparative table below highlights the key differences between conventional treatment methods and hydrogen peroxide-based advanced oxidation processes for spent caustic wastewater. Conventional methods provide a cost-effective solution for basic treatment but fall short in handling complex pollutants. AOPs, with their high oxidation potential, offer a powerful alternative capable of achieving superior treatment outcomes. The integration of both approaches in hybrid systems emerges as the most promising strategy for efficient and sustainable wastewater management.

Table: 1 Comparison of Conventional vs Advanced Oxidation processes

Criteria	Conventional Methods	AOPs (H_2O_2-Based)	Remarks	References
Treatment Efficiency	Moderate (50–80% COD removal)	High (80–99% COD removal)	AOPs provide superior pollutant degradation	(Manna & Sen, 2023; Mukherjee et al., 2023)
Refractory Compound Removal	Limited	Excellent	Effective degradation of phenols, sulfides, and mercaptans	(Hubner et al., 2024)
Reaction Rate	Slow	Fast	Rapid oxidation due to hydroxyl radicals	(Zheng et al., 2025)
Sludge Generation	High	Low (except Fenton)	Reduced sludge production improves sustainability	(Manna & Sen, 2023)
Operational Complexity	Low to moderate	Moderate	Requires precise control of operating parameters	(Mukherjee et al., 2023)
Capital Cost	Low (except WAO)	Moderate to high	Higher initial investment for AOP systems	(Mousset et al., 2021)
Operating Cost	Low to moderate	Moderate to high	Increased due to chemical and energy usage	(Zhou et al., 2025)
Energy Requirement	Low	High (UV/O_3 systems)	Energy-intensive depending on AOP type	(Wang et al., 2021)
Environmental Impact	Secondary pollution possible	Environmentally friendly	Produces fewer harmful by-products	(Alazaiza et al., 2026)
Odor Issues	Present (H_2S release)	Minimal	AOPs reduce odor-causing compounds	(Mukherjee et al., 2023)
Space Requirement	Large	Compact	Suitable for space-constrained facilities	(Bracamontes-Ruelas et al., 2024)
Scalability	Well-established	Emerging but growing	Increasing industrial adoption	(Hubner et al., 2024)
Process Control	Less stringent	Highly controlled	Critical for optimal AOP performance	(Zheng et al., 2025)
Suitability for High-Strength Wastewater	Limited	Highly suitable	Effective for toxic and refractory streams	(Ahmed et al., 2025)
Overall Performance	Moderate	Superior	AOPs outperform conventional methods in most aspects	(Mukul et al., 2026)

6. Case Studies and Industrial Applications

6.1 Introduction

The treatment of spent caustic wastewater has been widely studied and implemented across petroleum refineries and petrochemical industries due to its hazardous nature and stringent environmental regulations. While laboratory-scale studies provide valuable insights into treatment mechanisms, real-world industrial applications demonstrate the practical feasibility, efficiency, and limitations of various treatment technologies. This chapter presents selected case studies and industrial implementations of both conventional treatment methods and hydrogen peroxide-based advanced oxidation processes (AOPs), along with hybrid treatment approaches.

6.2 Refinery-Based Treatment Systems

Petroleum refineries are one of the primary sources of spent caustic wastewater, particularly from processes such as mercaptan removal (Merox units), LPG sweetening, and caustic washing units. Traditionally, refineries have relied on neutralization followed by biological treatment for wastewater management (Rahmanisa & Widiasa, 2020) .In several refinery applications, neutralization is carried out using mineral acids to adjust pH, followed by air stripping to remove hydrogen sulfide (H_2S) (Bahri et al., 2018). The neutralized effluent is then treated in biological systems such as activated sludge or sequencing batch reactors (SBR). While these systems are effective for reducing biodegradable organics, they often fail to achieve complete removal of refractory compounds.To overcome these limitations, many refineries have integrated Wet Air Oxidation (WAO) units as a pre-treatment step. WAO significantly reduces COD and converts sulfides into sulfates, thereby improving the efficiency of downstream biological treatment (Suárez, 1996). However, due to high capital and operating costs, WAO is typically applied in large-scale facilities (Kumfer et al., 2010).

