Applied Chemical Engineering (2026) Volume 9 Issue 1 ISSN: 2578-2010 (O)
doi: 10.59429/ace.v9i1.5871

ORIGINAL RESEARCH ARTICLE

Heterogeneous Fenton - Based Treatment for Petroleum Refinery Wastewater: A Systematic Review

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ABSTRACT

Environmentally friendly methods are recommended for the petroleum refining industries, for treatment of the generated wastewater. Ammonia, sulfides, phenol, oil and grease, and petroleum hydrocarbons, and other chemical compounds are only a few of the many pollutants found in effluent from petroleum refineries. Major disadvantages of conventional treatment systems for refinery effluent include low effectiveness, high operating and capital costs, and susceptibility to low toxicity and biodegradability. Refinery wastewater has been treated using a variety of techniques, such as chemical, biological, physical, and hybrid approaches. Advanced oxidation processes (AOPs) have elaborated improved efficacy. Because of its multiple uses, affordability, and environmental friendliness, the Fenton process has emerged as a desirable substitute for other AOPs in the removal of contaminants from water. Therefore, the full comprehension of the Fenton process in petroleum refinery wastewater management is the main subject of this study by going over the major developments in the catalytic oxidation of nano-based Fenton materials for the treatment of petroleum refinery wastewater. Nano-based particles are widely used in Fenton catalysis because of their cheap cost and plentiful supply, particularly α-Fe2O3, as well as their high removal efficiency of chemical oxygen demand (COD) and concentrations of phenol, with an average elimination efficiency surpassing 90%. The current review discusses current developments in the manufacture and use of Fenton catalysts that are heterogeneous for the reduction of organic contaminants. Since the reaction between solid Fenton catalysts and H2O2 can produce extremely reactive hydroxyl radicals (HO%), heterogeneous Fenton reactions have drawn a lot of interest in eliminating stubborn organic pollutants. The aim of this study was to thoroughly examine the studies that have been conducted to improve heterogeneous Fenton reactivity for effective application in treating.

Keywords: wastewater; petroleum industry; heterogeneous Fenton process; nanoparticles

ARTICLE INFO

Received: 26 December 2025
Accepted: 16 January 2026
Available online: 22 January 2026

1. Introduction

Petroleum industries often have a negative impact on the environment through discharge of significant volumes of oily wastewater resulting from the use of large volumes of water [1-2]. Depending on the kind of treated crude oil, different industries release different wastewater from oil refining operations as shown in fig. 1.1 [3]. Numerous organic and inorganic elements, such as dissolved oil, ammonia, dyes, and heavy metals, are present in these wastewaters. As already stated in the literature, it is estimated that 60 to 90 gallons of water are needed to refine one barrel of crude oil, or roughly 246 to 341 L. There is a growing awareness of the need to prevent pollution from oil refinery wastewaters that may endanger human health and harm ecosystems [4-5].

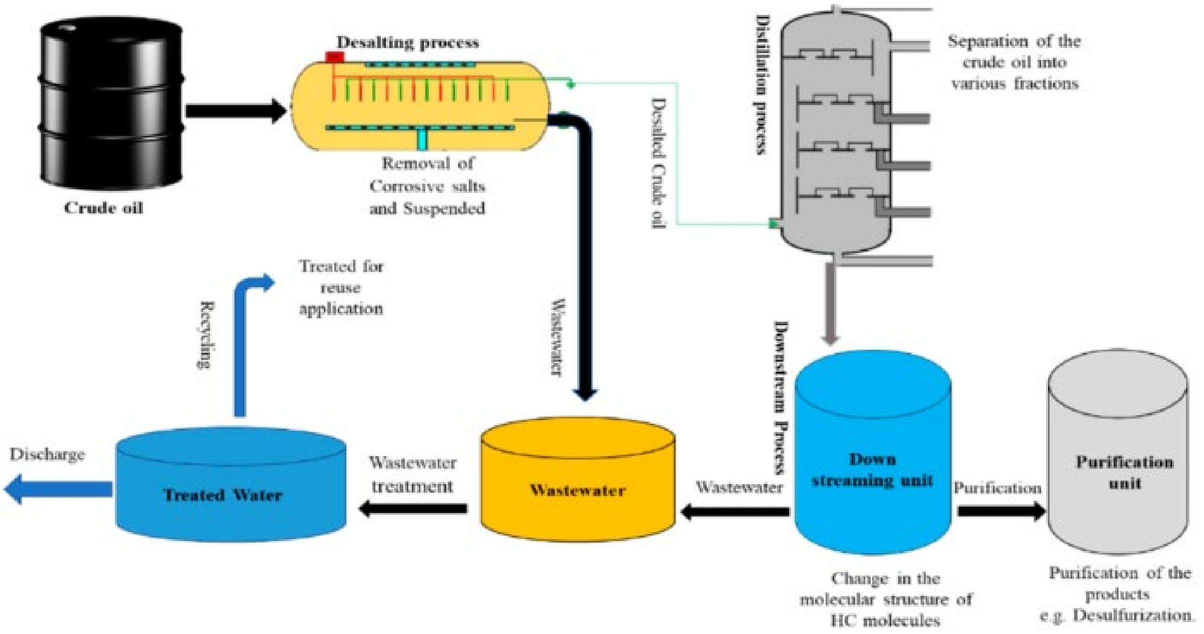


Figure 1. Simplified procedure for refining crude oil and producing the petroleum refinery wastewater (PRWW) [3]

Various petroleum refineries release numerous wastes from oil refining activities, depending on the type of the treated crude oil. Thus, it is necessary to develop efficient treatment techniques to reduce their detrimental effects on ecosystems. The use of photocatalytic agents is one of the crucial techniques that is very successful in managing oil pollution [4-5]. Physical, chemical, and biological methods form the other methods used to treat wastewater from the petroleum industry; however, most of these methods are best suited to meet specific treatment needs for each application and typically do not advise treating the wastewater to separate the different groups of pollutants [6-11]. One strategy for treating wastewater is chemical oxidation as an example of chemical methods for treating wastewater that can be divided into two categories: advanced oxidation procedures (AOPs) and standard chemical treatments. Several wastewater kinds, such as those from the oil and gas and pharmaceutical industries, need the use of extremely effective advanced oxidation procedures. Numerous studies have been conducted in the past to investigate the effectiveness of advanced oxidation techniques in treating various wastewater types that contain harmful and recalcitrant contaminants [12-14].

Chemical treatment, conversion, and separation are the three fundamental steps that make up the refining process. However, the kind of crude oil and the selected refined products determine the particular industrial processes of each refinery. Because of this fundamental factor, practically all petroleum oil refineries operate differently from one another.

2. Wastewater characterization from petroleum refineries

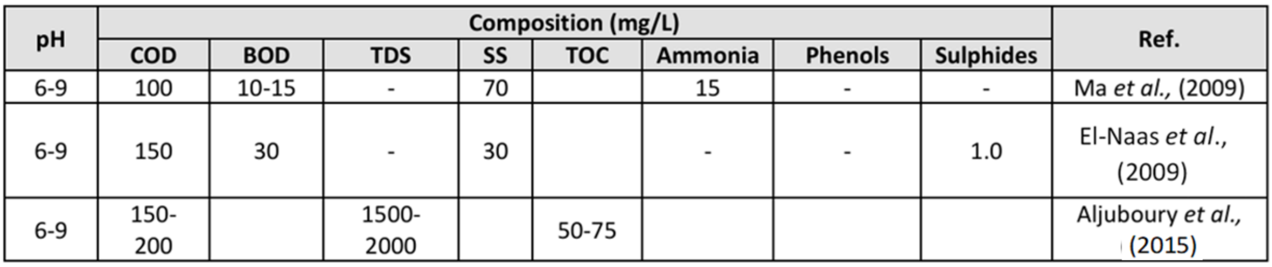
Petroleum refinery activities typically have the ability to damage the environmental ecosystem, which also has an impact on the quality of the air and land because of their toxicity [15].

