Wastewater Treatment with the Fenton Process
Principles and Applications

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3 Catalysts

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3 Catalysts

The catalyst has a significant role in the heterogeneous Fenton process the type as well as size determine the specific surface area, where the reaction takes place, the number of iron ions, the rate of leaching metallic iron and iron compounds, and the possibility of reusing the catalyst. Compounds such as metal compounds, and materials with carbon in their structure, can be used as catalysts [1]. The most popular ones are iron-based materials due to their highly active and promote decomposition compounds. The type of catalyst can also influence the radical generation, which is dependent on the oxygen deficiency on their surface due to charge exchange and cation deficiency in the compounds, which can react in the process. The sites of oxygen deficiency constitute the active specific surface, where the decomposition of H_2O_2 takes place and the process accelerates. Moreover, iron catalysts are cheap, low toxic, and easy to gather and reuse in the process. Additionally, the catalysts could be used in different configurations, modifications, and structural forms as catalysts do decompose huge types of pollutants in various conditions and parameters of the process (see Table 3.1). One of the significant problems is the deactivation of the catalyst and the leaching of material. However, in the heterogeneous Fenton process, the leaching of Fe^{2+} from the catalyst depends on compounds and the kind of support used in the process. Also, the catalyst can be separated and reused by recycling the material. Moreover, the catalysts have a porous structure, which enables the adsorption of pollutants on their surface. The assessments and properties of iron compounds such as crystallinity [2], surface area [3], and activity are related to the leaching of a metal compound in an acidic environment, which affects the effectiveness of catalyst in heterogeneous Fenton process [4]. Besides, it is also essential to choose the correct dose of the catalyst because too little can be ineffective due to the small surface area in which the process takes place [5]. Zhang *et al.* [6] noted that applying the process with additional catalysts is more effective. They confirmed it by the results of K_{obs} values (observed rate constant), which were 1.68, 0.69, and 0.28 1/h in processes ZVI/ethylenediaminetetraacetic acid/air, ZVI/Air, and ZVI/ethylenediamine-N,N'-disuccinic acid/air, respectively. The catalysts can be modified and used in various combinations by altering their structure, contributing to the increased adsorption and degradation of organic pollutants [7]. To increase the magnetite adsorption capacity and introduce other transition metals into their structure scientists used chelating agents, pillar clays, activated carbon, especially carbon-containing materials [8], carbon xerogels [9], carbon nanotubes, foam, and graphite; and alumina support [10,11]. Catalysts differ in their physical, chemical, and reactive properties. Scientists divided them into five categories: zero-value iron, iron minerals, iron oxides (hydrogen), multi-metals, iron-based materials, and supported iron-based materials [12].

TABLE 3.1

The Types of the Catalysts and Their Efficiency in the Heterogenous Fenton Process in Various Parameters and Conditions

Ref.	Brief Description of the Experiment	Catalysts and Other Process Reagents	Industry/Type of Pollution	Pollution Parameters	Analysis of Catalysts	Reagent Doses and Process Parameters	Optimal Conditions	Process Efficiency (Decrease in Parameters)
[104]	Decolorization and mineralization of textile wastewater in a heterogeneous Fenton like system with/ without ultrasound and ultraviolet	ZVI (Zero Valent Iron)	Reactive Black 5 (RB5) EDTA	RB5 = 100 mg/L EDTA = 0,4 mM	HPLC, IC, UV-vis, pH meter, TOC analyzer	pH = 2.0, 3.0, 4.0, 7.0 Time = 0-180 min EDTA = 0.1, 0.4, 1.0, 5.0 mM ZVI = 1, 5, 25, 50 g/L	pH = 7.0 Time = 180 min EDTA = 0.1 – 1.0 mM ZVI = 25 g/L	RB5 = 100%, EDTA = 96.5% TOC = 68.6% COD = 92.2%
[6]	Removal of 2,4-dichlorophenol from contaminated soil by a heterogeneous ZVI/EDTA/Air Fenton-like system	ZVI/EDTA/Air ZVI/Air ZVI/EDDS/Air	2,4-dichlorophenol from contaminated soil	20 g	HPLC, IC, XCT ion trap, ART-FTIR, atomic absorbing spectrometer, pH meter, dissolved oxygen meter	Time = 0, 15, 30, 45, 60, 90, 120, 180 min EDTA = 0.2, 0.4, 0.75, 1.6, 2.0 mmol/L ZVI = 2.5, 7.5, 12.5 g/L Air = 0.5, 1.0, 2.0 L/min	Time = 45 min/L EDTA = 0.4 mmol/L ZVI = 7.5 g/L Air = 1.0 L/min	96% 2,4-DCP = 96% degradation
[5]	Heterogeneous Fenton Process using the mineral hematite for discoloration of a reactive dye solution	Hematite	Drimarene Red X-6BN (C.I. Reactive Red 243)	100 mg/L	UV-VIS, atomic absorption spectrometry, colorimetric method, BET	pH = 2.5, 3.5, 5.0 Time = 0, 20, 40, 60, 80, 100, 120 min H_2O_2 = 0, 200, 500, 800 mg/L Hematite = 1, 5, 10, 20 g/L Temp = 25, 35, 45, 55°C	pH = 2.5 Time = 120 min H_2O_2 = 800 mg/L Hematite = 20 g/L Temp = 25	Reactive Red 243 = 99% degradation

Ref	Description	Catalyst	Pollutant	Concentration	Analysis	Parameters	Optimum conditions	Results
[105]	Heterogeneous Fenton-type processes for the degradation of organic dye pollutants in water — The application of zeolite-assisted AOPs	$FeZSM_5/H_2O_2$, $UV/FeZSM_5/$ H_2O_2, UV, UV/ $FeZSM_5$, UV/ Fe^{3+}, UV/ H_2O_2,	RB137 (C.I. Reactive Blue 137	20 mg/L in 0.5 L	FTIR spectroframs, IC-MSP analyses	Time = 0, 2, 5, 10, 20, 30, 40, 50, 60 min pH = 2.0–8.0 ZSM_5 = 0.745 i 1.49 g/L Fe = 0, 5, 1.0 mM H_2O_2 = 10 mM	$UV/FeZSM_5/H_2O_2$ $FeZSM_5$ = 1.49 g/L H_2O_2 = 10 mM pH = 6	TOC = 81.1% RB 137 = 100%
[95]	Graphene-modified iron sludge derived from an efficient heterogeneous Fenton catalyst for degradation of organic pollutant	Iron sludge with a low amount (0–2 wt%) of graphene	Rhodamine B, 23 acid red G, metronidazole	10 mg/L	XRD, FESEM, TEM, Raman, XPS, BET, FTIR UV-vis	pH = 3.03, 6.01, 9.44 Fe-G = 0.2, 0.5, 1.0 g/L H_2O_2 = 0, 1, 5, 10 mmol/L	pH = 3.03 Fe-G = 1 g/L H_2O_2 = 10 mmol/L	Rhodamine B = 99.0% 23 acid red G = 98.5% Metronidazole = 91.8%
[96]	Heterogeneous Electro-Fenton Using Modified Iron-carbon as Catalyst for 2,4-dichlorophenol	Fe-C catalyst	2,4-dichlorophenol (2,4-DCP)	2,4-DCP = 120 mg/L TOC = 81 I 277 mg/L	FE-SEM, XPS, XRD, HPLC, TOC analyzer, ion chromatography	Time = 0–120 min Current = 50–200 mA Fe-C = 2–6 g/L pH = 3.0, 5.0, 6.0, 7.0, 9.0	pH = 2.72 Fe-C = 6 g/L Current = 100 mA Time = 120	2,4-DCP = 100% degradation TOC = 47.3%
[136]	Azo-dye Orange II degradation by heterogeneous Fenton-like reaction	Fe-supports: an activated carbon and a carbon aerogel.	Azo dye Orange II (OII)	0.2 L of a 0.1 mM	SEM, HRTEM, XRD, XPS, BET, FTIR, UV-Vis	H_2O_2 = 3–48 mM M-Fe/H-Fe = 0.15, 0.20, 0.30 g/L pH = 2.0–4.0 T = 10–70°C	T = 30°C, pH = 3.0 H_2O_2 = 6 mM M-Fe/H-Fe = 91.5 mg/L	For M-Fe OII = 94.6%
[144]	Heterogeneous photo-Fenton processes using zero-valent iron microspheres for the treatment of wastewater contaminated with 1,4-dioxane	Zero Valent Iron (Fe^0) microsphere	1,4-Dioxane	COD = 450 mg/L; alkalinity = 900 mgCaCO3/L; conductivity = 810 IS/cm; 1,4 dioxane = 248 mg/L	SEM, EDS, BASF, TOC/TN, GC	H_2O_2/COD = 1.625, 2.125, 2.625 4.00 pH = 2.8; 7.0, 8.2 H_2O_2/Fe^0 = 1, 15, 30, 60	H_2O_2/COD = 2.625 pH=2.8 H_2O_2/Fe^0 = 60	TOC = 94% ChZT = 99% and 60%

TABLE 3.1 (Continued)
The Types of the Catalysts and Their Efficiency in the Heterogenous Fenton Process in Various Parameters and Conditions

Ref.	Brief Description of the Experiment	Catalysts and Other Process Reagents	Industry/Type of Pollution	Pollution Parameters	Analysis of Catalysts	Reagent Doses and Process Parameters	Optimal Conditions	Process Efficiency (Decrease in Parameters)
[28]	Continuous-flow heterogeneous electro-Fenton reactor for Tartrazine degradation	Iron-carbon granules	Tartrazine	40, 60, 80, 100 mg /L,	TOC, spectrophotometer	Fe-C = 86, 120, 160, 195 g; Time = 0–30 min; pH = 3.0, 5.0, 7.0, 9.0; H_2O_2 = 0.05, 3.0, 20.0 mL/min; The flow of pollutant = 10, 15, 20, 30 mL/min	The flow of pollutant = 20 mL/min; pH = 3.0; Fe-C = 160 g; H_2O_2 = 20 mg/L	Tartrazine = 80% degradation; TOC = 30%
[86]	Fabrication of magnetic carbon composites from peanut shells and its application as a heterogeneous Fenton catalyst in the removal of methylene blue	Magnetic carbon composites from peanut shells (PMC-1, PMC-2, PMC-3 + $K_2S_2O_8$), $FeCl_2$ + $K_2S_2O_8$, Fe_3O_4 + $K_2S_2O_8$	Methylene blue	5, 10, 20, 25, 35 mg/L	LC-MS, MÖssbauer spectroscopy, XPS, SEM, XRD, the Brunauer-Emmett-Teller surface area method, BET, VSM analyses,	$K_2S_2O_8$ = 0.1, 0.25, 0.5, 0.8, 1.0 g/L; pH = 3.0, 4.0, 5.0, 6.0, 8.0; Catalyst = 10, 20, 40, 60, 80 mg	$K_2S_2O_8$ = 1 g/L; pH = 3.0; Catalyst = 60 mg	PMC-2 + K2S2O8 degradation 90% dye
[87]	Novel magnetic porous carbon spheres derived from the chelating resin as a heterogeneous Fenton catalyst for the removal of methylene blue from aqueous solution	Porous magnetic carbon spheres (MCS) pore-size-distribution curves the MCS-500, MCS-800, MCS-1100	Methylene blue	20 ml, 40 mg/L	X-ray diffraction, MÖssbauer spectroscopy, Raman spectroscopy, XRS, Brunauer–Emmett–Teller surface area method, SEM, VSM, LC-MS,	NH_2OH = 2.5, 5.0, 10.0 mmol/L, H_2O_2 = 1.5, 2.5, 5.0 mmol; pH = 3.76, 5.14, 7.08; Catalyst = 10, 20, 30 g	H_2O_2= 5.0 mmol/L; NH_2OH = 2.5 mmol/L; pH = 3.76; Catalyst = 20 g	100% degradation dye (40 mg/L MB)