6.3 Application of AOPs in Petrochemical Industries

Petrochemical industries generate highly toxic spent caustic streams containing phenols, cresols, and sulfur compounds. In recent years, hydrogen peroxide-based AOPs have been increasingly adopted to treat such wastewater. The Fenton process is one of the most widely implemented AOPs at the industrial scale. In a typical petrochemical plant, spent caustic is first neutralized and then subjected to Fenton oxidation (Gholami et al., 2024). The process effectively reduces COD by up to 90% and significantly improves biodegradability, allowing for subsequent biological treatment (Shokri & Fard, 2023). Similarly, UV/H_2O_2 systems have been used as polishing units to remove residual contaminants after primary treatment (Wang & Wang, 2016) . These systems are particularly effective in achieving stringent discharge limits for phenols and color (Andreozzi et al., 1999). Another emerging application is the use of the O_3/H_2O_2 (peroxone) process, which enhances oxidation efficiency and enables complete mineralization of pollutants. Although relatively expensive, this method is gaining attention for high-value applications requiring near-zero discharge.

6.4 Hybrid Treatment Approaches

Hybrid treatment systems that combine conventional methods with AOPs have shown significant promise in treating spent caustic wastewater (Mirzaei et al., 2017). These systems leverage the advantages of both approaches while minimizing their individual limitations.

A typical hybrid treatment sequence for complex industrial wastewater involves multiple integrated steps designed to maximize treatment efficiency. Initially, neutralization is carried out to adjust the pH to optimal levels for subsequent processes. This is followed by pre-treatment using techniques such as wet air oxidation or the Fenton process, which help break down high-strength and toxic organic compounds. The partially treated wastewater is then subjected to biological treatment to remove biodegradable organics. Finally, an advanced oxidation polishing step, such as UV/H_2O_2 or O_3/H_2O_2, is applied to eliminate any remaining contaminants and ensure high-quality effluent. Such integrated systems offer several advantages, including higher overall treatment efficiency, reduced chemical and energy consumption, and improved compliance with environmental regulations. In practice, several industrial installations have reported chemical oxygen demand (COD) removal efficiencies exceeding 95% using these hybrid approaches, along with significant reductions in toxicity and odor (Prabakar et al., 2018).

6.5 Performance Evaluation of Treatment Technologies

The performance of different treatment technologies for complex wastewater such as spent caustic can be evaluated based on key parameters including COD removal, phenol degradation, sulfide oxidation, and overall toxicity reduction. Conventional treatment systems typically achieve COD removal efficiencies in the range of 50–80%, but they are often limited in their ability to remove refractory compounds and tend to generate large amounts of sludge, although they are relatively low in operational cost. In contrast, AOP-based systems offer significantly higher COD removal efficiencies, typically between 80–99%, along with effective degradation of complex organic pollutants and lower sludge production; however, these benefits come at the expense of higher operational costs (Barbusiński, 2009). Hybrid systems, which combine conventional and advanced processes, demonstrate superior performance with COD removal efficiencies exceeding 95%, comprehensive pollutant removal, optimized cost-performance balance, and high reliability (Pawar & Gawande, 2015). Overall, this comparison clearly indicates that hybrid systems outperform standalone conventional or AOP-based treatments in terms of both efficiency and sustainability.