2.1. Contaminants identified in pollutants from oil refineries

The wastewater generated by oil refineries contains a variety of toxins, including organic compounds, heavy metals, and other dangerous substances. The wastewater from oil refineries has been found to contain a variety of pollutants. Ammonia, dissolved minerals, heavy metals, oil, phenols, suspended particles, are the most important contaminants that have a significant effect when their levels become higher than permissible levels considered safe for the environment that cause the reduction in oxygen level as measured by biological oxygen demand (BOD) and chemical oxygen demand (COD). A typical PRWW effluent is frequently characterized by high BOD and COD due to the widespread distribution of aliphatic and aromatic hydrocarbons, grease and emulsified oils, ammonia, cyanides, and other inorganic compounds [16].

In most typical PRWW specimens, the average documented values for BOD and COD can be up to 400 mg/L and 600 mg/L, respectively. It was also reported about 150–250 mg/L, 300–600 mg/L, and 20–200 mg/L for BOD, COD and oil concentrations in desalted PRWW effluent, respectively [2,3,17]. Refinery effluents' minimum standard discharge limit is shown in **Table 2.1** [18-20].

Table 1. Refinery effluent minimum standard discharge limit [18-20]



pH	Composition (mg/L)								Ref.
	COD	BOD	TDS	SS	TOC	Ammonia	Phenols	Sulphides	
6-9	100	10-15	-	70		15	-	-	Ma *et al.*, (2009)
6-9	150	30	-	30		-	-	1.0	El-Naas *et al.*, (2009)
6-9	150-200		1500-2000		50-75				Aljubory *et al.*, (2015)

2.1.1. Organic compounds

Chemicals with carbon-based structures are referred to as "organic compounds" when discussing pollutants discovered in oil refinery wastewater. These compounds may be hazardous, persistent, and accumulative, endangering both the environment and public health. Similar to those present in crude oils, refinery wastewaters comprise aliphatic, aromatic, alkyl aromatic chemicals [16].

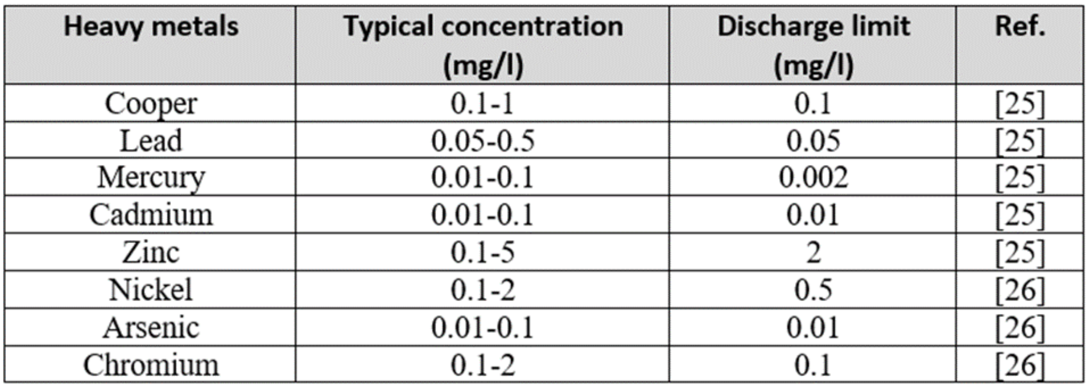
2.1.2. Sulphates and chloride

Refinery effluent has high amounts of dissolved solids, such as sulfates and chlorides, which are harmful to aquatic life and water quality. These substances have the power to destroy chlorides, sulfates, and dissolved particles in aquatic settings. Reverse osmosis membranes and ion exchange resins are two common techniques for extracting certain ions from water. Ion exchange resins reduce the concentration of specific ions in wastewater by exchanging ions like sulfate and chloride with other ions in the resin [16,21].

2.1.3. Heavy metals

Copper (Cu), lead (Pb), mercury (Hg), cadmium (Cd), zinc (Zn), nickel (Ni), arsenic (As), and chromium (Cr) are examples of common heavy metals. Even while there may be trace levels of certain heavy metals, they are nonetheless harmful. To reduce contamination and protect ecosystems and human health, refinery effluent must be managed and treated effectively. To remove heavy metals from wastewater, methods include ion exchange, membrane filtration, chemical precipitation, and biological processes are essential. The advantages and disadvantages of recent advancements and different methods for eliminating heavy metals were reviewed. In particular, novel methods such as biosorption, biological adsorption, and photocatalysis [22-24].
Likewise, there are notable differences in the heavy metal concentrations from PRWW seen in **Table 2.2** Copper (Cu), lead (Pb), mercury (Hg), cadmium (Cd), zinc (Zn), nickel (Ni), arsenic (As), and chromium (Cr) are examples of common heavy metals. Even though these heavy metals could be found in trace amounts, they are nevertheless harmful [25,26].

Table 2. Concentrations of certain heavy metals in effluent from normal refineries [25,26]



Heavy metals	Typical concentration (mg/l)	Discharge limit (mg/l)	Ref.
Cooper	0.1-1	0.1	[25]
Lead	0.05-0.5	0.05	[25]
Mercury	0.01-0.1	0.002	[25]
Cadmium	0.01-0.1	0.01	[25]
Zinc	0.1-5	2	[25]
Nickel	0.1-2	0.5	[26]
Arsenic	0.01-0.1	0.01	[26]
Chromium	0.1-2	0.1	[26]

It is typically challenging to comprehend the full chemistry of PRWW contaminants and connect their toxicity to the receiving natural ecosystem because to their extremely complex and dynamic nature [17]. In addition to harming the soil and reducing its usefulness, the release of contaminated material into the ground increases the possibility that the contaminants will find their way into the groundwater [27]. Therefore, in order to comply with discharge regulations and for recycling purposes, an efficient treatment strategy must be created.

3. Handling wastewater from petroleum refineries

3.1. Traditional wastewater treatment approaches

Refinery effluent must be managed effectively by proper treatment to reduce contamination and protect environment from harm. Heavy metal removal from wastewater requires the use of methods such chemical precipitation, ion exchange, membrane filtration, and biological processes [28,29]. In particular, novel approaches like biological adsorption, A mix of chemical, biological, and physical methods must be used to treat refinery effluent in order to eliminate or break down these hazardous substances. Combining treatment techniques before discharge is frequently the standard due to the complexity and diversity of refinery contaminants [30]. ideally, in order to produce an effluent that conforms with the current effluent disposal standards, a refinery wastewater treatment facility should have the units at described in **Figure 3.1** [31].

It is worth noting that, if a complete wastewater treatment system with three stages of treatment—primary, secondary, and tertiary is operational, an effluent can be effectively treated to meet the recommended standards. The criteria: chemical oxygen demand (COD), biological oxygen demand (BOD), oil and grease (O&G), benzene, toluene, ethylbenzene, and xylene (BTEX), suspended solids (SS), NH3, and heavy metals may be eliminated in 90% to 99% of cases [32,33].