Ref	Description	Water	Concentration	Analysis	Conditions	Optimal conditions	Results
[91]	Niobium substituted magnetite as a strong heterogeneous Fenton the catalyst for wastewater treatment	$Fe_{3-x}Nb_xO_4$ (x = 0.0, 0.022, 0.049, 0.099, 0.19)	Methylene blue	12.5, 50, 75 i 100 mg/L	XRD, BET surface area, TEM, VSM, XPS, chemical experiments, SCA	$Fe_{3-x}Nb_xO_4$ (x = 0.0, 0.022, 0.049, 0.099, and 0.19), Time = 30–180 min, pH = 4.0, 7.0, 8.0, 10.0	$Fe_{3-x}Nb_xO_4$ series, x = 0.19 Time = 180 min pH = 7.0, 10.0	Degradation = 100% degradation dye
[145]	Treatment of textile wastewater by heterogeneous Fenton process using a new composite Fe_2O_3/carbon	Composite Fe_2O_3/carbon	Textile wastewater	Dye = 100–300 g/L COD = 1000 mg/L BOD_5 = 300 mg/L	BET, SEM/EDAX, PZC	Catalyst = 100–300 g/L H_2O_2 = 500–1000 mg/L pH = 3.0–9.0	Catalyst = 300 g/L H_2O_2 = 500 mg/L pH = 3.0	COD = 71%
[146]	Industrial wastewater treatment using hydrodynamic cavitation and heterogeneous Fenton processing	Zero valent iron (ZVI)	Industrial wastewater	ChZT = 42,000 mg/L TOC = 14,000 mg/L.	TOC analyzer	Hydrocavitator pressure = 500, 1000, 1500 psi	Hydrocavitator pressure = 1500 psi	TOC = 60%
[147]	Three-dimensional heterogeneous electro-Fenton oxidation of biologically pretreated coal gasification wastewater using sludge derived carbon as catalytic particle electrodes and catalyst	CPEs (SAC-Fe, SAC, CAC, Fe_3O_4 MNPs) were filled into real pure Fe_3O_4 magnetic nanoparticles (MNPs);	Biologically pretreated coal gasification wastewater	ChZT = 173.3 ± 14.1 mg/L TOC = 57.6 ± 4.2 mg/L BZT_5 = 14.6 ± 4.1 mg/L Total fenols = 48.3 ± 3.3 mg/L	BET, zeta potential analyzer, plasma atomic absorption spectrophotometry, SEM, XRF, XRD, FTIR, TOC analyzer, GC-MS, ESR	pH = 2.0, 3.0, 5.0, 7.0 Catalyst = 2.5, 5.0, 7.5, 10.0 g/L Current density = 10, 15, 20, 25 mA/cm^2	pH = 3.0 Catalyst = 2.5–10 g/L Current dentisity = 25 mA/cm^2	Total fenols = 78.1%, TOC = 93.5%, COD = 78.1%

TABLE 3.1 (Continued)
The Types of the Catalysts and Their Efficiency in the Heterogenous Fenton Process in Various Parameters and Conditions

Ref.	Brief Description of the Experiment	Catalysts and Other Process Reagents	Industry/Type of Pollution	Pollution Parameters	Analysis of Catalysts	Reagent Doses and Process Parameters	Optimal Conditions	Process Efficiency (Decrease in Parameters)
[148]	Heterogeneous photo-Fenton oxidation of acid orange II over iron-sewage sludge-derived carbon under visible irradiation	sewage sludge derived carbon (SC) employed as the support of iron oxide-containing catalyst (FeSC)	Acid orange II (AOII)	100 mg/L	inorganic elemental composition, XRD, SEM and TGA-FTIR, UV–vis	Catalyst = 0.5, 1.0, 1.5, 2, g/L; pH = 3.0, 4.0, 5.0	Catalyst = 1.5 g/L pH = 4.0	Decolorization = 100%
[149]	Treatment of textile wastewater by homogeneous and heterogeneous Fenton oxidation processes	Mesoporous Activated Carbon (MAC) with ferrite iron	Textile wastewater	COD = 564 mg/L BOD = 120 mg/L TOC = 144 mg/L Total solids = 7,508 mg/L Oxidation-reduction potencial = +525 mV Total dissolved solids = 7,148 mg/L Total suspended solids = 360 mg/L Chloride = 1749 mg/L Sulfate = 1,605 mg/L Ammonia = 8.4 mg/L TKN=16.2 mg/L Sulfacant =	FT-IR, UV–Visible spectroscopy, cyclic voltammetry, XRD, Diffuse Reflectance Spectroscopy	pH = 2.5, 3.5, 4.5, 5.5, 7.0 H$_2$O$_2$ = 3, 6, 9, 12,15 mM/L FeSO$_4$ = 0.4, 0.8, 1.0, 1.4,1.8 mM/L Catalys t = 2, 5, 7,5, 10, 15, 20, 25 g/L	pH = 3.5 H$_2$O$_2$ = 9–16 mM/L Catalyst = 10 g/L FeSO$_4$ = 0,8-1,8 mM/L	COD = 51 mg/L, BOD = 20 mg/L, TOC = 25 mg/L, Total solids = 7028 mg/L, Oxidation reduction potencial = +525 mV, Total dissolved solids = 6752 mg/L, Total suspended solids = 276 mg/L, chloride = 1582 mg/L, sulfate = 1281 mg/L, ammonia = 0

Ref	Title	Catalyst	Wastewater	Characteristics	Analysis	Operating conditions	Optimal conditions	Results
				9.71 mg/L Total hardness 400 Ca = 60 mg/L Volatile dissolved solids = 1,064 mg/L				mg/L, TKN = 6,0 mg/L, surfactant = 1,53 mg/L, total hardness 260, Ca = 46 mg/L, volatile dissolved solids = 0,347 mg/L
[150]	A Comparative Study of Homogeneous and Heterogeneous Photo-Fenton Process for Textile Wastewater Treatment	Copper Modified Iron Oxide	Textil wastewater	$COD = 780$ mg/L $BOD = 198$ mg/L $TSS = 48$ mg/L $TDS = 2,603$ mg/L Alkalinity = 700 mg/L	UV–Vis spectrophotometer	pH = 2.0, 3.0, 4.0, 5.0, Catalyst = 5, 10, 15, 20 mg/L $H_2O_2 = 50, 100, 150, 200$ mM UV power = 0, 8, 16, 24 W	pH = 3.0 Catalyst = 10 mg/L $H_2O_2 = 150$ mM UV = 16 W	COD removal of 62% and Dye removal of 85%
[151]	Application of heterogeneous photo-Fenton process for the mineralization of imidacloprid containing wastewater	Waste iron oxide	The imidacloprid-containing wastewater	0.58 g/L	XRD, TOC analyzer,	Time = 0–360 min pH = 3.0, 3.5, 4.0, 5.0 $H_2O_2 = 26.3, 52.5, 105.0, 125.5, 157.5$ mM Catalyst=1.0, 2.0, 5.0, 10.0 g/L^{-1}	Time = 6 h pH = 3.5 $H_2O_2 = 105.0$ mM Catalyst = from 1.0 to 5.0 g/L	97.7% = TOC
[152]	Photo-assisted heterogeneous Fenton-like process for treatment of PNP wastewater	$Fe-Ce/Al_2O_3$	The sodium salt of p-nitrophenol (PNP)	200 mg/L	SEM, BET	$H_2O_2 = 50, 75, 100, 150, 200$ mmol/L Catalyst = 30, 50, 100, 200, 300 g/L, pH = 3.0, 4.0, 5.0, 6.0, 7.0, 8.0, T = 15, 25, 35, 45, 55, 65, 75°C Time = 15, 30, 45, 60, 75, 90 min.	$H_2O_2 = 1.15$ mmol Catalyst = 10 g Fe-Ce/Al2O3, pH = 4 Temperature = 25°C, Time = 120 min	PNP = 98.7% COD = 72.9%

(Continued)

TABLE 3.1 (Continued)

The Types of the Catalysts and Their Efficiency in the Heterogenous Fenton Process in Various Parameters and Conditions

Ref.	Brief Description of the Experiment	Catalysts and Other Process Reagents	Industry/Type of Pollution	Pollution Parameters	Analysis of Catalysts	Reagent Doses and Process Parameters	Optimal Conditions	Process Efficiency (Decrease in Parameters)
[153]	Treatment of synthetic textile wastewater by homogeneous and heterogeneous photo-Fenton oxidation	Zero vailent iron (ZVI)	Remazol Red RR	100 mg/L	UV–vis spectrophotometer, lab kits LCK, LCI 500, LASA 100 spectrophotometer,	Catalyst = 0.25, 1, 3, 5 mM H_2O_2 = 1, 3, 10, 12, 15, 29 mM Time = 0–8 h	Catalyst = 0.25 mM H_2O_2 = 12–20 mM Time = 8 h	COD = 93%
[154]	Treatment of Actual Chemical Wastewater by a Heterogeneous Fenton Process Using Natural Pyrite	Pyrite FeS_2, Zero vailent iron (ZVI), Magnetite	Chemical wastewater	COD = 7500–8000 mg/L BOD_5/COD = 0.1 TOC = 2000 mg/L	excitation-emission matrix (EEM) analysis, BET, three-dimensional fluorescence	Catalyst = 5, 10, 20, 50 g/L, H_2O_2 = 1, 2, 5, 10, 50, 100 mmol/L pH = 1.8, 3.7 Time = 0–120 min	Catalyst = 10 g/L H_2O_2 = 50 mmol/L pH = 1.8 does 7. Time = 120 min	COD reduction of 36%
[155]	In-situ heterogeneous via photocatalysis-Fenton reaction with enriched photocatalytic performance for removal of complex wastewater	Fe-g-C_3N_4, M-Fe-g-C_3N_4 (Fe-doped g-C_3N_4)	Coking wastewater	COD =64.6 mg/L TOC = 25.3 mg/L	XRD, FE-SEM, FTIR, XPS, UV-vis, TEM, ZETA potential and nanoparticle size analyzer, LCMS, spectrometer,three-electrode quartz cell, atomic absorption spectrophotometer, HPLC, TOC analyzer	Catalyst = 1.5, 3.0 g/L H_2O_2 = 8, 16, 20 mM	Catalyst = 1.5 g/L H_2O_2 = 8 mM	COD = 57.2% TOC = 76.1%