Despite the successful implementation of these technologies, several industrial challenges and practical considerations remain. Wastewater composition can vary significantly, affecting treatment consistency and efficiency. AOPs often involve high chemical consumption, while processes such as the Fenton method generate sludge that require careful handling and disposal. Additionally, UV- and ozone-based systems demand substantial energy input, increasing operational costs. Challenges also arise during scale-up and integration of treatment processes within existing industrial infrastructure. To overcome these issues, industries are increasingly adopting advanced monitoring systems, process automation, and optimization strategies to ensure stable and efficient operation.Environmental and regulatory compliance is another critical factor driving the adoption of advanced treatment technologies. Regulatory authorities impose strict discharge limits on parameters such as COD, biological oxygen demand (BOD), phenols, sulfides, and total dissolved solids (TDS). AOPs and hybrid treatment systems have proven highly effective in meeting these stringent standards, enabling industries to remain compliant while minimizing environmental impact. Furthermore, the reduction in toxicity and odor achieved through these methods contributes to improved environmental sustainability and safer discharge practices.Looking ahead, the future of spent caustic wastewater treatment is shifting toward more sustainable, efficient, and technologically advanced solutions. Emerging trends include the integration of AOPs with membrane technologies, the development of improved catalyst-based systems that minimize sludge generation, and the use of renewable energy sources to power UV-based processes. In addition, digitalization and real-time process control are gaining importance for optimizing performance and reducing operational costs. The adoption of Zero Liquid Discharge (ZLD) systems is also increasing, reflecting a growing emphasis on complete wastewater reuse and minimal environmental discharge. Collectively, these advancements are expected to significantly enhance the feasibility and widespread implementation of advanced treatment technologies in industrial applications.

The case studies highlights the practical implementation of conventional and advanced treatment methods for spent caustic wastewater in industrial settings. While conventional methods remain widely used due to their cost-effectiveness, they are often insufficient for complete pollutant removal. Hydrogen peroxide-based AOPs provide a powerful alternative, offering high efficiency and environmental benefits. Hybrid treatment systems, combining both approaches, emerge as the most effective and sustainable solution for industrial wastewater management.

Table: 2 Real Case Studies on Spent Caustic Wastewater Treatment

Case Study	Industry / Source	Treatment Method	Key Conditions	Performance Results	Remarks	References
Case Study 1	Olefin Plant	Neutralization + Fenton Process	pH ≈ 5, Fe^{2+} = 100 mg/L, Reaction time = 50 min	COD removal >99.5%, Final COD <100 mg/L	Highly efficient hybrid system	(Gholami et al., 2024)
Case Study 2	Petrochemical Wastewater	Electro-Fenton Process	pH ≈ 5.46, H_2O_2/COD = 0.73, Time ≈ 70 min	COD removal ≈ 93–94%	Cost-effective AOP method	(Shokri & Fard, 2023)
Case Study 3	Refinery (Sulphidic Wastewater)	Electro-Fenton	Fe^{2+} ≈ 200 mg/L	COD removal ≈ 90%, Sulfide removal ≈ 98%	High efficiency for sulfur compounds	(Shokri et al., 2023)
Case Study 4	Bandar Abbas Oil Refinery	Sono - Electrocoagulation	Ultrasound + Electrocoagulation	COD removal ≈ 80%	Improved conventional process	(Ahmadi et al., 2025)
Case Study 5	Refinery Wastewater	Fenton Pre-treatment	pH 2.7–6, H_2O_2/Fe ratio optimized	COD removal ≈ 95.5%, Phenol removal ≈ 99.5%	Excellent for phenolic compounds	(Babuponnusami & Muthukumar, 2012)
Case Study 6	Oil Refinery Wastewater	Photo-Fenton (UV + H_2O_2 + Fe^{2+})	pH ≈ 3, UV irradiation	COD removal ≈ 75% (after pretreatment)	Effective as polishing stage	(Shokri & Fard, 2023)