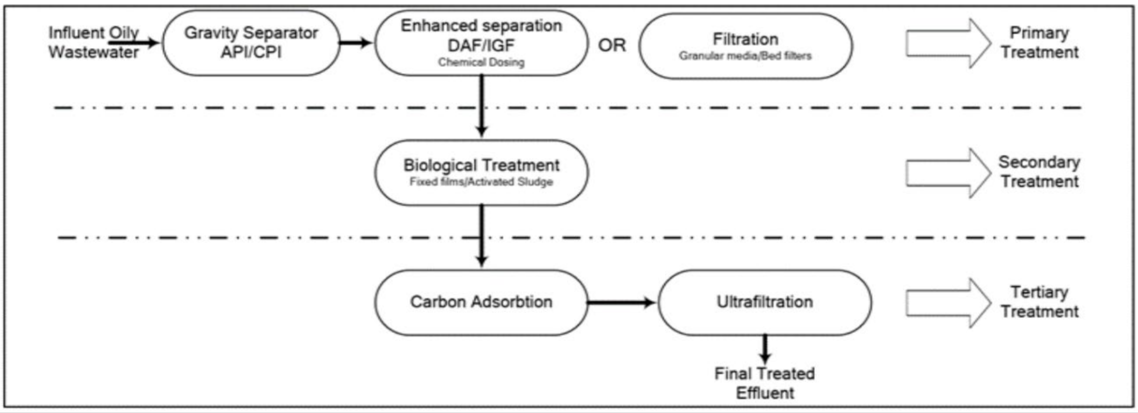


Figure 2. Typical stages of an oily wastewater refinery's treatment [31]

Physical, chemical, and biological treatment procedures were among the methodologies and approaches for treating petroleum wastewater, according to the literature review that was carried out.

3.1.1. Physical treatment

Physical treatment methods comprise procedures that enhance or treat wastewater using only physical phenomena and do not include significant chemical or biological changes. Sedimentation and coarse screening to eliminate bigger entrained particles are two examples [20]. When sulfide and salts are present in excess of 20 mg L-1, biological activity may be inhibited. In order to remove or separate suspended solids (SS), immiscible liquids, solid particles, and suspended substances from petroleum wastewater using sedimentation, coagulation, flocculation, and extended use of the secondary treatment unit, the physical treatment system is a primary treatment step. The majority of physical therapy approaches are regarded as traditional approaches. removed using physical methods like sedimentation before biological treatment. In separators or separation tanks, gravity mechanically accomplishes the sedimentation process, which is used to separate oil from water. Turbidity was eliminated and the organic load was reduced using the coagulation procedure. However, due to its complexity, physical methods were not very successful in treating petroleum effluent; consequently, alternative methods might be employed for pretreatment [20].

3.1.2. Membrane

In general, membranes can be divided into two categories: synthetic and biological. The use of membrane technologies like ultra-filtration and electrodialysis is growing. Compared to other physical treatment methods, membrane separation was shown to be more acceptable and cost-effective when treating organic matter.It is demonstrated that heavy metals were removed from petrochemical effluent by membrane bioreactors (MBRs) in varying percentages, ranging from 40% to 70%. Iron removal was the process's maximum removal, exceeding 70%..fluent, membrane technologies—in particular, reverse osmosis—seem to be a more efficient option than traditional techniques [34]. The procedure entails using a semipermeable membrane to separate two solutions with varying concentrations. Water would inevitably move from the less concentrated solution to the more concentrated one. However, there are a few significant drawbacks to membrane processes, including membrane fouling and the production of a significant amount of residual concentrate. Membrane fouling shortens the membranes' lifespan and reduces process efficiency, necessitating chemical cleaning or extensive preparation.

3.1.3. Flocculation / Coagulation

One significant and traditional technique for treating wastewater is the chemical coagulation process, which lowers or eliminates turbidity, color, COD, and TSS. When applied as a final polishing treatment or before to biological or membrane treatment, it is an effective pretreatment method for reducing or getting rid of non-biodegradable organic waste in petroleum effluent [20,34].

As an important example, in Iraq five petroleum refineries release their liquid waste into water sources, along with a treatment facility. The production processes in these oil refineries produce a significant amount of liquid waste, which is characterized by a high content of oil pollutants. If these discharges are released untreated or with ineffective treatment, they pose a serious threat to the environment because they pollute water resources and harm various aquatic resources. In addition, the release of contaminated trash into the soil damages it and reduces its usefulness, and there is a chance that the contaminants will find their way into groundwater. Sampling of these discharges, regular visits, and laboratory testing are used to monitor and assess the refineries in different governorates. Test findings are compared with the factors in effect, with an emphasis on the value of oils and fats, which should not exceed 10 mg/liter, in accordance with the parameters that apply, while the other parameters are monitored [1]. **Table 3.1** illustrates how Iraqi refineries dispose their wastewater.

Table 3. The techniques employed for removal of waste for Iraqi refineries [1]

No	Name of the refinery	Place of Effluents discharge	Rriver's name
1	Southern Refineries Company / Basra Refinery	Adjacent lands	----
2	North Refineries Company / Qayyarah Refinery	River	Tigris
3	North Refineries Company / Kasak Refinery	Water trocar	-----
4	Northern Refineries Company / Baiji Refinery	River	Tigris
5	North Refineries Company / Haditha Refinery	Adjacent lands	----
6	Mid Land Refineries Company / Dora Refinery	River	Tigris
7	Mid Land Refineries Company/Samawah Refinery	Adjacent lands	-----
8	North Oil Company / Kirkuk refinery	River	Tigris
9	Diwaniyah Refinery	Septic tanks	-----
10	Alsinsinah Refinery / Baiji	Adjacent lands	------
11	Najaf Refinery	Septic tanks	-----
12	Dhi Qar Refinery	Adjacent lands	-----
13	Maysan Refinery	Adjacent lands	-----

With the traditional approach, solid particles are separated and permitted to sink due to gravity during sedimentation. As water flows through media, particles are captured by filtration. Chemical techniques for disinfection and coagulation-based pollution removal. While disinfection uses ozone or chlorine to destroy disease-causing germs, coagulation joins tiny particles into larger clumps for easy removal [27]. However, there are a number of drawbacks to traditional methods, including their inefficiency, high cost, and potentially dangerous byproducts; also, they necessitate extensive resources and highly skilled workers.

3.2. Treatment using advanced oxidation processes

Advanced oxidation processes (AOPs), which are characterized by the production of hydroxyl radicals, are one of the promising alternatives. The main goal of the AOPs is to generate highly reactive and highly sensitive free radicals and use non-selective substances to lessen organic composites that are polluted that are found in a medium, such soil, wastewater, or marine media, etc. Due to their reactivity: electrophiles, hydroxyl radicals are effective for of organic compounds removal. They are strong oxidizers that can break down substances that the typical oxidant is unable to oxidize [32]. Generally by, combining O_3, H_2O_2, TiO_2, UV, ultrasonic, and electron beam irradiation increases the production of hydroxyl radicals. Among the main benefits of AOPs over conventional methods of water treatment are the elimination of impurities and the prevention of the synthesis of harmful substances [70]. **Figure 3** provides a summary of the AOP in the treatment of petroleum effluent [35].

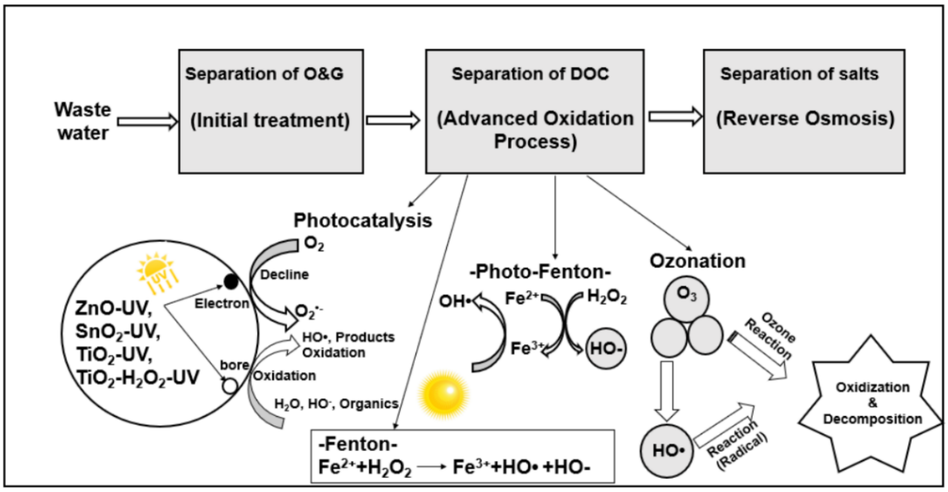
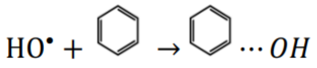