Ref.	Study	Catalyst	Pollutant	Concentration	Analytical methods	Parameters studied	Optimal conditions	Result
[108]	Heterogeneous Fenton process using steel industry wastes for methyl orange degradation	Steel industry wast (diffraction as magnetite Fe_3O_4, hematite Fe_2O_3, and wuestite).	Orange II	20 mg/L	XRD, atomic absorption spectrometer, UV–vis spectrophotometer	pH = 2.0, 3.0, 4.0, 5.0 H_2O_2 = 12, 24, 48, 68 mM Catalyst = 50, 100, 200, 250 mg/L Time = 15, 30, 45, 60, 90, 120 min	pH = 2.0 H_2O_2 = 34 mM Catalyst = 200 mg/L Time = 120 min	Orange II = 98% degradation
[99]	Hydroxamic acid mediated heterogeneous Fenton-like catalysts for the efficient removal of textile wastewater	iIron-Hpo ligand catalyst supported on granular activated carbon (GAC) HpOFe-GAC, HqFe-GAC and FeCit-GAC	Acid Red 88	30, 50, 70, 90 μM	UV–vis absorption spectra, atomic absorption spectroscopy (AAS), SEM, EDS,	Catalyst = 2.5, 5, 7.5, and 10 g/L H_2O_2 = 40 mM pH = 3.0, 5.0, 7.0, 9.0, 11.0 Temperature = 30, 40, 50, 60°C Time = 10, 20, 30, 40, 50, 60 min	Catalyst = 5 g/L, H_2O_2 = 40 mM pH = 7.0 Temperature = 50°C, Time = 60 min	Acid Red = 99.8% degradation
[102]	Removing organic contaminants with bifunctional iron-modified rectorite as efficient adsorbent and visible light photo-Fenton catalyst	Iron-modified rectorite (FeR)	Rhodamine B	80 mM	TOC analyzer, atomic absorption spectroscopy (AAS), UV–vis spectrophotometer, FTIR–ATR, ESR, XRD, XPS, SEM, BET, HRTEM	pH = 2.0, 4.0, 6.0, 8.0, 10.0 H_2O_2 = 2, 4, 6, 8, 10 mM FeR-B = 0.2, 0.4 g/L Time = 2, 4, 6 h	pH = 4.5 H_2O_2 = 6.0 mM FeR = 0.4 g/L Time = 6 h	Rhodamine B = 99% degradation
[156]	Influence of Operational Parameters in the Heterogeneous PhotoFenton Discoloration of Wastewaters in the Presence of an IronPillared Clay	Iron-pillared Tunisian clay (Fe-PILC)	Congo Red	230 mg/L	XRF, XRD, BET, FTIR methods, SEM, IR spectroscopy, UV–vis spectroscopy	Catalyst = 0.2, 0.4, 0.6, 0.8, 1.0, 1.2 g/L H_2O_2 = 100, 200, 300, 400 mg/L pH = 2.0, 4.0, 6.0, 8.0 Time = 10, 20, 30, 40, 50, 60 min	Catalyst = 0.3 g/L, H_2O_2 = 200 mg/L pH = 3.0 Time = 60 min	Congo Red = 100% degradation

(Continued)

TABLE 3.1 (Continued)
The Types of the Catalysts and Their Efficiency in the Heterogenous Fenton Process in Various Parameters and Conditions

Ref.	Brief Description of the Experiment	Catalysts and Other Process Reagents	Industry/Type of Pollution	Pollution Parameters	Analysis of Catalysts	Reagent Doses and Process Parameters	Optimal Conditions	Process Efficiency (Decrease in Parameters)
[157]	Degradation of Methylene Blue by Heterogeneous Fenton Reaction Using Titanomagnetite at Neutral pH Values	Titanomagnetite, magnetite	Methylene Blue	100 mg/L	SEM, XRD, Mossbauer spectroscopy, BET, gas sorption analyzer, FTIR, UV-vis	Titanomgnetite = 0.5, 1.0, 2.0, 3.0 g/L, H_2O_2 = 0.075, 0.15, 0.30, 0.45 mol/L	Titanomagnetite = 1 g/L, H_2O_2 = 0.3 mol/L	Methylene blue = 100% degradtion
[110]	Degradation of mixed dye via heterogeneous Fenton process: Studies of calcination, toxicity evaluation, and kinetics	Iron was impregnated in black soil (Fe-BS)	The mixture of Azure B and Congo red	200 mL	FTIR, XRD, UV-Vis spectroscopy	H_2O_2 = 0.1, 0.2, 0.3, 0.4, 0.5 ml Catalyst = 2, 4, 6, 8% iron loaded into the black soil (0.1, 0.2, 0.3, 0.4 g) pH = 2.0, 3.0, 4.0, 5.0	H_2O_2 = 0.4 mL Catalyst = 0.3 g dose of 8% Fe Temperature = 150°C pH = 5.0	Degradation = 99,82%
[98]	Efficient degradation of tetracycline by a heterogeneous electro-Fenton process using Cu-doped Fe@Fe$_2$O$_3$	Cu-doped Fe@ Fe$_2$O$_3$	Tetracycline	20 mg/L	SEM, TEM, XRD, XPS, EDX, STEM, UV-visible spectrophotometer, HPLC-MS, TOC analyzer, ICP-OES, high-performance liquid-chromatography	Time = 20, 40, 60, 80, 100, 120 min pH = 3.0, 5.0, 7.0 Cu-doped Cu/Fe mass ratio = 5, 10, 30, 50, 60%	Time = 120 min pH = 3.0 Ratio = 50 wt% Cu and 0.1 L/min aeration rate	98.1% degradation (2 h) mineralization efficiency of TC 89.8% after 6 h

Ref	Title	Catalyst	Pollutant	Analytical methods	Conditions	Optimal conditions	Results
[158]	Treatment of pharmaceutical wastewater by heterogeneous Fenton process: an innovative approach	ZnO nanoparticles	Pharmaceutical wastewater 100 mg/L norfloxacin	TEM, UV-vis spectrophotometer, SPR, XRD, SEM, UV-vis measurements, LC-MS	Time = 20, 40, 60, 80, 100, 120 min H_2O_2 = 50, 100, 200, 300, 400, 500 mg/L ZnO = 0, 10, 20, 30, 40, 50 mg/L pH = 2.0, 4.0, 6.0, 8.0, 10.0, 12.0	Time = 120 min H_2O_2 = 300 mg/L ZnO = 30 mg/L pH = 10.0	Norfloxacin = 98% degradation
[159]	High-efficiency heterogeneous Fenton-like catalyst biochar modified $CuFeO_2$ for the degradation of tetracycline	Biochar modified $CuFeO_2$	Tetracycline 20 mg/L	XRD, SEM, EDX, SAED, HRTEM, FTIR, XPS, BET, HPLC	H_2O_2 = 5, 10, 20, 50, 80, 100 mM Catalyst = 50, 100, 200, 500, 800, 1000 mg/L pH = 3.0, 5.0, 7.0, 9.0, 11.0	H_2O_2 = 50 mM Catalyst = 500 mg/L pH=5.0	Tetracycline = 89.12% degradation
[160]	Remediation of organic arsenic contaminants with heterogeneous Fenton process	SiO_2-coated nano zero-valent iron	p-Arsanilic acid (p-ASA) 10 mg/L	UPLC, GC-MS, ICP-MS, LiquiTOC trace, EPR, XRD, XPS	pH = 2.0, 3.0, 4.0, 5.0, 6.0, 7.0 Time = 10, 20, 30, 40, 50, 60 min	pH = 3.0 Time = 60 min	99.6% degradation of p-ASA
[161]	Application of Mineral Iron-Based Natural Catalysts in Electro-Fenton Process: A Comparative Study	Four natural catalysts, namely ilmenite ($FeTiO_3$), pyrite (FeS_2), chromite ($FeCr_2O_4$), and chalcopyrite ($CuFeS_2$)	Cefazolin antibiotic (CFZ) 0.2 mM	XRD, RAMAN, HEF	I = 50, 100, 200, 400, 500 mA, Catalyst = 0.5, 1, 2 g/L	I = 200 mA Catalyst = 1 g/L	Degradation = 100%
[162]	Magnetite and Hematite in Advanced Oxidation	$Fe_2O_3/Fe^0/$ H_2O_2, $Fe_3O_4/$ Fe^0/H_2O_2, light/$Fe_2O_3/$	Cosmetic wastewater TOC = 146.4 mg/L COD = 819 mg/L BOD = 102 mg/L	TOC analyzer, HS-SPME-GC-MS, mass spectrometer, ChromaTOF software	H_2O_2/COD = 0.5:1, 1:1, 2:1, 4:1 Time = 15, 30, 60, 120 min	H_2O_2/COD = 0.5:1, 1:1, 2:1, 4:1 Time = 120 min Catalyst = Fe^0/Fe_3O_4	COD = 74.5 BOD_5 = 12 mg/L TOC = 69% removal

(Continued)

TABLE 3.1 (Continued)
The Types of the Catalysts and Their Efficiency in the Heterogenous Fenton Process in Various Parameters and Conditions