7. Process Optimization and Integration

The treatment of spent caustic wastewater requires not only appropriate technology selection but also effective optimization of operating conditions to achieve maximum efficiency and cost-effectiveness. Due to the complex nature of spent caustic—characterized by high alkalinity, elevated COD, and the presence of refractory compounds—standalone treatment methods often fail to deliver satisfactory results. Process optimization focuses on key parameters such as pH, chemical dosage, reaction time, temperature, and mixing conditions (Shokri & Fard, 2023). In conventional systems, proper neutralization and controlled biological conditions improve performance, while in advanced oxidation processes (AOPs), parameters such as acidic pH, optimized hydrogen peroxide dosage, and catalyst concentration significantly enhance hydroxyl radical generation and pollutant degradation.Optimization of hydrogen peroxide-based AOPs plays a crucial role in improving treatment efficiency while minimizing operational costs. For instance, maintaining an optimal pH range of 2.5–3.5 in the Fenton process ensures maximum radical production, whereas excessive hydrogen peroxide can lead to scavenging effects and reduced efficiency (Barbusiński, 2009). Similarly, reaction time and mixing intensity influence the extent of oxidation and mass transfer. In UV/H_2O_2 systems, energy optimization and water clarity are critical for effective UV penetration. These optimization strategies ensure higher COD removal efficiency, reduced chemical consumption, and improved process stability, making AOPs more viable for industrial applications. Integration of conventional treatment methods with AOPs has emerged as the most effective approach for handling spent caustic wastewater (Mirzaei et al., 2017). In a typical integrated system, neutralization is followed by primary treatment (such as wet air oxidation or Fenton oxidation), biological treatment for biodegradable organics, and finally AOP polishing to remove residual refractory compounds. This hybrid approach combines the cost advantages of conventional methods with the high efficiency of AOPs, resulting in overall COD removal exceeding 95% and improved compliance with environmental regulations. Additionally, integrated systems reduce sludge generation and optimize energy consumption, enhancing overall sustainability.Despite these advantages, challenges remain in scaling up and implementing optimized systems at the industrial level. Variations in wastewater composition, high chemical and energy requirements, and operational complexities must be carefully managed through proper design and automation. Emerging technologies such as real-time monitoring, artificial intelligence-based optimization, and advanced catalytic systems are expected to further improve process efficiency and reliability. Overall, optimized and integrated treatment systems provide a practical and sustainable solution for effective management of spent caustic wastewater in modern industrial applications.

Table 3: Summary of Process Optimization and Integration (Mirzaei et al., 2017; Brillas et al., 2009; Barbusiński, 2009; Rajaee et al., 2020)

Aspect	Conventional Methods Optimization	AOP Optimization (H_2O_2-Based)	Integrated/Hybrid Approach
pH Control	Neutralization to ~6–8	Acidic (pH 2.5–3.5 for Fenton)	Multi-stage pH adjustment
Chemical Dosage	Acid/alkali optimization	Precise H_2O_2 and catalyst dosing	Reduced overall chemical use
Reaction Time	Longer (biological systems)	Shorter (rapid oxidation)	Optimized overall retention time
Temperature	Ambient (biological) / High (WAO)	Moderate	Balanced energy use
Sludge Generation	High	Low (except Fenton)	Reduced sludge via integration
Energy Requirement	Low–High (WAO)	Moderate–High (UV/O_3)	Optimized through combination
Treatment Efficiency	Moderate	High	Very High (>95%)
Operational Control	Simple	Requires precision	Automated & optimized
Cost Efficiency	Low initial cost	Higher operating cost	Optimized lifecycle cost
Environmental Impact	Secondary pollution possible	Cleaner (CO_2, H_2O)	Sustainable solution
System Reliability	Moderate	High (if controlled)	Very high
Best Application	Primary treatment	Advanced/polishing	Complete treatment solution

8. Future Trends and Research Directions

8.1 Introduction

The treatment of spent caustic wastewater continues to evolve with advancements in environmental regulations, sustainability goals, and technological innovations. While conventional treatment methods and hydrogen peroxide-based advanced oxidation processes (AOPs) have demonstrated significant effectiveness, ongoing research is focused on improving efficiency, reducing operational costs, and minimizing environmental impact. Future trends emphasize the development of integrated, energy-efficient, and sustainable treatment systems capable of handling complex industrial wastewater streams.