Figure 3. An outline for the AOP in wastewater treatment from petroleum refineries [35]

Nowadays, AOPs are receiving greater attention since they are eco-friendly methods that produce less secondary byproducts and have demonstrated good treatment efficiency in the elimination of organic compounds, regardless of low amounts [36]. Due to its significant reactivity with organic chemicals and propensity for color degradation, the strong hydroxyl radical (−OH) is responsible for the treatment capability [37-39]. This has led to reports that AOPs are an effective treatment technology for sludge treatment as well as the decrease of COD, color, odor, and other particular contaminants. During the (AOPs) process, the following equations will take place:



(1)

$$\mathrm{HO^{\bullet} + R - H \rightarrow R^{\bullet} + H_2O} \quad (2)$$

$$\mathrm{HO^{\bullet} + R - X \rightarrow [R - X]^{+\bullet} + HO^{-}} \quad (3)$$

$$\mathrm{HO^{\bullet} + HCO_3{}^{-} \rightarrow CO_3{}^{\bullet -} + H_2O} \quad (4)$$

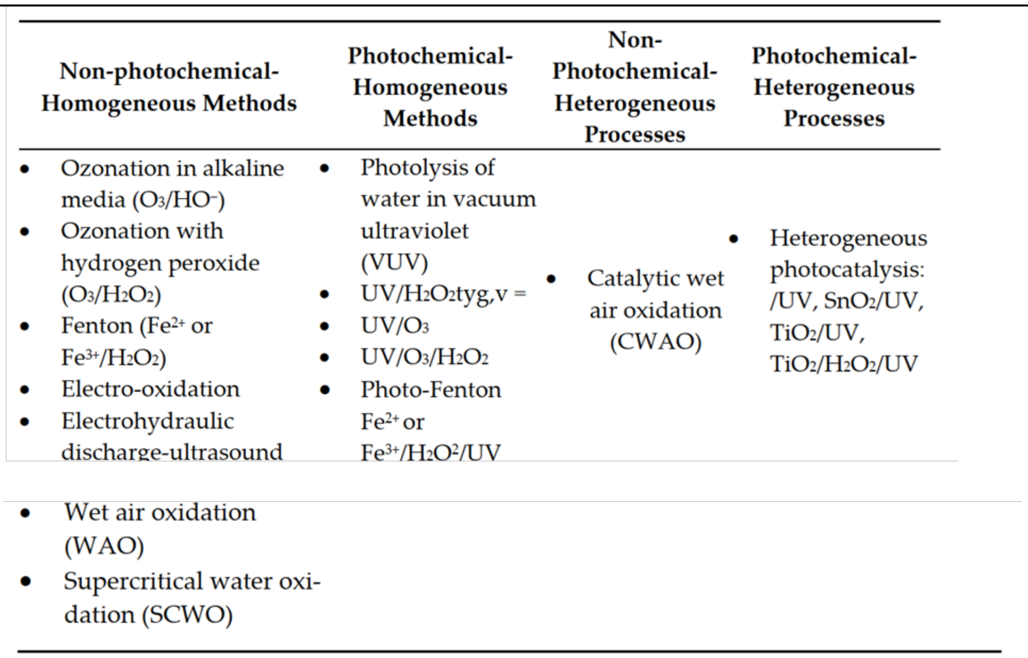
$$\mathrm{HO^{\bullet} + CO_3{}^{2-} \rightarrow CO_3{}^{\bullet -}\ HO^{-}} \quad (5)$$

Organic composite of the petroleum wastewater is attacked by hydroxyl radicals (HO•), and react with the saturated aliphatic molecule to remove hydrogen leading to the formation of a hydroxyl.

By reacting with the HO• radicals (Equations (4) and (5)), these ions can subsequently confront the organic substrates through the HO• radicals. Due to the high cost of the chemicals used (such as H_2O_2 and O_3) and the electric energy required for UV radiation, AOPs are an expensive procedure. Pretreatment procedures including dilution, coagulation, and flocculation are required for high organic wastewaters in order to reduce the initial concentrations of the pollutants [40,41].

There are two main types of AOP: homogeneous and heterogeneous processes as shown in **Table 3** [42].

Table 4. Advanced oxidation techniques (AOPs) and their classification [42]



Non-photochemical-Homogeneous Methods	Photochemical-Homogeneous Methods	Non-Photochemical-Heterogeneous Processes	Photochemical-Heterogeneous Processes
• Ozonation in alkaline media (O_3/HO^-) • Ozonation with hydrogen peroxide (O_3/H_2O_2) • Fenton (Fe^{2+} or Fe^{3+}/H_2O_2) • Electro-oxidation • Electrohydraulic discharge-ultrasound • Wet air oxidation (WAO) • Supercritical water oxidation (SCWO)	• Photolysis of water in vacuum ultraviolet (VUV) • UV/H_2O_2tyg,v = • UV/O_3 • $UV/O_3/H_2O_2$ • Photo-Fenton Fe^{2+} or $Fe^{3+}/H_2O^2/UV$	• Catalytic wet air oxidation (CWAO)	• Heterogeneous photocatalysis: /UV, SnO_2/UV, TiO_2/UV, $TiO_2/H_2O_2/UV$

3.3. Mechanism of fenton advanced oxidation process

Iron (II) and hydrogen peroxide, sometimes known as Fenton's reagents, oxidize organic substrates in the Fenton process. The Fenton process employs Fe^{2+} as a catalyst and hydrogen peroxide as an oxidant [43].

The Fenton method is used for a variety of industrial waste, including waste with a high phenolic chemical content, textile waste, laboratory waste, and pharmaceutical waste. The Fenton process has several benefits, including the ability to oxidize certain low molecular weight organic compounds (like paraffin, chlorinated alkanes, and some short-chain carboxylic acids), high efficiency, ease of use due to room temperature and atmospheric pressure, and a waste effluent that is more environmentally friendly [43]. However, the Fenton process has a number of limitations, including high running costs, a limited pH range (it operates best at pH 3), a large volume of sludge iron, and a challenging Fe^{2+} catalyst recycling procedure. The Fenton process could be widely taken into consideration to lower high pollution levels because of its low operating cost in comparison to other sophisticated oxidation processes, low toxicity of iron ions and hydrogen peroxide, simple technology, potential application in ambient temperature and pressure, high biocompatibility, short process duration, and low energy consumption. The ideal pH range for Fenton's reaction, which takes place in an acidic environment, is between 2.8 and 3 [44,45].

Despite being a potent oxidant, hydrogen peroxide (H_2O_2) by itself is ineffective for high concentrations of some refractory pollutants due to low reaction rates at a suitable H_2O_2 concentration [46]. In the Fenton technique, metal salts, such as iron salts, activate H_2O_2 to produce OH• radicals, which are potent oxidants that target and eliminate a variety of dangerous organic contaminants in water. Additionally, the reaction produces radical HO_2• as active intermediates. The creation of radical OH• is a complicated process. The single electron transfers reactions between Fe^{2+} and H_2O_2, OH• and H_2O_2, HO_2• and H_2O_2, and the resulting oxygen free radicals start the chain growth process (OH•, HO_2•). Reactions (6-8) represent a chain initiation phase. The ferric ions generated in reaction (6) further catalyze the breakdown of hydrogen peroxide into oxygen and water. The organic substrate (RH) of wastewater can be oxidized by hydroxyl radicals produced during the process, as illustrated below [43]:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH\bullet + OH- \qquad (6)$$

$$OH\bullet + H_2O_2 \rightarrow HO_2\bullet + H_2O \qquad (7)$$

$$HO_2\bullet + H_2O_2 \rightarrow H_2O + O_2 + OH\bullet \qquad (8)$$

$$RH + OH\bullet \rightarrow H_2O + R\bullet \qquad (9)$$

$$R\bullet + H_2O_2 \rightarrow ROH + OH\bullet \qquad (10)$$

$$R\bullet + O_2 \rightarrow ROO\bullet \qquad (11)$$

The extremely reactive organic radical (R•) is created when protons are abstracted. According to multiple studies, the standard pH in Fenton's reaction is 3, which can be regarded as the appropriate operational pH. The production of chemicals that produce fewer hydroxyl radicals at a very low pH (<2.5) lowers the system's efficiency. Therefore, before adding Fenton reagents to wastewater, a pH adjustment is required [47].