Ref.	Brief Description of the Experiment	Catalysts and Other Process Reagents	Industry/Type of Pollution	Pollution Parameters	Analysis of Catalysts	Reagent Doses and Process Parameters	Optimal Conditions	Process Efficiency (Decrease in Parameters)
	Processes Application for Cosmetic Wastewater Treatment	Fe0/ H_2O_2, light/Fe_3O_4/ Fe0/ H_2O_2				Catalyst = Fe_2O_3/Fe0/ H_2O_2, Fe_3O_4/Fe0/ H_2O_2, light/Fe_2O_3/ Fe0/ H_2O_2, or light/ Fe_3O_4/Fe0/ H_2O_2 = 25/75, 50/50, 75/25, 0/100, 100/0 mg/ L with and without light	= 75/25 mg/L with light	
[45]	Magnetite, Hematite, and Zero-Valent Iron as Co-Catalysts in Advanced Oxidation Processes Application for Cosmetic Wastewater Treatment	Fe_3O_4/ Fe_2O_3/Fe0	Cosmetic wastewater	TOC = 306.3 mg/L	TOC analyzer, HS-SPME–GC–MS	H_2O_2/COD = 1:1, 2:1, Time = 15, 30, 60, 120 min Catalyst: UV/ H_2O_2/ Fe_2O_4/Fe_2O_3/Fe0 and the H_2O_2/Fe_3O_4/ Fe_2O_3/Fe0 (500/500/ 3000, 1500/1500/ 1000, 500/500/1000, 125/125/750/ 375/ 375/250, 1000/1000/ 2000, 250/250/1500, 750/750/500, 250/ 250/500) pH = 2.0, 3.0, 4.0, 5.0, 6.0	H_2O_2/COD = 1:1 Time = 120 min Catalyst: 500/500/ 1000 mg/L Fe_3O_4/ Fe_2O_3/Fe0 pH = 3.0	TOC = 134.1 mg/ L (56.2%)
[163]	Insights into the novel application of Fe-MOFs in ultrasound-assisted heterogeneous Fenton system	Fe-MOFs (MIL-53, MIL-88B and MIL-101)	Tetracycline hydrochloride	10 mg/L	XRD, FTIR, SEM, XPS, N_2 sorption-desorption isotherms and CO-FTIR, BET, TOC analyzer, ICP, UV-vis spectrometer, EPR	US power = 40, 60, 80, 100 W Catalyst = 0.2, 0.3, 0.4 g/L H_2O_2 = 22, 44, 88 mM pH = 5.0, 7.0, 9.0, 11.0	US Power = 60 W Catalyst = 0.3 g/L H_2O_2 = 44 mM pH = 5.0–11.0 (efficiency not change)	TOC = 42.5% (after 7 minutes) for MIL.88B

Ref	Title	Catalyst	Pollutant	Concentration	Analysis	Conditions	Results
[164]	Decolorization of wastewater by heterogeneous Fenton reaction using MnO_2-Fe_3O_4/CuO hybrid catalysts	MnO_2-Fe_3O_4/CuO hybrid, Fe_3O_4/CuO	Methylene blue		XRD, EDS, FE-SEM, and BET techniques	H_2O_2 = 2, 4, 8, 16, 32 mmol/L, pH = 2.0, 4.0, 5.0, 7.0, 9.5, 12.0 Catalyst = 10, 25, 50, 75, 100 mg/L; H_2O_2 = 16/32 mmol/L, pH = 2.0/4.0, Catalyst = 10 mg/L	Methylene blue = 90% degradation for MnO_2-Fe_3O_4/CuO
[165]	Decolorization and mineralization of commercial reactive dyes by using homogeneous and heterogeneous Fenton and UV/Fenton processes	Fe^{2+} and Fe^0 concentrations, Fe^{2+}, Fe^0	Reactive Yellow 3 (RY3), C.I. Reactive Blue 2 (RB2), and C.I. Reactive Violet 2 (RV2)	100 mg/L	UV-vis Spectrophotometer, TOC analyzer	$FeSO_4 \cdot 7H_2O$ = 0.2, 0.5, 1.0, 2.0 mM H_2O_2 = 2.5, 5, 10, 20, 50 mM Fe^{2+}/H_2O_2 = 1/5, 1/10, 1/20, 1/40, 1/100 Fe^0/H_2O_2 = 1/0.2, 1/ 0.4, 1/2, 1/20, 1/200 H_2O_2 (on mineralization) = 0.01, 0.1, 1.0, 5.0, 10.0 mM Fe^0 = 0.1, 0.2, 0.4, 1.0, 2.0 mM Time = 0, 5, 10, 30, 40, 60, 70, 90 min; Fe^{2+}/H_2O_2 = 0.5 mM/ 20 mM Fe^0/H_2O_2 = 2 mM/ 1 mM	TOC = 78-84% Decolourization = 95-100%

DIVISION OF CATALYSTS IN THE FENTON PROCESS

In the heterogeneous Fenton process, iron catalysts are used to promote the oxidation of organic compounds in contaminated water and soil. Several different kinds of iron catalysts can be used in this process, including:

- Iron oxides: Iron oxides, such as goethite, hematite, and magnetite, are naturally occurring minerals that can act as catalysts in the Fenton reaction. These minerals are often found in iron-containing soils, and their high surface area and reactivity make them effective catalysts for the oxidation of organic pollutants.
- Iron-modified zeolites: Zeolites are porous materials that can be modified with iron ions to create an effective catalyst for the Fenton reaction. Iron-modified zeolites have a high surface area and reactivity and can be tailored to optimize their catalytic properties for specific applications.
- Iron-doped carbon materials: Carbon materials, such as activated carbon or carbon nanotubes, can be doped with iron ions to create a catalyst for the Fenton reaction. Iron-doped carbon materials have a high surface area and reactivity and can be easily synthesized and tailored to optimize their catalytic properties.
- Iron-based nanoparticles: Iron-based nanoparticles, such as zero-valent iron (ZVI) or iron oxide nanoparticles, can be used as catalysts in the Fenton reaction. These nanoparticles have a high surface area and reactivity and can be easily dispersed in water or soil for effective treatment of contaminated sites.
- Iron-based waste materials: Waste materials, such as blast furnace slag or steel slags, can be used as catalysts in the Fenton reaction. These materials contain high levels of iron, and their use as catalysts can provide an economical and environmentally friendly solution for the treatment of contaminated water and soil.

The choice of iron catalyst depends on several factors, including the type and concentration of contaminants present in the water or soil, the pH and temperature of the system, and the desired reaction rate and efficiency. Further research is needed to better understand the properties and limitations of different types of iron catalysts in the heterogeneous Fenton process and to develop methods for optimizing their use in environmental remediation [13].

ZERO-VALENT IRON

Zero-valent iron (ZVI) is a form of iron that has a high reactivity due to the lack of valence electrons in its outer shell. ZVI is often used as a catalyst in environmental remediation applications, including the treatment of contaminated water and soil.

When ZVI is used as a catalyst in the Fenton reaction, it can promote the oxidation of organic contaminants in water and soil by generating hydroxyl radicals. ZVI can also be used as a reducing agent to convert contaminants, such as heavy

metals or chlorinated solvents, into less toxic or non-toxic forms through a process called reductive dechlorination. ZVI is often used in permeable reactive barriers (PRBs), which are barriers made of a reactive material, such as ZVI, placed in the subsurface to intercept and treat contaminated groundwater as it flows through. The PRB allows the contaminated water to come into contact with the ZVI, which can remove or transform the contaminants through a variety of chemical processes. ZVI has several advantages as a remediation technology, including its low cost, high reactivity, and compatibility with other remediation technologies. However, the use of ZVI also has some limitations, including the potential for passivation, which occurs when the ZVI becomes coated with corrosion products or other materials that limit its reactivity. The use of ZVI also requires careful consideration of site-specific factors, including the type and concentration of contaminants present, the hydrogeological conditions, and the potential for off-site impacts. Overall, ZVI is a promising and widely used remediation technology that can effectively treat contaminated water and soil through a variety of chemical processes. Further research is needed to better understand the properties and limitations of ZVI as a catalyst and to develop methods for optimizing its use in environmental remediation. The disadvantage of the catalyst is deactivation in neutral and alkaline conditions [14].

Zero valent iron is one of the most popular solid catalysts used in the heterogeneous Fenton process and is the zero-valent iron (ZVI), characterized by activity, environmental friendliness, cost-effective preparing [15], non-toxicity [16], as well as effectiveness to remove halogenated compounds [17,18], nitrate [19], phosphate [20], polycyclic aromatic hydrocarbons [21,22], heavy metals [19,23,24], arsenic [25], dyes [26,27], phenol [28–30], nitrobenzene, chlorophenol, pharmaceutical compounds, or wastewater from the food industry, mining, and during the remediation of land contaminated with oil derivatives [31].

IRON-CONTAINING SOILS

Iron-containing soils have been used as heterogeneous catalysts in Fenton-like processes for the treatment of contaminated water and soil. These soils have a high content of iron oxides, such as goethite, hematite, and magnetite, which can act as a source of Fe^{2+} and Fe^{3+} ions for the Fenton reaction.

In Fenton-like processes that use iron-containing soils as catalysts, the soil is typically first pretreated to remove any organic matter or other contaminants that may interfere with the catalytic activity. The soil is then activated by reducing the Fe^{3+} ions to Fe^{2+} ions using a reducing agent, such as sodium dithionite or sodium borohydride. The activated soil is then mixed with the contaminated water or soil, and hydrogen peroxide is added to initiate the Fenton reaction.

The use of iron-containing soils as catalysts in Fenton-like processes has several advantages. These soils are abundant and widely available, making them a low-cost and environmentally friendly alternative to synthetic catalysts. They also have a high surface area, which can increase the efficiency of the reaction. Additionally, the soil can act as a filter or adsorbent, removing some of the pollutants from the water or soil before they even reach the catalytic sites.

However, the use of iron-containing soils in Fenton-like processes also has some limitations. The catalytic activity of the soil can be affected by factors such as pH, temperature, and the presence of other ions or contaminants. The soil may also contain other minerals or compounds that can interfere with the Fenton reaction or form by-products. The stability and reusability of the soil as a catalyst may also be a concern, as the soil may become saturated with contaminants over time or lose its catalytic activity through repeated use.

Overall, iron-containing soils are an important and promising natural resource for the remediation of contaminated water and soil. Further research is needed to better understand the properties and limitations of these soils as catalysts for the Fenton reaction and to develop methods for optimizing their use in environmental remediation [32–34].

IRON MINERALS AND IRON (HYDR)OXIDES

In the heterogeneous Fenton process, compounds such as solid iron oxides can be easily prepared in the laboratory and used as catalysts. In addition, their nanoforms have strong adsorption and catalytic activities [7,35,36]. In the heterogeneous Fenton process, popular iron oxides used as a catalyst are magnetite [37], hematite [38], ferrihydrite [39], ferrites [40,41], goethite [38], and schorl [42].