8.2 Emerging Advanced Oxidation Technologies

Recent developments in AOPs have led to the emergence of novel techniques that enhance hydroxyl radical generation and improve treatment efficiency. These include electro-Fenton, photo-Fenton, catalytic ozonation, and plasma-based oxidation processes (Brillas et al., 2009). These technologies offer advantages such as higher oxidation rates, reduced chemical consumption, and improved adaptability to varying wastewater compositions.

Electro-Fenton processes, for instance, generate hydrogen peroxide in situ, reducing the need for external chemical dosing. Similarly, photo-Fenton processes utilize solar or UV energy to enhance radical production, making them more energy-efficient. These advancements are expected to play a significant role in future wastewater treatment systems.

8.3 Integration with Membrane and Hybrid Systems

The integration of AOPs with membrane technologies such as ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO) is gaining increasing attention (Shon et al., 2013). Membrane systems provide effective separation of suspended solids and dissolved contaminants, while AOPs ensure degradation of organic pollutants. Hybrid systems that integrate biological treatment, advanced oxidation processes (AOPs), and membrane filtration offer multiple advantages for industrial wastewater management. These systems provide enhanced treatment efficiency by combining the strengths of each individual process, ensuring more complete removal of organic and toxic pollutants. The integration also helps reduce fouling in membranes, extending their operational lifespan and lowering maintenance requirements. Additionally, such hybrid approaches improve the potential for water reuse by producing high-quality effluent suitable for various industrial applications. These benefits make integrated systems particularly valuable for industries striving to implement Zero Liquid Discharge (ZLD) strategies and achieve sustainable wastewater management.

8.4 Digitalization and Smart Process Control

The adoption of digital technologies is transforming wastewater treatment processes. Advanced sensors, real-time monitoring systems, and automation tools enable precise control of operating parameters, improving process efficiency and reliability. Artificial Intelligence (AI) and Machine Learning (ML) algorithms are increasingly being applied in wastewater treatment systems to improve efficiency and operational reliability (Rajaee et al., 2020). These technologies enable predictive process optimization by analyzing historical and real-time data to determine optimal operating conditions. They also play a crucial role in fault detection and prevention by identifying anomalies and potential system failures before they occur. Additionally, AI and ML facilitate the dynamic adjustment of chemical dosing, ensuring precise control over reagent usage based on varying wastewater characteristics. As a result, these advanced digital tools reduce the need for manual intervention while significantly enhancing the overall performance, stability, and efficiency of treatment systems.

8.5 Sustainable and Green Treatment Approaches

Sustainability is a key focus area in future wastewater treatment research. Efforts are being made to reduce energy consumption, minimize chemical usage, and utilize renewable energy sources. Key approaches for advancing sustainable wastewater treatment include the development of solar-driven UV/AOP systems, which utilize renewable energy to reduce operational costs and environmental impact (Malato et al., 2009). The use of biodegradable and recyclable catalysts is another important strategy, as it minimizes chemical waste and enhances process sustainability. Energy recovery from treatment processes can further improve overall efficiency by capturing and reusing energy generated during treatment. Additionally, reducing sludge generation not only lowers disposal challenges but also contributes to a cleaner and more environmentally friendly process. Collectively, these strategies support the development of cost-effective, efficient, and environmentally responsible wastewater treatment solutions.