Since iron hydroxide is often produced at pH 6, the pH of the solution in the Fenton process should be changed to preserve catalyst stability. The optimal catalyst to peroxide ratio is typically 1:5 wt/wt, and the ideal pH for the Fenton reaction for a variety of materials is between 2.8 and 3. The decrease of free iron forms in the solution at an acidic pH of more than three causes the breakdown rate to decrease, potentially due to the formation of Fe(II) complexes with the barrier preventing the synthesis of free radicals. The generation of ferrous ions is reduced as pH rises over 3 because Fe^{3+} starts to precipitate as ferricoxy-hydroxides and breaks down the H_2O_2 into O_2 and H_2O. Furthermore, it is known that as pH rises, the •OH radical oxidation potential decreases. However, at low pH (pH = 2.5), Fe(II) $(H_2O)^{2+}$ is created, which combines with hydrogen peroxide more slowly, producing fewer reactive hydroxyl radicals and, as a result, lowering the degradation efficiency [48-50]. It is worthy to mention that, the ferrous ion is a component of the oxide crystal structure in iron oxide systems. This characteristic reduces the leaching of ferrous ions from the catalyst by increasing the stability of the catalyst towards the splitting of H_2O_2. Fig. 3.3 demonstrates the mechanism of Interfacial processes of iron-based materials-catalyzed heterogeneous Fenton reactions [51]

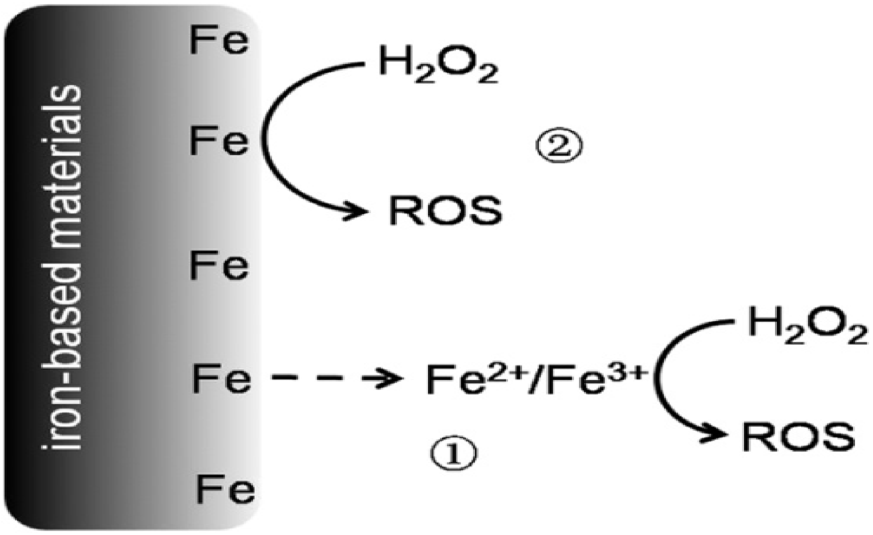
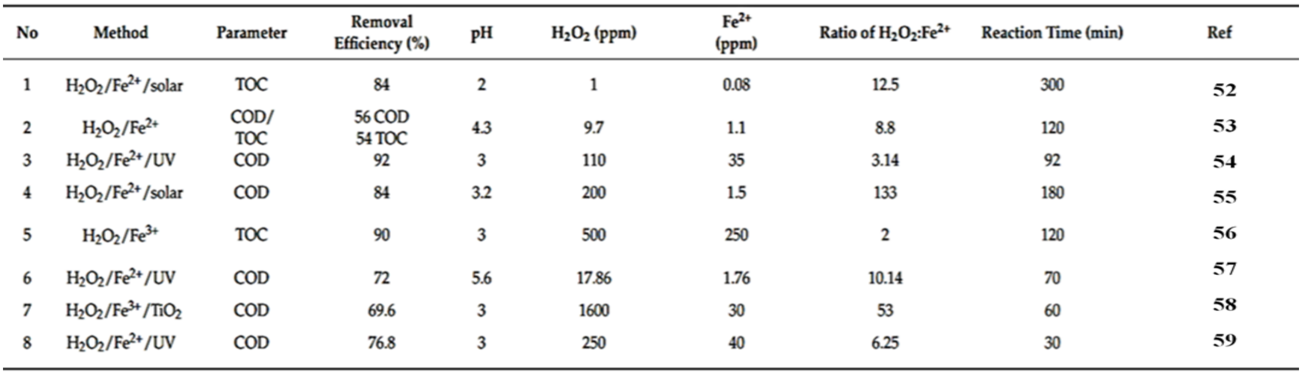


Figure 4. Diagrammatic representation of the interfacial mechanisms in iron-based materials-catalyzed heterogeneous Fenton systems: 1. surface-leached iron-induced homogeneous Fenton process and 2. heterogeneous catalysis mechanism.
(The surface of materials based on iron in aqueous solution is simplified.)[51]

Table 5 provides an overview of the Fenton and photo-Fenton technologies' efficacy in treating petroleum effluent. The Fenton and photo-Fenton processes' efficiency in treating petroleum refinery effluent and separating various contaminants, such as COD and TOC compounds, are displayed in **Table 3.3**. The tests demonstrated that Fe^{+2} concentrations under both procedures were successful in removing pollutants from the wastewater at various parameters, such as pH, reaction duration, and H_2O_2 concentration, although they required large volumes of reagents.

Table 5. the effectiveness of Fenton and Photo-Fenton techniques for treating effluent from petroleum [52-59]



No	Method	Parameter	Removal Efficiency (%)	pH	H_2O_2 (ppm)	Fe^{2+} (ppm)	Ratio of H_2O_2:Fe^{2+}	Reaction Time (min)	Ref
1	H_2O_2/Fe^{2+}/solar	TOC	84	2	1	0.08	12.5	300	52
2	H_2O_2/Fe^{2+}	COD/ TOC	56 COD 54 TOC	4.3	9.7	1.1	8.8	120	53
3	H_2O_2/Fe^{2+}/UV	COD	92	3	110	35	3.14	92	54
4	H_2O_2/Fe^{2+}/solar	COD	84	3.2	200	1.5	133	180	55
5	H_2O_2/Fe^{3+}	TOC	90	3	500	250	2	120	56
6	H_2O_2/Fe^{2+}/UV	COD	72	5.6	17.86	1.76	10.14	70	57
7	$H_2O_2/Fe^{3+}/TiO_2$	COD	69.6	3	1600	30	53	60	58
8	H_2O_2/Fe^{2+}/UV	COD	76.8	3	250	40	6.25	30	59

Wastewater degradation is significantly improved by the use of energy-dispersing components and both homogeneous and heterogeneous catalysts.

Under atmospheric pressure and at ambient temperature, the Fenton process can be performed. Furthermore, the necessary reagents are easily accessible, safe, easy to handle and store, and do not harm the environment. Nonetheless, two primary disadvantages were noted. The first has to do with oxidant waste because of hydrogen peroxide's ability to scavenge radicals and its own breakdown. The second relates to the production of solid sludge and the ongoing loss of iron ions. Fenton sludge has been linked to a number of negative economic and environmental effects. Therefore, it is necessary to research methods that enable an effective use of H_2O_2. Additionally, an effort must be made to recover iron ions and then recycle and reuse them [60,61].