Magnetite

Magnetite with the formula Fe_3O_4 consists of 73% iron, which makes it one of the highest iron-content minerals. It is composed of Fe^{2+} oxides and iron Fe^{3+} oxides, where there are two Fe_3O_4 ions per one Fe^{2+} ion. The properties of magnetite such as low price, no toxicity, and strong magnetic properties, guarantee its usage in environmental protection. It is also a popular catalyst in advanced oxidation processes (AOPs) due to its ability to remove pollutants based on redox reactions. In addition, we can separate magnetite from post-process sludge due to its magnetic properties. Magnetite owns its properties to many octahedral sites in its structure. As a result, it can hold many Fe^{2+} ions, which speeds up and increases the reaction for initiating H_2O_2 activation [37]. However, the usage of magnetite in pure form is limited due to a lower degree of oxidation when compared to iron soluble in the heterogeneous Fenton reaction [10]. Magnetite nanoparticles can be modified by an organic disulfide polymer (PTMT) and used in the adsorption of heavy metals coming from simulated high-salinity wastewater [43]. In other effective and innovative research, the photocatalytic ozonation process has been used. Magnetite and titania support onto graphene were applied for micropollutants removal [44]. Magnetite with zero-valent iron and hematite as a catalyst were used to remove pollutants in cosmetic wastewater. The best wastewater treatment results were obtained for 500 mg/L Fe_3O_4, 500 mg/L Fe_2O_3, and Fe^0 1,000 mg/L [45]. We also used magnetite with hematite as a catalyst in AOP applications for cosmetic sewage treatment plants. In this research, the heterogeneous Fenton process was efficient and innovative. What is more, we noticed high efficiency of wastewater treatment, such as 75.7% TOC removal and 90.5% total nitrogen removal [45].

Hematite

Hematite is one of the most durable forms of trivalent iron oxide with high thermodynamic stability. It is a common material of natural sediments and soil, which contains about 70% iron. Hematite is an inexpensive and crude material that is applied as a combustible material in pig iron production after the process. Due to burning it in a furnace, hematite does not adversely affect the environment. However, before using the material in research, hematite is subjected to crushing, dispersing, and cleaning. The specified particle size (less than 60 nm) is achieved using the sedimentation process. The iron sample is sonicated in 95% ethanol for 5 min, washed with 0.1 M HNO_3 and rinsed with water, and mixed with 95% ethanol. The last stage of hematite sample preparation is drying at 30°C [46]. The freshly precipitated and amorphous iron oxide such as ferrihydrite is a precursor of hematite [47]. Hematite has a lower ability to degrade hydrogen peroxide than other minerals with higher efficiency in catalytic decomposition and a high degree of diffusion. Among the used catalysts, hematite was distinguished by the highest activity in catalyzing the oxidation reaction. The iron with lower valence is oxidized the fastest by H_2O_2. Lei *et al.* [48] noticed that the oxidation of CO in nanopores is more effective due to the higher density of iron and exposed active surface involved in the reaction [38]. The exposed surface of the crystals, in which the reaction takes place, size, and morphology, the arrangement of atoms on the surface of the compound, and the number and type of hydroxyl groups bonding to iron atoms influence hematite catalytic activity. Nanostructures of compounds and their modification such as Nb-containing hematite [49], Nb-doped hematite [50], Fe_2O_3 core-shell nanowires [51], S-doped hematite [52], N-co-doped hematite [53], are increasingly used as catalysts in heterogeneous Fenton process.

Ferrihydrite

Ferrihydrite is an iron oxide mineral (oxy)hydrate most often used in the form of a nanomaterial with a large specific surface area (SSA > 200 m^2/g) and many Fe-OH groups. Mineral has a structural formula $5Fe_2O_3 \cdot 9H_2O$. It occurs naturally in the earth's crust in the form of hydrated Fe^{3+} hydroxide. Ferrihydrite has a large SSA of 250–275 m^2/gL as well as high reactivity [39], which allows greater contact between the ferrihydrite and hydrogen peroxide. It also has a nanometric structure, which enables its more excellent contact between reactants and impurities and is a reasonable basis for dispersing functional materials [54]. Using ferrihydrite as a catalyst in the heterogeneous Fenton process is more and more popular [39]. Matt *et al.* [55] confirmed the well activity of catalysts in the heterogeneous Fenton process. They noticed that ferrihydrite achieved higher removed of 2,4,6-trinitrotoluene than with used other compounds such as hematite as well as goethite as the catalyst. The ferrihydrite also can be modified, which was done by Yanping *et al.* [56]. They synthesized Ag/AgBr/Ferrihydrate due to placing various Ag/AgBr on the ferrihydrite surface and using it as a catalyst. Results of the research presented that in the process, shows that electrons accelerate the formation of Fe^{2+}. In the process, in which electrons increase the efficiency of using H_2O_2, scientists noticed extend of pH values. During Fe^{3+} reduction, electrons can increase the structural stability of catalysts [57,58]. Wu *et al.* [59] used another modification of

the process with the additional UV radiation to obtain dissolved ferrihydrite. Barreiro *et al.* [60] used ferrihydrite as a catalyst to remove atrazine with H_2O_2. While Zhang *et al.* [61] used citrate-modified ferrihydrite microstructures as a catalyst, synthesized via a simple aqueous solution route. The modified ferrihydrite microstructures adsorption well methylene blue and Cr^{6+} ions. The authors noticed also high activity in the generation of hydroxyl radicals by the usage of these compounds as catalysts [61].

Ferrites

Another popular catalyst applied in the heterogeneous Fenton process is ferrite. It is a metal oxide of the general formula AB_2O_4 is spinel. The structural formula is as follows MFe_2O_4, where M = Mn, Fe, Co, Ni, Zn, etc. [7]. Magnetite is an iron ferrite, in which Fe is siding in A and B positions. Magnetite is used in industry as powder or ceramics in electronic devices, magnetic nanodevices, optics, bio-medicine, and telecommunications [40,41]. The ferrite has a crystalline structure, magnetic properties, and favorable adsorption properties. The three spinel ferrite structures depend on the M^{2+} and Fe^{3+} site position in the MFe_2O_4 pattern such as normal structure with M^{2+} in tetrahedral places and Fe^{3+} in octagonal places. Another structure is an inverse pattern with evenly distributing Fe^{3+} and M^{2+} in octagonal places. In mixed structures of spinel ferrite, the ions occupy tetrahedral and octahedral sites randomly. Normal structure spinel ferrite is $ZnFe_2O_4$, an inverse spinel ferrite is $NiFe_2O_4$ and Fe_3O_4 and the mixed spin ferrite includes $MnFe_2O_4$ [62]. Scientists also utilized nickel ferrite [63], bismuth ferrite [64], mesoporous silica magnetically surrounded [65], transition metals substituted with cobalt nano ferrites [66], nickel doped cobalt ferrite [67], as the catalyst. Scientists also used ferrihydrite as a photocatalyst, due to noticed effect of UV on ferrihydrite. Jauhar *et al.* [68] noticed the high effectiveness of cobalt ferrite with the addition of manganese and used it as a catalyst in the removal of methyl blue even in the absence of light [68]. Based on the research of Wu *et. al.* [59], it was found that cobalt ferrites used as catalysts have a high treatment efficiency of anionic and cationic compounds. Liu *et al.* [63], Soltani *et al.* [64], Sahoo *et al.* [65], and Singh *et al.* [67] also used ferrite as catalysts. In all processes, an effective evaluation of degradation of the pollutant over 80% was achieved.

Goethite

Goethite, a common iron oxide mineral, has been found to be an effective catalyst for the Fenton process in wastewater treatment. Goethite is a naturally occurring mineral that is abundant and inexpensive. It has a high surface area and is capable of adsorbing a range of organic and inorganic pollutants from wastewater. Studies have shown that goethite can enhance the efficiency of the Fenton process in re-moving pollutants such as dyes, pesticides, phenols, and heavy metals. The goethite catalyst can be easily synthesized and has a longer lifespan compared to other iron-based catalysts, making it a promising candidate for industrial wastewater treat-ment. However, like other iron-based catalysts, goethite has limitations such as pH dependency, iron leaching, and the need for a high concentration of hydrogen peroxide. Researchers are still exploring ways to optimize the use of goethite in the

Fenton process to overcome these limitations and improve its efficiency and applicability in wastewater treatment.

Goethite is an iron oxyhydroxide with a surface area (of 100–200 m^2/g), thermodynamically stable at "room temperature". It rusts in almost all kinds of soils in the natural environment and other surface formations containing iron, which structure (α-FeOOH) consists of double strands edge dividing $FeO_3(OH)_3$ octahedrons. The construction of goethite consists of double fringes connected by dividing the corners and forming octagonal "tunnels" crossing hydrogen bridges. In the heterogeneous Fenton process, goethite is applied as a catalyst due to its parameters such as widespread occurrence, low price, and environmental friendliness. It occurs in water as a chemically active compound with low energy demand [69]. Goethite is slightly soluble, and its dissolution by the leaching process is caused by the proton in the Fenton reaction with Fe^{3+} (Eq. 3.1).

$$\alpha - FeOOH + 3H^+ \rightarrow Fe^{3+} + 2H_2O \qquad (3.1)$$
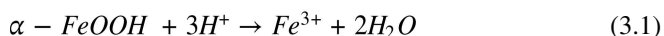
One of the advantages of using goethite as a catalyst in the Fenton process is that it can be used under a wide range of pH conditions. This is because goethite has a surface charge that allows it to be stable over a broad range of pH values, making it suitable for treating wastewater with varying pH levels. Another advantage is that goethite has a high selectivity towards the target pollutants, which means it can effectively remove the pollutants without causing further harm to the environment. This is because goethite has a specific surface area that allows it to selectively adsorb and oxidize the pollutants, leaving behind harmless by-products. Moreover, goethite can also be used in conjunction with other catalysts such as activated carbon, which can enhance the removal efficiency of pollutants in wastewater. This combination is effective in treating complex wastewater containing various contaminants. Overall, the use of goethite as a catalyst in the Fenton process has great potential for improving wastewater treatment processes. Its abundance, low cost, and high efficiency make it an attractive option for industrial wastewater treatment. However, further research is needed to optimize the use of goethite in the Fenton process and to investigate its long-term stability and environmental impact. After the removal of the organic compounds, the leaching process continues with Fe^{3+} by non-reducing dissolution with by-products. The dissolution of goethite increases during the degradation by-products of the process [70,71]. However, Lin *et al.* [72] showed no dissolving iron in basic conditions, which confirms the poor solubility of the compound.