Table 4: Emerging Trends in Spent Caustic Wastewater Treatment

Technology / Approach	Key Features	Advantages	Challenges	Future Potential	References
Electro-Fenton	In-situ H_2O_2 generation	Reduced chemical usage, high efficiency	Electrode cost, maintenance	High	(Brillas et al., 2009)
Photo-Fenton (Solar/UV)	Light-assisted oxidation	Energy-efficient, enhanced radical generation	Requires light source	Very High	(Malato et al., 2009)
Membrane + AOP Hybrid	Combined separation and oxidation	High-quality effluent, reuse potential	Membrane fouling	High	(Shon et al., 2013)
Catalytic Ozonation	Catalyst-enhanced ozone oxidation	Faster reaction rates	Catalyst cost	Moderate to High	(Kasprzyk-Hordern et al., 2003)
AI/ML Optimization	Data-driven control systems	Real-time optimization, efficiency	Implementation complexity	Very High	**(Rajaee et al., 2020)**
Zero Liquid Discharge (ZLD)	Complete water recovery	No wastewater discharge	High capital cost	Growing rapidly	(Tong & Elimelech, 2016)
Green Catalysts	Eco-friendly materials	Reduced environmental impact	Development stage	High	(Navalon et al., 2017)

8.6 Challenges and Research Opportunities

Despite significant advancements, several challenges remain in the widespread implementation of advanced treatment technologies. High operational costs, energy requirements, and process complexity are major barriers. Additionally, variability in wastewater composition requires adaptable and robust treatment systems. Future research in wastewater treatment, particularly in advanced oxidation processes, should focus on developing cost-effective catalysts that can enhance reaction efficiency while minimizing operational expenses. Improving the energy efficiency of AOPs is also essential to reduce overall process costs and environmental impact. Additionally, efforts should be directed toward enhancing the scalability of advanced treatment technologies to ensure their successful implementation in large-scale industrial applications. The integration of renewable energy sources into treatment systems presents another promising avenue for improving sustainability. Furthermore, reducing sludge generation and addressing disposal challenges remain critical areas requiring innovation. Addressing these key challenges will be vital for achieving efficient, economical, and sustainable wastewater management systems.

8.7 Future Outlook

The future of spent caustic wastewater treatment lies in the development of integrated, intelligent, and sustainable systems. The combination of advanced oxidation processes, membrane technologies, and digital tools is expected to revolutionize the field. Industries are increasingly moving towards resource recovery and water reuse, driven by environmental regulations and economic considerations.

With continuous research and technological advancements, it is anticipated that next-generation treatment systems will achieve higher efficiency, lower costs, and minimal environmental impact.

9. Conclusion

The treatment of spent caustic wastewater remains a significant challenge due to its high alkalinity, elevated chemical oxygen demand (COD), and the presence of toxic and refractory compounds such as phenols, sulfides, and mercaptans. This study comprehensively reviewed conventional treatment methods and hydrogen peroxide-based advanced oxidation processes (AOPs), highlighting their performance, limitations, and applicability in industrial wastewater treatment. Conventional methods, including neutralization, wet air oxidation, and biological treatment, are widely used due to their cost-effectiveness and established infrastructure. However, these methods often exhibit limited efficiency in removing refractory pollutants and may lead to secondary environmental issues such as sludge generation and odor emissions. In contrast, AOPs, particularly those based on hydrogen peroxide, demonstrate superior treatment efficiency through the generation of highly reactive hydroxyl radicals capable of degrading complex organic compounds. Processes such as Fenton, UV/H_2O_2, and O_3/H_2O_2 have shown remarkable potential in achieving high COD removal and improved effluent quality.

The comparative analysis clearly indicates that while AOPs offer enhanced performance and environmental benefits, their higher operational costs and process control requirements pose challenges for large-scale implementation. To address these limitations, hybrid treatment systems integrating conventional methods with AOPs have emerged as the most effective solution. These systems combine the economic advantages of conventional processes with the high efficiency of advanced oxidation, resulting in improved overall performance, reduced sludge generation, and compliance with stringent environmental regulations.

Furthermore, the incorporation of process optimization techniques, digital monitoring tools, and sustainable practices has significantly enhanced the feasibility of advanced treatment systems. Emerging technologies such as electro-Fenton, membrane-AOP hybrids, and AI-based process control are expected to play a crucial role in the future of wastewater treatment. Overall, this study concludes that optimized and integrated treatment approaches provide a practical, efficient, and sustainable solution for managing spent caustic wastewater in modern industrial applications.

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