Wastewater Treatment with the Fenton Process
Principles and Applications

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4 Nanomaterials

NANOPARTICLES

Iron-based nanoparticles have shown promise in heterogeneous Fenton processes. They exhibit superb reactivity and specificity towards pollutants due to their small size and high surface-to-volume ratio. This allows for the efficient oxidation of contaminants in wastewater. Further, ion-based nanoparticles have a redox potential that allows for the reduction of hydrogen peroxide to form hydroxyl radicals ($^{\bullet}OH$), which are strong oxidizing agents that can effectively degrade pollutants in wastewater. Their solubility is low under anaerobic conditions, making them suitable for anaerobic environments. Nanoparticles are relatively low cost compared to other advanced oxidation processes, such as photocatalysis, and can be easily synthesized. They can also be recovered and reused, which makes them a more sustainable and cost-effective option for wastewater treatment. Examples of iron minerals and iron-based materials in the nanoparticulate form include magnetite (Fe_3O_4), goethite (α-FeOOH), hematite (Fe_2O_3), ferrihydrite ($Fe_5HO_8 \cdot 4H_2O$), akaganeite (β-FeOOH), greigite (Fe_3S_4), or zero-valent iron nanoparticles (nZVI). These nanoparticulate forms of iron minerals and iron (hydr)oxides can have unique properties and reactivity compared to their bulk counterparts, making them attractive for various applications, including Fenton processes [1]. Examples of the nanostructures used in the Fenton process are shown in Table 4.1.

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Magnetite is a naturally occurring iron oxide with magnetic properties that is commonly used in various applications, including environmental remediation and

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TABLE 4.1
Examples of the Nanostructures Used in the Fenton Process (Self-prepared)

Nanostructure	Size	Shape	Reference
Fe-G graphene-modified iron sludge	–	curled sheet	[2]
Cu-doped Fe/Fe_2O_3	20–100 nm	abundant spherical nanoparticles	[3]
Iron-modified rectangle	500 nm	–	[4]
Fe-SBA-15 nanocomposites	–	–	[5]
Magnetite nanostructure	20–40, 100–200 nm	–	[6]
a-Fe2O3 nanograins	40–280 nm	grains	[7]
Nanophotocatalyst modified by graphite electrode	8–15, 3–5 nm	nanotubes	[8]
$FeVO_4$ with CeO_2	–	nanotubes	[9]
$BiFeO_3$ nanostructures	100–150 nm	–	[10]
$AlSi_2Fe_6$	215.7	–	[11]
Nanometric magnetite (Fe_3O_4)	17–25 nm	ball-milled	[12]
Fe_3O_4	75 nm	spherical particles with rough surface	[13]
Chlorpheniramine	50 ± 20 nm	powder	[14]

biomedical imaging. Due to their unique properties, magnetite nanoparticles have been explored as an alternative to traditional iron-based catalysts in Fenton processes. The magnetic nature of magnetite nanoparticles allows for easy separation from the reaction mixture using an external magnetic field, which can reduce the cost and complexity of the separation process. Additionally, the high surface area-to-volume ratio of nanoparticles can enhance the catalytic activity of the magnetite catalyst, leading to improved Fenton process efficiency [17].

Recent studies have reported the successful application of magnetite nanoparticles in Fenton processes for the degradation of various organic contaminants in wastewater. For example, magnetite nanoparticles were used as catalysts in the Fenton process to degrade methyl orange and Congo red dyes, resulting in high degradation efficiencies. Additionally, magnetite nanoparticles were found to be effective catalysts in the Fenton-like process for the removal of organic pollutants from landfill leachate [18]. The use of magnetite nanoparticles in Fenton processes has also been investigated in combination with other advanced oxidation processes, such as photocatalysis and electro-Fenton [19]. In these combined processes, magnetite nanoparticles are used as a catalyst to generate hydroxyl radicals through the Fenton reaction, while other mechanisms generate additional reactive species. This synergistic effect has been shown to enhance the degradation efficiency of various organic contaminants in wastewater. Altogether, data shows that magnetite nanoparticles have shown great potential as catalysts in Fenton processes for degrading organic contaminants in wastewater. Their magnetic nature and high surface-area-to-volume ratio make them efficient catalysts with easy separation. At the same time, their unique properties also make them promising candidates for combined advanced oxidation processes.

Goethite, an iron hydroxide mineral, also can form nanoparticles of needle-like whiskers and has applications in catalysis, adsorption, and water treatment. Its unique crystal structure and surface chemistry make it an effective catalyst for degrading various organic pollutants in wastewater [20]. Goethite nanoparticles can be synthesized through multiple methods, such as hydrothermal synthesis, sol-gel synthesis, and coprecipitation [21]. In the Fenton processes, goethite nanoparticles can act as a heterogeneous catalyst, where the pollutants in the wastewater can adsorb onto the surface of the goethite particles, facilitating their oxidation by the hydroxyl radicals generated from the Fenton reaction. However, the efficiency of goethite as a catalyst in Fenton processes can be influenced by various factors, such as the size, shape, and surface area of the nanoparticles, as well as the pH and temperature of the reaction. Recent studies have shown that goethite nanoparticles can be modified with other metal ions, such as Cu^{2+} and Ni^{2+}, to enhance their catalytic activity in Fenton processes [22]. These modified goethite nanoparticles have been found to exhibit improved degradation efficiency towards various organic pollutants, including dyes and pharmaceuticals, in wastewater treatment.