Schorl

Schorl (chemical formula: $NaFe_3Al_6(BO_3)3\text{-}Si_6O_{18}(OH)_4$) is a natural, complex borosilicate mineral containing iron, which is a tourmaline group, which confirms they are the trigonal space group R3m – static crystal structures [42]. The formula of tourmaline is XY_3Z_6 $[Si_6O_{18}]$ $[BO_3]$ W_4, where X = Ca, Na, K or vacancy; Y = Li, Mg, Fe^{2+}, Mn^{2+}, Al, Cr^{3+}, V^{3+}, Fe^{3+}; Z = Mg, Al, Fe^{3+}, V^{3+}, Cr^{3+}; and W = OH, F, O [73]. Spontaneous and permanent poles characterize the tourmaline. The electric dipoles, which guarantee an electric field on the surface of a compound,

were noticed on the surface of poles [7,74], which is unique pyroelectric properties and piezoelectricity. Schorl is classified as terminal members, gravity (Y = Mg), schorl (Y = Fe^{2+}), tsilaisite (Y = Mn), olenite (Y = Al), and elbait (Y = Li, Al), depending on the occupancy of the Y and X sites [75]. The mineral can produce an electrostatic charge if subjected to a slight pressure or temperature change [42]. Schorl is a catalyst in many kinds of industries such as water treatment, air purification systems, and medicine. Schorl, a mineral of the tourmaline group, has also been investigated as a catalyst for Fenton-like reactions in wastewater treatment. Studies have shown that schorl has the potential to enhance the Fenton process by generating hydroxyl radicals that can effectively degrade organic pollutants. Schorl has a unique crystal structure that provides a large surface area for catalytic activity. It contains iron and other trace elements that can act as catalysts to generate hydroxyl radicals in the Fenton reaction. Schorl is effective in removing various pollutants, including dyes, phenols, and pharmaceuticals, from wastewater. The study reported that schorl had a higher catalytic activity than other iron-containing minerals such as magnetite and hematite in the Fenton process. Additionally, schorl is stable under acidic conditions, which is necessary for the Fenton reaction. However, further research is needed to optimize the use of schorl as a catalyst in the Fenton process for wastewater treatment. Other studies are required to understand the mechanism of catalytic activity and to determine the optimal conditions for schorl to enhance the Fenton process. Research has shown that schorl can effectively catalyze the Fenton reaction, leading to the degradation of a variety of pollutants in wastewater. In one study, schorl was used as a catalyst in the Fenton process to remove phenol from aqueous solutions. The results showed that schorl was effective in degrading phenol, achieving a degradation efficiency of 96% after just 15 minutes of reaction time. Schorl has also been investigated as a catalyst for the degradation of other pollutants in wastewater, such as dyes and pharmaceuticals. In one study, schorl was shown to be an effective catalyst for the degradation of the antibiotic sulfamethazine in the Fenton process. The study found that schorl achieved a degradation efficiency of 91% after 60 minutes of reaction time. Overall, schorl has shown promise as a catalyst in the Fenton process for the treatment of wastewater. Further research is needed to fully understand the potential of schorl and to optimize its use in the Fenton process [76–78].

Pyrite

Pyrite, also known as iron sulfide (FeS_2), is a mineral that is commonly found in natural environments. Pyrite has been studied in the context of the Fenton process due to its ability to catalyze the generation of hydroxyl radicals ($^{\bullet}OH$) in the presence of hydrogen peroxide (H_2O_2). The Fenton process with pyrite (FeS_2) involves the oxidation of Fe^{2+} to Fe^{3+} by $^{\bullet}OH$, which is generated by the reaction between H_2O_2 and pyrite. The oxidation of Fe^{2+} to Fe^{3+} produces Fe^{3+} ions, which can then react with H_2O_2 to generate more $^{\bullet}OH$. This process leads to a chain reaction that generates a large number of $^{\bullet}OH$, which can then react with pollutants to break them down into simpler, less harmful compounds. Pyrite can be used as a low-cost alternative to ferrous ions (Fe^{2+}) as a catalyst in the Fenton process. Pyrite has a high surface area and a high affinity for H_2O_2, which makes it a highly

effective catalyst for the generation of $^\bullet$OH. In addition, pyrite is abundant and widely available, which makes it an attractive option for large-scale applications. However, the use of pyrite in the Fenton process can also present some challenges. Pyrite is a highly reactive mineral that can undergo rapid oxidation in the presence of air and water, which can lead to the formation of acidic conditions that can inhibit the Fenton process. In addition, the presence of other minerals in the natural environment can also affect the effectiveness of pyrite as a catalyst.

Overall, pyrite is an effective catalyst in the Fenton process, and its use can offer several advantages in terms of cost and availability. However, the use of pyrite in the Fenton process requires careful consideration of the environmental conditions and the presence of other minerals in the system. Pyrite has several advantages as a catalyst in the Fenton process. First, pyrite has a high surface area and a high affinity for H_2O_2, which makes it a highly effective catalyst for the generation of $^\bullet$OH. Second, pyrite is abundant and widely available in nature, which makes it a low-cost and sustainable option for large-scale applications of the Fenton process. Finally, pyrite is highly effective in the treatment of a wide range of pollutants, including organic compounds, dyes, and pharmaceuticals.

However, the use of pyrite in the Fenton process also presents some challenges. Pyrite is a highly reactive mineral that can undergo rapid oxidation in the presence of air and water, which can lead to the formation of acidic conditions that can inhibit the Fenton process. In addition, the presence of other minerals in the natural environment can also affect the effectiveness of pyrite as a catalyst.

To address these challenges, researchers have studied various methods for stabilizing pyrite and enhancing its effectiveness as a catalyst in the Fenton process. These methods include the use of organic coatings to protect pyrite from oxidation and the addition of surfactants to enhance the dispersion of pyrite in solution.

Overall, pyrite has shown great potential as a catalyst in the Fenton process, and its use can offer several advantages in terms of cost and sustainability. However, the use of pyrite in the Fenton process requires careful consideration of the environmental conditions and the presence of other minerals in the system to ensure its effectiveness as a catalyst. Ammar *et al.* used pyrite to decompose tyrosol in the electro-Fenton process and obtain about 90% mineralization of solutions [79–81].

BIMETALLIC

Various types of metallic catalysts characterized significant effectiveness in the Fenton process and could be used in industry [19]. A bimetallic material is one of modification ZVI, in which their structure settles on transition metals. Transition metals simplify the production of activated atomic hydrogen (H^+), strengthening the reducing agent characterized by accelerating iron corrosion. Also, bimetallic materials can create galvanic cells and increase the oxidation of ZVI [82]. Isomorphic iron is often replaced with other transition metals to increase the catalytic activity of the compound. One kind of modification uses oxygen vacancy (OV), *i.e.*, active places on the catalyst's surface, formed during adaptation to unequal substitutions or cation deficiency in the magnetite structure. Costa *et al.* [83] used oxygen vacancy and noticed the synergistic effect of a used compound on

the decomposition of hydrogen peroxide during the usage of magnetite, Co, and Mn. Magalhães *et al.* [84] introduced chromium in the magnetite structure to produce for the first time a Cr–Fe spinel active heterogeneous Fenton system. It was noticed that chromium shows ionic width compatible with the magnetite spinel structure and high reactivity towards H_2O_2 activation [84]. Another factor is the importance of ions in preventing the recombination of photogenerated electrons (e⁻) and holes h⁺ on the catalyst surface [85]. Another kind of modification applied porous magnetic composites, characterized by a high degree of magnetism and catalytic property, containing electron-carrying composite structures and exhibiting large surfaces with active centers. Other advantages of mentioned modification are larger pores, the grid structure favoring the diffusion of pollutants on the activated carbon, and the improvement of active adsorption sites [86]. Ma *et al.* [87] used magnetic porous carbon bullets derived from microporous chelating resin with cheap and environmentally friendly material, modified with ethylenediaminete-traacetic acid (EDTA), and loaded with iron composite. Chelating agents are alternative compounds that increase the efficiency of the heterogeneous Fenton process [88–90]. Catalyst can also be modificative by doping magnetic metal on the surface of compounds, which improves the catalytic properties. Pouran *et al.* [91] modified the magnetite by deposition of niobium on the catalyst structure. The researchers noticed that with a higher niobium content and a molar content, the degradation degree of methylene blue has increased. Using niobium as a catalyst with greater adsorption capacity increases the degradation efficiency of hydroxyl peroxide, and causes smaller elation of Nb ions. Moreover, an increase in the amount of niobium caused the catalyst crystal sizes to be smaller, and the surface area was larger in the compound due to the deficiency of cations in the catalyst structure. After doubling the amount of introduced Nb and Nb^{5+} ions, scientists noticed that with the replacing of Fe^{3+} cations in the crystal structure, and increasing particle size. Comparing the surface area of Fe^{3+} and Nb^{5+}, niobium has a larger radius than iron (55 *vs.* 64 μm). Because of that, it is characterized by a larger active surface area than iron [92]. The treatment process can also be effective due to the participation of Nb^{4+}/Nb^{5+} redox pairs in the H_2O_2 decomposition cycle. This process increases because of the rate of Fe^{3+} reduction to Fe^{2+} [91].

Other advantages of the process include increasing the adsorption on the surface of the catalyst, enhancing the oxygen quantity on the catalyst surface, and the regeneration of Fe^{2+} cations. One can also use an interesting and innovative solution as iron modified with graphene as a catalyst (0–2 wt.%). The iron deposited begins in the form of FeOOH on a graphene sheet showing a wide pH value range, sta-bility, and reusability. All catalysts have unique properties such as the mesoporous structure and the large room for adsorption. Also, graphene has excellent electron conductivity (4,000 K/Wm) and a positive effect on the transfer of electrons between molecules, which leads to a reduction of iron Fe^{3+} to Fe^{2+}. Qui *et al.* [93] and Yang *et al.* [94] confirmed that using of modificative catalyst, which caused the process, could be cheaper and easier to use [95].

The iron-carbon with polytetrafluoroethylene (PTFE) was used by Zhang *et al.* [96], who used Fe^{2+} as the source of iron generated by anodic oxidation of Fe-C during micro-electrolysis. Scientists used molecules, with low process prices and

high catalytic properties, and the long life of a galvanic cell. The PTFE used to modify the surface properties of Fe-C (iron with carbon) caused the limitation of iron ions leaching. The modification achieved good process efficiency at an initially neutral pH value [97]. Another modification of the process conducted Luo et al. [98] used a two-electron reduction of dissolved oxygen with carbon nanotubes coated with Fe_2O_3 with nickel foam as the cathode substrate to degrade pollutants. The advantages of carbon usage were a rapid reduction of O_2 and accumulation of H_2O_2 due to the high mass transfer efficiency and large active surface [98].