Figure 5 depicts the solid-liquid separation, oxidation reaction, neutralization, and acid regulation in the standard Fenton continuous flow process configuration, and catalyst mixing [62].

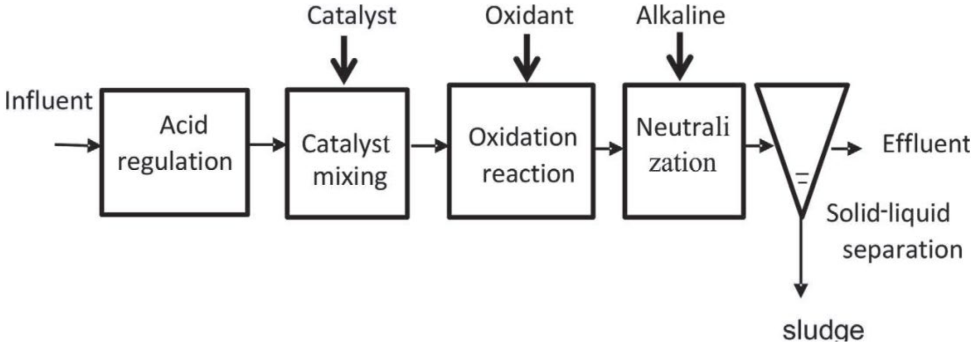


Figure 5. Illustration of the Fenton process [62]

Researchers have focused a lot of emphasis on improving the Fenton process in order to get beyond the aforementioned drawbacks. Ferric oxide, iron minerals, and nano zero-valent iron were among the heterogeneous and homogeneous catalysts that were utilized to replace Fe2+ [63,64]**.** On the one hand, a heterogeneous Fenton process can be created by employing a reductant or transition metal to lessen the loss of iron and the resulting sludge production.

3.4. Variables impacting the fenton process

Factors including pH, H_2O_2 dose, catalyst concentration, and the initial concentration of contaminants in wastewaters have a significant impact on the efficiency of Fenton and related processes. These elements are essential to the Fenton process because they produce OH, which helps break down contaminants in wastewater. Therefore, it is essential to understand how these parameters relate to the generation and consumption of OH in the Fenton process [65].

1. Pollutants' initial concentration

Degradation of pollutants in wastewater is one of the main goals of any Fenton process; therefore, the initial concentration of pollutants has a considerable impact on degradation efficiency. While lower pollution concentrations are advantageous for the Fenton process, they can also have negative effects when handling huge volumes of wastewater. A rise in the initial concentration of pollutants in a heterogeneous system may cause the total process efficiency to decline [65,66].

2. Reagents of Fenton

In terms of the rate at which contaminants in wastewater degrade, Fenton reagents (Fe^{2+} or catalyst and H_2O_2) have a significant impact on the overall process efficiency. The concentration of pollutants in a solution determines the ideal H_2O_2dosage for the Fenton process. Despite this, it is significantly greater than the predicted threshold required for pollutants to fully mineralize. In particular, non-radical routes may facilitate H_2O_2's breakdown into O_2 and H_2O. Pollutant degradation in wastewater can be accelerated by an increase in H_2O_2 content. However, large amount of H_2O_2 can also lead to a high COD content and higher operating costs, particularly when wastewater volume is quite high. Furthermore, specific organisms are harmed by high H_2O_2 [66,67]. As a result, choosing the H_2O_2 concentration for the Fenton process requires careful consideration. However, a higher dose of Fe^{2+} or catalyst can boost the production of additional OH radicals that can be used to eliminate contaminants from wastewater. Nevertheless, OH radical scavenging effects may also result from high catalyst loading. Furthermore, the price of solid catalysts in a heterogeneous environment may potentially be a barrier to their widespread use. The rate at which organic contaminants in wastewater are attacked by OH radicals determines the effectiveness of the Fenton process. In the Fenton process, contaminants often degrade quickly during the first reaction, which is followed by a gradual reaction. In order to prevent the radical scavenging effect and lower costs, Fenton reagent optimization is crucial [67].

3. pH Value

Because of the Fe and H_2O_2 speciation considerations, pH has a significant impact on the efficiency of the Fenton process. Diverse conclusions have been published by researchers regarding the ideal pH for Fenton processes. But according to numerous studies, the ideal pH for Fenton systems is 3. Fenton's reagent activity may be impacted by the formation of inactive Fe oxyhydroxides and iron hydroxide ($Fe(OH)_3$) precipitate at higher pH levels. However, the Fenton reaction is dominated by OH radical scavenging actions at pH values below 3. However, the ideal pH for the Fenton process is a difficult but crucial component that can only be ascertained by experimentation. The pH dependency of the Fenton process has been expanded in previous literature, particularly on heterogeneous systems, and further research is anticipated in the years to come [65-67].

4. Impact of inorganic ions

Due to chemicals are used during manufacturing processes, inorganic ions are typically found in industrial wastewaters. High levels of nitrates, chlorides, carbonates, and sulfides ions can be found in industrial wastewaters. When found in wastewater, these background contaminants may have an impact on the oxidation process by scavenging OH radicals. Despite the fact that inorganic ions have different effects on the Fenton process, matrix compositions of these ions must be taken into account because of their inhibitory effects [65].

3.5. Fenton process using heterogeneous catalysts

3.5.1. Materials based on multi-metallic iron

A homogeneous Fenton procedure is the Fenton reaction that uses iron salts as a catalyst. However, there are certain drawbacks, such as (i) the development and removal of ferric hydroxide sludge at pH values above 4.0, (ii) the difficulty of recycling and reusing catalysts, (iii) significant energy consumption, and (iv) a limited operational pH range [68]. In order to address the drawbacks of homogeneous catalysis, using sources of modified iron as heterogeneous catalysts in the Fenton reaction has been extensively researched. Numerous heterogeneous catalysts have been used in Fenton reactions, such as iron minerals [68], iron pillared clays [69], and zero valent iron [70]. Different kinds of heterogeneous Fenton-like catalysts are depicted in Figure 3.5 [62].

These catalysts break down H_2O_2 into HO without clearly leaching iron ions or producing iron hydroxide precipitate. Consequently, these catalysts have high activity even after several uses and are quickly recovered after the reaction [74]. In the meanwhile, these catalysts' high stability allows them to mediate heterogeneous Fenton reactions throughout a broad pH range, including neutral pH. For this reason, during the past ten years, the scientific community's interest in this topic has steadily grown [74,75]. However, there are still a lot of contentious issues with the development of Fenton catalysis in heterogeneous state. For instance, in a heterogeneous Fenton catalytic system, the presence of high-valent iron species (such as Fe(IV)) and how to increase the heterogeneous Fenton catalytic activity are important factors.

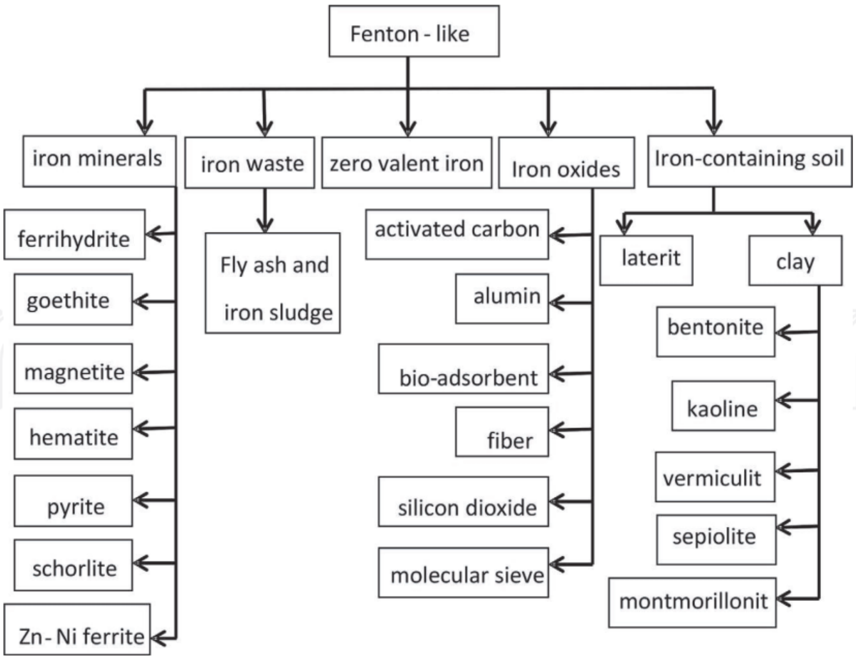


Figure 6. Heterogeneous catalysts used in Fenton process [62]

It is worthwhile to investigate whether the irons in the solid phase or the dissolved irons take the lead in a heterogeneous Fenton catalysis system. The contribution of both homogeneous and heterogeneous Fenton catalysis was shown to be strongly influenced by the catalyst's stability and the existence of potent complexing agents in the heterogeneous Fenton reaction system.