Saratale et al. [99] used the aromatic hydroxamic acid derivative of 2-hydroxypyridine-N-oxide (HpO) to build a catalyst with iron-HpO ligand deposited on granular activated carbon (GAC). The catalyst consisted of acid groups and N-derivatives of hydroxamic products, including chelating products and Fe^{3+} bond insurance [100]. Additionally, scientists formed hydroxypyridine N-oxide by the stable bidentate complexes with Fe^{3+} [101]. Another modification carried out by Zhao et al. [102] used a bifunctional recite (FeR) modified with iron as a catalyst. Hussain et al. [103] used strontium-doped copper deposited on zirconium oxide ZrFeSr as a catalyst in the heterogeneous Fenton process. Zhou et al. [6] noticed decomposed pollutants in the soil treatment in the heterogeneous Fenton process due to the use of ZVI/EDTA/Air as catalysts. The hydrogen peroxide quickly decomposes during contact with soil. By the reaction of ZVI with air, iron precipitates under neutral or alkaline conditions. Therefore, scientists utilized chelated acids to increase the efficiency of the process. They also used EDTA in the reaction with Fe^{2+}. The effect of the process was the formation of H_2O_2 [6]. Zhou et al. [104] based their process on hydrogen peroxide production by activating dioxygen in the reaction of iron-EDTA ligands. In this modification, it is important to activate oxygen from the iron- EDTA ligand reaction to form the O_2-Fe^{2+}-EDTA complex, which has a coordination number of 7 with metal in the hub [104]. Also, excess iron can reduce EDTA degradation, which accelerates the decomposition of H_2O_2 and the higher use of oxidants. Moreover, too much EDTA can slow down the kinetic reactions, especially O_2 activation and H_2O_2 reduction. The excessive EDTA (molar ratio [EDTA]:[Fe^{2+}/Fe^{3+}] greater than 1:1) can reduce the coordination number and prevent the formation of O_2 ligands F-Fe^{2+}/Fe^{3+}-EDTA and/or O_2-Fe^{2+}/Fe^{3+}-EDTA. Aleksić et al. [105] used Fe in the form of ZSM_5 zeolite and noticed the higher efficiency of the process at a higher pH value. At a higher pH value, the leaching of iron on the zeolite support was smaller than in an acidic environment. As a result, they lost less catalyst, and therefore it can be used with better results. During the reaction of H_2O_2 with iron ions, it bound on the zeolite skeleton and diffuses with the resulting radicals penetrating the mass, mostly $^•OH$ radicals being formed on the inner part of zeolites [106]. During the process at a higher (almost neutral) pH value, the reaction of positively charged iron with the ions of the negatively charged zeolite backbone slows down or delays the generation of hydro complexes with iron ions, which are stable in water [107]. Ma et al. [87] used NH_2OH to accelerate the redox reaction of Fe^{3+}/Fe^{2+}, which resulted in a relatively constant recovery of Fe^{2+}. The recovery of Fe^{2+} increased the pseudo-first-order reaction rate and the pH range in which the treatment process could be carried out [87].

WASTE MATERIALS

The Fenton-iron process is an effective method for the treatment of wastewater that contains organic pollutants. One of the key components of the Fenton-iron process is the use of iron catalysts, which can be obtained from various waste materials.

Iron-based waste materials such as iron filings, scrap iron, steel slag, and iron oxide nanoparticles have been used as catalysts in the Fenton-iron process. These waste materials are attractive for use as catalysts due to their low cost, abundance, and environmental benefits of waste recycling [108].

Iron filings are commonly used as catalysts in the Fenton-iron process due to their high reactivity and low cost. They can be obtained from various sources, including metalworking shops and waste recycling centers. Similarly, scrap iron and steel slag, which are by-products of the steel industry, can also be used as catalysts in the Fenton-iron process [108].

In addition, iron oxide nanoparticles have shown promise as effective catalysts for the Fenton-iron process. These nanoparticles can be synthesized from various waste materials, such as waste iron sludge or iron-rich wastewater, through simple and low-cost methods.

The use of waste materials as catalysts in the Fenton-iron process not only reduces the cost of the treatment process but also provides an environmentally friendly solution for waste recycling. It also helps to reduce the burden on landfills and promotes the circular economy concept [108].

However, it is important to note that the quality of the waste materials used as catalysts can affect the efficiency of the Fenton-iron process. The waste materials should be carefully selected and processed to ensure their purity and effectiveness as catalysts.

In conclusion, waste materials containing iron can be used as effective catalysts in the Fenton-iron process for the treatment of wastewater containing organic pollutants. This provides an environmentally friendly and cost-effective solution for waste recycling and the treatment of wastewater [109].

Waste iron materials such as iron filings, scrap iron, and steel slag can be used as catalysts in the Fenton-iron process for the treatment of wastewater. However, these materials may contain impurities that can affect their catalytic activity. Therefore, it is important to properly prepare the waste iron materials before use in the Fenton-iron process.

Here are some steps for preparing waste iron materials for use in the Fenton-iron process:

- Collect the waste iron materials: The first step is to collect the waste iron materials from various sources, such as metalworking shops and waste recycling centers.
- Clean the waste iron materials: The waste iron materials should be cleaned to remove any contaminants, such as oil, grease, or dirt. This can be done by washing the materials with water and soap and then rinsing them thoroughly with clean water.

- Dry the waste iron materials: The waste iron materials should be dried completely to prevent any residual moisture from affecting their catalytic activity. This can be done by air-drying the materials or by placing them in an oven at a low temperature.
- Grind the waste iron materials: The waste iron materials can be ground into smaller particles to increase their surface area and improve their catalytic activity. This can be done using a ball mill or a mortar and pestle.
- Test the catalytic activity: Finally, the prepared waste iron materials should be tested for their catalytic activity in the Fenton-iron process. This can be done by conducting batch experiments with different concentrations of hydrogen peroxide and iron catalysts and measuring the degradation of organic pollutants in the wastewater [108].

In conclusion, preparing waste iron materials for use in the Fenton-iron process requires careful cleaning, drying, grinding, and testing to ensure their effectiveness as catalysts. Proper preparation can help to improve the efficiency of the Fenton-iron process for the treatment of wastewater containing organic pollutants.

Waste iron materials can be obtained from various sources for use in the Fenton-iron process. Some common sources of waste iron include:

- Metalworking shops: Waste iron materials such as iron filings, scraps, and turnings are generated in metalworking shops as byproducts of metal processing and machining.
- Steel industry: The steel industry generates large amounts of waste iron materials, such as steel slag, which is a by-product of steel production.
- Waste recycling centers: Waste recycling centers collect and process various types of waste materials, including scrap iron and other metals, that can be used as catalysts in the Fenton-iron process.
- Construction sites: Construction sites generate waste iron materials such as steel reinforcement bars, which can be recycled and used in the Fenton-iron process.
- Landfills: Landfills contain a significant amount of waste iron materials that can be recycled and used in the Fenton-iron process. However, the quality of the waste materials obtained from landfills may be lower than those obtained from other sources [108].

In general, waste iron materials can be obtained from a wide range of sources, and their availability and quality may vary depending on the location and type of industry. It is important to properly select and prepare the waste iron materials for use in the Fenton-iron process to ensure their effectiveness as catalysts.

Overall, the use of waste iron materials as catalysts in the Fenton-iron process can be effective and efficient, with several advantages over other types of catalysts. Some of the advantages include:

- Low cost: Waste iron materials are readily available and inexpensive compared to other types of catalysts, such as noble metals.

- Environmental benefits: The use of waste iron materials in the Fenton-iron process promotes waste recycling and reduces the burden on landfills, thereby promoting a circular economy concept.
- High reactivity: Iron-based catalysts are highly reactive and can effectively degrade a wide range of organic pollutants in wastewater.
- Long-term stability: Iron-based catalysts are relatively stable and can maintain their catalytic activity over a long time, reducing the need for frequent replacement [108].

However, the efficiency of the Fenton-iron process using waste iron materials can be influenced by factors such as the particle size, purity, and concentration of the catalysts, as well as the operating conditions of the process, such as pH and temperature. Therefore, it is important to carefully select and prepare the waste iron materials for use in the Fenton-iron process to ensure their effectiveness as catalysts and optimize the treatment efficiency [108].

In the heterogeneous Fenton process, scientists utilized waste materials as a catalyst, thus saving money and natural materials. For example, Kumar *et al.* [110] used black soil from black iron-laden soil as a catalyst, which was prepared for the process by wet impregnation with iron (Fe-BS) and ticking at various temperatures in calcination. The calcination process was caused by the removal of volatile substances and impurities to increase the active surfaces on the catalyst and create large surfaces or active sites. Due to the various parameters of the process, especially the temperatures, the catalyst can be stiffer, more active, and more stable [111,112]. Mashayekh-Salehi *et al.* [113] in their research, used pyrite-induced waste rock from the Ahan-Lajaneh mine in Iran as a catalyst. They used nanoparticles with mesoporous powder, which are characterized by the presence of FeS_2 without additional compounds. Van *et al.* [114] used iron slag as a catalyst in the Fenton process from metallurgy processes in Thai Nguyen Non-Ferrous Metals Limited Company in Vietnam. Industrialists estimated producing of metal slag is about 250,000 tons per year. To prepare the catalyst, iron was dried at 105°C for 48 h. In the next stage, it was crushed and sieved. Therefore using waste in the Fenton process is cheaper and more friendly for the environment than their utilization. Chu *et al.* [115] used magnetic biochar derived from food as the catalyst. To prepare magnetic biochar scientists used food waste, for example from a food-waste disposal facility, which is located in Korea. The most abundant components of food were glucan (23.1%) and protein (21.5%). In food were also ash (16.6%) and other components (36.5%). They mixed Fe^{2+} with chloride tetrahydrate, Fe^{2+} with chloride hexahydrate, food waste, and distilled water to prepare the magnetic biochar. In the next step, pH was adjusted to 7.6–8.2 and dried in a furnace. The compound was pyrolyzed at 300°C for 7 h as well as dried in a vacuum oven [115]. Additionally, Hong-Chao *et al.* [116] used ionothermal carbonization of biomass to construct Fe, N-doped biochar with prominent activity and recyclability as cathodic catalysts in heterogeneous electro-Fenton (see Figure 3.1). Tan *et al.* [85] used waste iron oxide obtained from the tannery wastewater process as a catalyst. XRD analysis showed the goethite-compatible compound in the wastewater, which confirms the presence of iron-containing compounds [85]. Bansal *et al.* [117] used
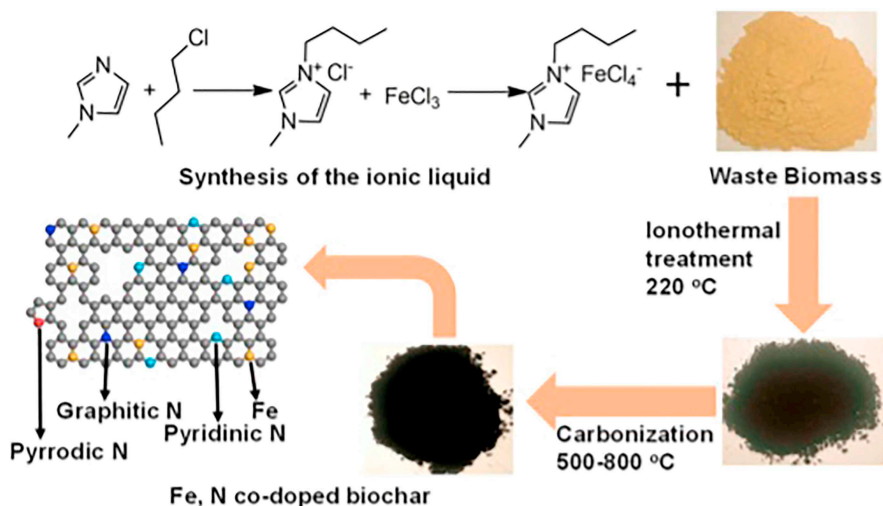
FIGURE 3.1 The schematic diagram for the synthesis of Fe, N cooped biochar materials.

remnants of car destruction such as the fly ash Fenton process with UV light as a catalyst for the removal of tetracycline. Usually, industrialists deposit about 5 million tons of automotive waste in landfills yearly. This type of waste has metals such as copper and aluminum in their structure, which are popularly used as catalysts in wastewater treatment [117].

Fly ash is a by-product of coal combustion in power plants and is a common waste material. Fly ash contains various elements and minerals, including iron, which can be used as a potential source of iron in the Fenton process. Fly ash iron has been investigated for its potential use as a catalyst in the Fenton process to degrade organic pollutants in wastewater.

Studies have shown that fly ash iron can be effective in generating hydroxyl radicals and degrading various types of organic pollutants. The use of fly ash iron in the Fenton process has several advantages. Firstly, fly ash is a low-cost and abundant waste material, making it an attractive option for wastewater treatment applications. Secondly, the use of fly ash iron can reduce the amount of waste material that needs to be disposed of, providing an environmentally sustainable solution. However, the use of fly ash iron in the Fenton process also has some limitations. The iron content of fly ash can vary significantly, which can affect its catalytic activity in the Fenton process. The presence of other elements and minerals in fly ash can also affect its catalytic activity and stability in the Fenton process.

To address these limitations, various methods have been proposed to prepare fly ash iron for use in the Fenton process. For example, acid leaching can be used to extract iron from fly ash and increase its iron content. Thermal treatment can also be used to enhance the catalytic activity of fly ash iron. In conclusion, fly ash iron is a potential source of iron in the Fenton process, and its use can provide a low-cost and sustainable solution for wastewater treatment. However, the iron content and properties of fly ash

can vary significantly, and preparation methods should be carefully considered to optimize its catalytic activity and stability in the Fenton process.

Further research is needed to explore the potential of fly ash iron and other waste materials as catalysts in the Fenton process. In addition to its use as a catalyst in the Fenton process, fly ash iron has also been investigated for other applications in environmental remediation. For example, fly ash iron can be used to remove heavy metals and other contaminants from water and soil. The high surface area and porous structure of fly ash iron allow for the effective adsorption of heavy metals and other contaminants. The iron oxide present in fly ash can also form complexes with heavy metals, making them less bioavailable and less toxic.

However, the use of fly ash iron for environmental remediation also has some limitations. The variable composition and properties of fly ash can affect its effectiveness in removing contaminants. The presence of other elements and minerals in fly ash can also affect the stability and performance of fly ash iron in environmental remediation. To address these limitations, various modifications have been proposed to enhance the effectiveness of fly ash iron in environmental remediation. For example, fly ash can be modified through acid or alkaline treatments to increase its iron content and improve its adsorption capacity. Other modifications, such as the addition of organic matter, can also enhance the performance of fly ash iron in environmental remediation [112,118–120].

Iron sludge is a by-product generated from the iron-based coagulants used in wastewater treatment. Due to its high iron content, it has the potential to be used as a catalyst in the Fenton process for wastewater treatment. The iron sludge can act as a heterogeneous catalyst in the Fenton reaction, providing a high surface area for the reaction to occur and facilitating the production of hydroxyl radicals. Research has shown that the addition of iron sludge to wastewater can enhance the performance of the Fenton process. The iron sludge can act as a source of iron ions, which can participate in the Fenton reaction and promote the formation of hydroxyl radicals. Additionally, the use of iron sludge can reduce the amount of waste generated from the wastewater treatment process. However, the use of iron sludge in the Fenton process also presents some challenges. The quality and composition of the iron sludge can vary, which can affect its catalytic activity. In addition, the presence of other impurities in the iron sludge, such as heavy metals, can negatively impact the performance of the Fenton process and lead to environmental concerns. Overall, the use of iron sludge in the Fenton process shows promise as a way to enhance the efficiency and sustainability of wastewater treatment. Further research is needed to optimize the use of iron sludge as a catalyst and to address any environmental concerns associated with its use. Iron sludge, also known as ferric sludge or iron hydroxide, is a by-product generated in various wastewater treatment processes, such as coagulation/flocculation with ferric chloride or ferric sulfate. Iron sludge contains a high amount of iron, which makes it a potential candidate for use as an iron source in the Fenton process. Studies have shown that iron sludge can be used effectively as an iron source in the Fenton process for the treatment of various wastewater contaminants, such as dyes, phenols, and organic acids. However, the effectiveness of iron sludge as an iron source depends on several factors, including its iron content, the type of contaminants present in the wastewater, and the

operating conditions of the Fenton process. One of the major advantages of using iron sludge in the Fenton process is that it is a low-cost source of iron, which can significantly reduce the overall cost of the Fenton process. Additionally, the use of iron sludge can also reduce the amount of waste generated from wastewater treatment processes, as it can be used as a value-added product instead of being disposed of as a waste material. However, the use of iron sludge in the Fenton process also has some limitations. For example, the composition of iron sludge can vary depending on the source and treatment process, which can affect its performance in the Fenton process. Moreover, the presence of impurities in iron sludge, such as heavy metals, can pose a risk to the environment and human health if not properly handled.

Overall, the use of iron sludge in the Fenton process has shown promise as an alternative to commercial iron salts for the treatment of wastewater contaminants. However, further research is needed to optimize its use and to evaluate its potential risks and benefits [13,121].

IRON CARRIERS IN CATALYSTS

Iron carriers used in the Fenton process can include various materials such as iron filings, scrap iron, iron oxide, iron hydroxide, iron carbonate, and iron-containing clays. These materials can act as carriers for iron particles and enhance the performance of the Fenton process. The choice of iron carrier depends on the specific wastewater treatment application and the properties required for the carrier. One of the commonly used iron carriers in the Fenton process is iron oxide, specifically magnetite and hematite. These materials have a high surface area, thermal stability, and resistance to acidic and basic environments, which makes them ideal carriers for the iron catalyst in the Fenton process. Iron oxide carriers can also provide a high concentration of iron particles, leading to enhanced catalytic activity in the degradation of organic pollutants [122,123].

Another common iron carrier in the Fenton process is iron-containing clays, such as montmorillonite and bentonite. These clays have a high surface area and cation exchange capacity, allowing them to effectively immobilize iron particles and enhance their reactivity in the Fenton process.

The use of iron carriers in the Fenton process can improve the stability and efficiency of the iron catalyst, leading to enhanced degradation of organic pollutants in wastewater. However, the choice of carrier material and its properties should be carefully considered to ensure optimal performance of the Fenton process.

In conclusion, iron carriers play an important role in the Fenton process by immobilizing or dispersing the iron catalyst and improving its stability and reactivity. Various iron carriers can be used in the Fenton process, including iron oxide and iron-containing clays, and their properties should be carefully considered to optimize the performance of the process [124,125].

In addition to the iron carriers mentioned above, other materials have been investigated for their potential use as iron carriers in the Fenton process. For example, activated carbon has been shown to effectively immobilize iron particles and enhance their reactivity in the Fenton process. Activated carbon has a high surface

area and porous structure, which allows for effective adsorption and immobilization of iron particles.

Various modifications have also been made to iron carriers to enhance their performance in the Fenton process. For example, iron oxide nanoparticles have been coated with various materials, such as silica and chitosan, to improve their stability and reactivity in the Fenton process. Iron-containing materials have also been immobilized on various carrier materials, such as graphene oxide and carbon nanotubes, to improve their dispersibility and catalytic activity. It is worth noting that the choice of iron carrier and its properties can also affect the kinetics of the Fenton process. For example, the size and shape of iron particles can affect their reactivity and the rate of hydroxyl radical production. The concentration and distribution of iron particles on the carrier material can also affect their catalytic activity. Overall, the use of iron carriers in the Fenton process is an important strategy to enhance the performance and stability of the iron catalyst. The choice of carrier material and its properties should be carefully considered to optimize the performance of the Fenton process in the treatment of various types of wastewater. Further research is needed to explore the potential of new iron carriers and modifications to improve the efficiency of the Fenton process [124,125].

To reuse catalysts and increase the efficiency of the process scientists immobilized iron compounds on carriers or insoluble iron oxides such as goethite, magnetite, and hematite [126]. Microelectrolysis may take place during the heterogeneous Fenton process in which carbon is used as the catalyst carrier. Process microelectrolysis consists of mixing carbon or a composite of carbon or graphite with steel and iron. As a result of the process, microcells are formed, but the dominant process is adsorption [127–129]. The iron-based catalyst was also immobilized on a carrier such as silica [130], polymer [131], single silica batch [132], as well as clay [133] and clay oxides [134], or hydrogels [131,132,135].

Moreover, iron oxides were placed on commercial or developed materials such as FexOy - MWNT (multi-walled carbon nanotubes), Fe/C, Fe-ZSM$_5$ (Zeolite Socony Mobil-5), and Fe-Beta, to increase the active surface of the catalyst and facilitate its separation [136–138]. Another type of catalyst is mesoporous silicates, with long-range structural systems, such as SBA-15 molecular sieves, and a broad spectrum of activity. Using the modified compounds is popular in the absorption, catalysis, and separation process [139]. Benzaquén *et al.* [140] synthesized catalysts of mesoporous materials modified with iron (Fe-SBA-15 nanocomposites). Niveditha *et al.* [141] immobilized iron-on molybdophospahate (FeMoPO$_4$) with a tetrahedral structure to effectively form the catalyst. It was noticed that iron and silica are stable and effective catalysts. Moreover, silica has a lot of advantages such as the possibility of replacing it with phosphate [142]. Remirez *et al.* [136] noticed the adsorption process taking place in macropores. They analyzed it by the current microscope in the sample of coal from stone [136]. Another disadvantage is decreasing efficiency of the catalyst. During the recycling of Fe^{2+}/Fe^{3+}, sunlight is an essential element supporting the Fenton reaction. The use of a carrier can slightly limit light access to the catalyst during the regeneration of iron oxides [143].

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