The most important question is how to increase heterogeneous Fenton catalytic efficiency. The most effective and crucial stage for eliminating impurities in the heterogeneous Fenton system is the generation of HO by the reaction between Fe(II) and H_2O_2. Therefore, certain methods that can speed up Fe(II) regeneration, encourage H_2O_2 breakdown, and produce H_2O_2 in situ could greatly increase the heterogeneous Fenton reactivity [76]. Heterogeneous Fenton oxidation is a quick and effective way to break down contaminants. Hydroxyl radicals (•OH) are produced when Fe (II) and H_2O_2 combine, and these radicals can react quickly with contaminants. Fe_3O_4 has garnered a lot of interest recently as a heterogeneous Fenton catalyst. Organic pollutants can be broken down in a broader pH range (pH 3–7) , Fe (II) and Fe (III) on the surface of the Fe_3O_4 can accomplish reversible oxidation and reduction by electron transfer to limit the iron loss . Furthermore, because the catalysts' surface free energy would be altered and the reaction would be hastened, Fe (II) on their surface was more reactive than Fe (II) in solution [76,77].

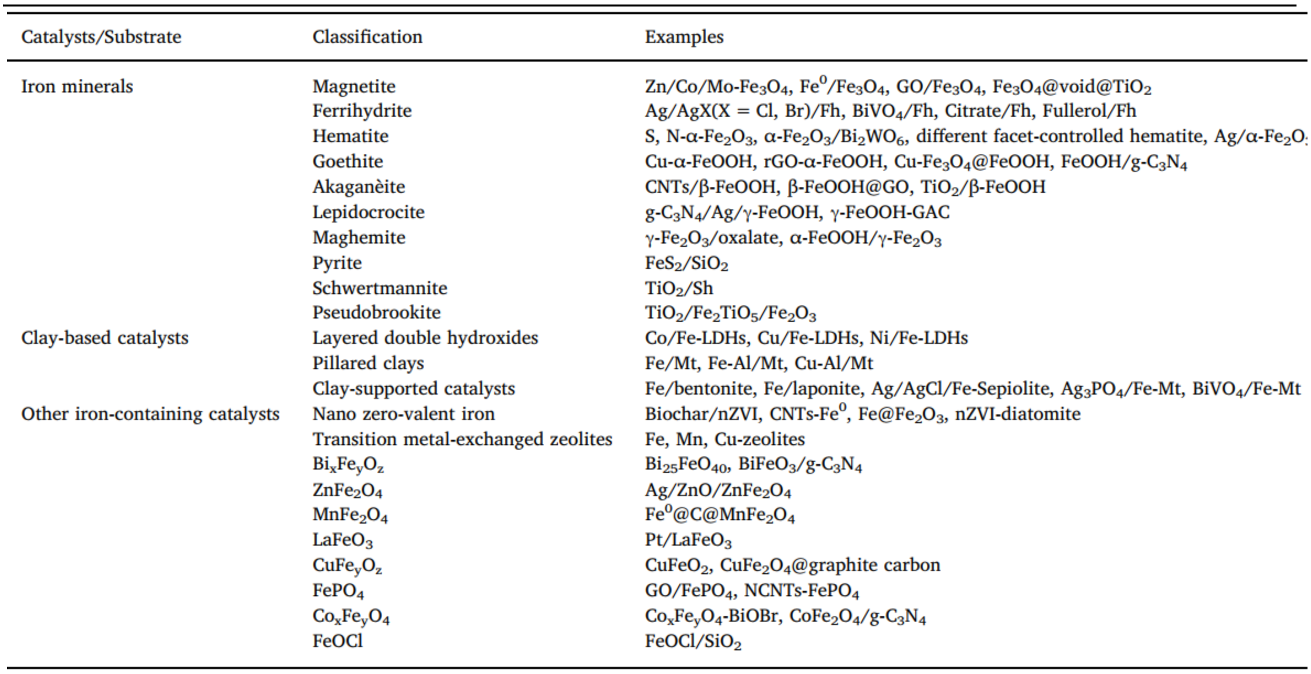
Iron oxides are typically regarded as non-toxic, environmentally benign, and biodegradable. The specific surface area, particle size, morphology, and other characteristics of synthesized materials often determine their physical characteristics, which differ significantly depending on the synthesis methods used. Solvothermal, hydrothermal, thermal decomposition, microemulsion, and co-precipitation are a few of the widely used techniques for the synthesis of iron-based compounds. The literature nowadays lists sixteen pure faces of oxides, hydroxides, and oxy-hydroxides [76,77]. Due to their inexpensive cost, minimal toxicity, strong catalytic activity, and simple recovery techniques, iron-based materials are typically regarded as excellent heterogeneous Fenton catalysts. The ferrous ion is a component of the oxide crystal structure in iron oxide systems. This characteristic reduces ferrous ion leaching from the catalyst by increasing the catalyst's stability with respect to the splitting of H_2O_2 [78]. Among the iron mineral types used as Fenton-catalysts are magnetite, goethite, hematite , schwertmannite, lepidocrocite, and maghemite. Numerous publications exist regarding the use of the iron oxide family of materials for microbial inactivation and wastewater treatment. The catalyst's concentration was 0.6 mg/L Fe^{3+}, and natural water sources typically have iron concentrations on this magnitude. This approach appears to be effective for inactivating bacteria on large scales [78].

3.5.2. Supported materials based on iron

Carbon-based materials, such as graphene oxide (GO), carbon nanotubes (CNTs),,activated carbon (AC) , multi-wall carbon nano-tubes (MWCNTs) as well as silicate substances, such as quartz, zeolite, mesoporous silica, and saponite have been used in heterogeneous Fenton reactions as the support for effective heterogeneous Fenton catalysts because of their inexpensive cost, strong mechanical strength, and outstanding chemical stability. Although, to a much lesser extent, the above materials can also stimulate the active breakdown of H_2O_2. [79]. By improving adsorption, certain supports can concentrate organic molecules close to the catalytic active center of iron oxides, increasing the degradation efficiency [80].

Some recent studies have demonstrated that the fast single electron transfer ability of heterogeneous Fenton catalysts in combination with carbon compounds facilitates the rapid reduction of Fe(III) to Fe(II). Considering their unique chemical characteristics, such as their large surface areas, abundant electrons, functional groups, and strong electrical conductivity, carbon materials have become widely used entities in heterogeneous Fenton reactions within these methodologies, facilitating the Fe(III)/Fe(II) redox cycle. It has been demonstrated that the deliberate addition of iron species to carbonaceous matrices (such as graphene, carbon nanotubes, and activated carbon) greatly increases electrical conductivity and catalytic activity [81-83] .The intrinsic conductivity of the carbon framework, the accessibility of iron active sites, and the synergistic interfacial contacts between the metallic and carbon phases are the main factors that dictate electron transfer pathways in iron-carbon composites, which demonstrate higher catalytic activity.Graphene is a two-dimensional carbon atom monolayer with exceptional mechanical stability, electrical conductivity, and electron mobility. According to reports, graphene supports the Fenton catalyst and improves the Fenton reaction's performance [84]. Therefore, one of the key factors contributing to the increased catalytic efficiency of heterogeneous materials supported by graphene Fenton catalysts are materials similar to graphene that have exceptional electron transport capabilities. **Table 3.4** illustrates the most widely used Fenton catalysts [85].

Table 6. Heterogeneous Fenton catalysts that are commonly utilized [85]



Catalysts/Substrate	Classification	Examples
Iron minerals	Magnetite	Zn/Co/Mo-Fe_3O_4, Fe^0/Fe_3O_4, GO/Fe_3O_4, Fe_3O_4@void@TiO_2
	Ferrihydrite	Ag/AgX(X = Cl, Br)/Fh, $BiVO_4$/Fh, Citrate/Fh, Fullerol/Fh
	Hematite	S, N-α-Fe_2O_3, α-Fe_2O_3/Bi_2WO_6, different facet-controlled hematite, Ag/α-Fe_2O
	Goethite	Cu-α-FeOOH, rGO-α-FeOOH, Cu-Fe_3O_4@FeOOH, FeOOH/g-C_3N_4
	Akaganèite	CNTs/β-FeOOH, β-FeOOH@GO, TiO_2/β-FeOOH
	Lepidocrocite	g-C_3N_4/Ag/γ-FeOOH, γ-FeOOH-GAC
	Maghemite	γ-Fe_2O_3/oxalate, α-FeOOH/γ-Fe_2O_3
	Pyrite	FeS_2/SiO_2
	Schwertmannite	TiO_2/Sh
	Pseudobrookite	TiO_2/Fe_2TiO_5/Fe_2O_3
Clay-based catalysts	Layered double hydroxides	Co/Fe-LDHs, Cu/Fe-LDHs, Ni/Fe-LDHs
	Pillared clays	Fe/Mt, Fe-Al/Mt, Cu-Al/Mt
	Clay-supported catalysts	Fe/bentonite, Fe/laponite, Ag/AgCl/Fe-Sepiolite, Ag_3PO_4/Fe-Mt, $BiVO_4$/Fe-Mt
Other iron-containing catalysts	Nano zero-valent iron	Biochar/nZVI, CNTs-Fe^0, Fe@Fe_2O_3, nZVI-diatomite
	Transition metal-exchanged zeolites	Fe, Mn, Cu-zeolites
	$Bi_xFe_yO_z$	$Bi_{25}FeO_{40}$, $BiFeO_3$/g-C_3N_4
	$ZnFe_2O_4$	Ag/ZnO/$ZnFe_2O_4$
	$MnFe_2O_4$	Fe^0@C@$MnFe_2O_4$
	$LaFeO_3$	Pt/$LaFeO_3$
	$CuFe_yO_z$	$CuFeO_2$, $CuFe_2O_4$@graphite carbon
	$FePO_4$	GO/$FePO_4$, NCNTs-$FePO_4$
	$Co_xFe_yO_4$	$Co_xFe_yO_4$-BiOBr, $CoFe_2O_4$/g-C_3N_4
	FeOCl	FeOCl/SiO_2

The physical and chemical properties that nanomaterials display are strongly correlated with their size and shape. The literature reports on hematite (α-Fe_2O_3) with morphologies such microtubes, nano-rods, and nano-rings. By varying the hydrothermal reaction time, the morphological evolution of hematite was examined. The nanoparticles developed a spherical shape after 6 hours of hydrothermal treatment. Following further heating, burger-like, olive-like, and elliptical shapes were seen at 12, 18, and 24 hours, respectively [86]. Burger-like α-Fe_2O_3 was shown to be stronger than other α-Fe_2O_3 morphologies, where 98% degradation efficiency was noted.

Iron minerals can be added to a variety of supporting materials, including as zeolites, clay, graphene oxide (GO), silica, etc., in addition to being directly used as heterogeneous Fenton catalysts [87]. The physical and chemical properties of nanomaterials are significantly correlated with their size and shape.

4. Conclusions

Among homogenous and heterogeneous AOPs, heterogeneous Fenton reactions are unique because of the catalysts' structural stability, reusability, broad pH range of application, high oxidation efficiency, and cheap operating costs. Utilizing such a potential innovation in the industry will be enhanced by a deeper understanding of reaction mechanisms. In heterogeneous Fenton chemistry, the interfacial electron-transfer process continues to be a fundamental scientific issue. High-valent iron must be directly detected or even quantified, regardless of whether it is present in a freely dissolved or surface-bound state. Magnetic qualities of materials like ferrites, magnetite, and their composites, which make it simple to separate and reuse them after wastewater treatment. The catalytic activity of heterogeneous Fenton catalytic systems can be changed by a variety of supporting materials. Incorporating carbon-based two-dimensional materials and semiconductor nanoparticles with iron minerals to accelerate electron transfer and Fe (II) regeneration has demonstrated potential and is anticipated to garner additional attention in the upcoming years.

When building and implementing heterogeneous Fenton systems, three main factors: the degradation efficiency, the catalyst's reactivity and stability, and the efficiency of H_2O_2 utilization should be taken into account concurrently. A promising heterogeneous Fenton catalyst may have the benefits of strong catalytic reactivity, low H_2O_2 consumption, and superior structural stability since pure iron oxides have severe iron leaching or comparatively moderate catalytic reactivity.

In terms of industrial applications, catalyst recycling and full organic mineralization can be accomplished by combining other treatment methods like filtering and biological treatment. Toxicity tests can also be included to assess Fenton's heterogeneous approach for treating drinking water.

Heterogeneous treatment is a developing method for eliminating microbiological, organic, and inorganic pollutants from water. Given their broad pH range of applicability, little sludge formation, and reusability, heterogeneous catalysts have shown significant promise for commercial applications when compared to the homogeneous Fenton reaction.

A review of the literature on the use of nanoparticle- based Fenton technology reveals that this procedure is crucial for destroying pollutants of rising concern and inactivating pathogenic microorganisms in a variety of wastewater types. Accordingly, including catalysts with good selectivity, synergistic action, and adaptability to treat various source waters and wastewaters contaminated with a variety of pathogenic microorganisms and problematic organic and inorganic pollutants may further improve process performance.

Many factors (pollutant type, wastewater volume, pollutant concentration, ability to recycle and recover valuable materials, local energy sources) influence the choice of treatment technology.

The application of homogeneous Fenton in treating resistant wastewater has continued to be delayed by constraints such as the requirement for acidic conditions, sludge formation, and high chemical inputs. Therefore, addressing these issues continues to be a major area of research in the field of advanced oxidation methods for wastewater treatment. This is seen in processes such as heterogeneous Fenton oxidation.

The majority of studies have been carried out on the laboratory size, lacking sufficient transposition to bigger scales; therefore, there is a necessity of conducting studies on larger operational scales in order to make the findings practical and relevant in industrial settings.

For reactions with different pollutants, the concentrations and ratios of basic chemical substances, such as hydrogen peroxide and catalysts based on the Fe^{2+} ion or other transition metals in heterogeneous arrangements, are currently determined experimentally using rather randomly chosen quantities, necessitating additional optimization studies.

Acknowledgments

The authors of the present article are indebted to Prof. Dr. Ali Abbar at the AL-Khwarizmi College of Engineering for his help and advice for this review.

Nomenclature

AC	activated carbon
AOP	advanced oxidation processes
BOD	biological oxygen demand
BTEX	benzene, toluene, ethylbenzene, and xylene
CNTs	carbon nanotubes
COD	chemical oxygen demand
DOC	dissolved organic carbon
GO	graphene oxide

MWCNTs	multi-wall carbon nano-tubes
O & G	oil and grease
PRWW	petroleum refinery wastewater
SS	suspended solids
TOC	total organic carbon

Conflict of interest

The authors declare no conflict of interest

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