Hematite is an iron oxide mineral with a reddish-brown color and is widely used in pigments and in environmental applications such as arsenic removal from water. Hematite nanoparticles have been investigated for their potential use as catalysts in Fenton-like reactions for wastewater treatment [23]. Research has shown that the addition of hematite nanoparticles can enhance the degradation of organic contaminants in wastewater through the Fenton-like reaction, by generating hydroxyl radicals from H_2O_2 in the presence of Fe^{2+} ions. The high surface area and porosity of hematite nanoparticles can also enhance their catalytic activity, allowing for more efficient and effective degradation of contaminants. Additionally, the stability and reusability of hematite nanoparticles make them a promising candidate for practical applications in wastewater treatment. Furthermore, recent studies have explored the use of modified hematite nanoparticles, such as those coated with graphene oxide or doped with other metals, to enhance their catalytic properties further and improve their performance in Fenton processes [24].

Ferrihydrite is a poorly crystalline iron oxide/hydroxide mineral with a high surface area commonly found in soils and sediments. Ferrihydrite nanoparticles have a unique crystalline structure with a high surface area, making them promising materials for advancing Fenton processes. The high surface area allows for more active sites for the catalytic reaction to take place, leading to increased efficiency in removing contaminants from wastewater [25]. In addition, ferrihydrite nanoparticles have been found to have good stability and reusability in Fenton processes, making them a cost-effective solution for wastewater treatment. Researchers have also explored modifying the surface chemistry of ferrihydrite nanoparticles to enhance their catalytic activity and selectivity for specific contaminants. These nanoparticles can potentially be effective catalysts for Fenton processes in wastewater treatment due to their unique structure, high surface area, and stability.

Akaganeite forms a corrosion product in acidic environments and has potential applications in water treatment and environmental remediation. Akaganeite is an iron hydroxide mineral with a unique crystal structure and surface reactivity compared to other iron oxides/hydroxides. Its high specific surface area, acidic properties, and ability to undergo phase transformations make it a promising material for Fenton processes [26]. The use of akaganeite nanoparticles in Fenton reactions has been shown to effectively degrade organic contaminants, such as bisphenol A and phenol, in wastewater treatment. In addition, akaganeite nanoparticles can be easily synthesized and have shown to be stable under a wide range of pH and temperature conditions, which makes them a suitable candidate for practical applications. However, more research is needed to optimize their performance and understand the underlying reaction mechanisms involved in Fenton processes with akaganeite nanoparticles. Their unique properties offer new opportunities for advancing the effectiveness and efficiency of Fenton processes in water treatment and environmental remediation.

Greigite (Fe_3S_4) is a magnetic iron sulfide mineral with considerable potential in environmental remediation and bioremediation. Greigite is a magnetic iron sulfide mineral that has been explored for its potential applications in environmental remediation and bioremediation [27]. It has a cubic crystal structure and is stable under various environmental conditions. Due to their magnetic properties, greigite nanoparticles can be manipulated and controlled using magnetic fields, which makes them useful for the targeted delivery and separation of pollutants in contaminated environments. In Fenton processes, greigite nanoparticles have been studied as potential catalysts for the degradation of organic pollutants. The greigite nanoparticles' high surface area and reactivity make them effective catalysts for the Fenton reaction. They have been shown to enhance the rate and efficiency of pollutant degradation. Additionally, the magnetic properties of greigite nanoparticles make them easy to separate from the treated wastewater, which could reduce the cost and complexity of the treatment process. However, further research is needed to fully understand their properties and optimize their use in Fenton processes.

Zero-valent iron nanoparticles (nZVI) are promising in heterogeneous Fenton processes. The nZVI has shown promising results for the removal of organic pollutants from wastewater, and ongoing research is focused on optimizing the synthesis, characterization, and application of nZVI in wastewater treatment [28]. Several types of zero-valent iron nanoparticles have been used in heterogeneous Fenton processes for wastewater treatment.

These include:

- Bare nZVI: This is the most common type of nZVI used in Fenton processes, where the iron nanoparticles are synthesized without any surface modification or coating [29].
- Coated nZVI: Iron nanoparticles can be coated with various materials to improve their stability, reactivity, and selectivity. For example, silica-coated nZVI (nZVI@SiO_2) and starch-coated nZVI (nZVI@starch).
- Supported nZVI: Iron nanoparticles can be supported on various materials to enhance their dispersion and stability. This can be nZVI supported on activated carbon (nZVI@AC) and nZVI supported on clay (nZVI@clay) have been used in Fenton processes.

- Composite nZVI: Iron nanoparticles can be incorporated into various composites to improve their performance and functionality. For example, nZVI/polymer composites, nZVI/activated carbon composites, and nZVI/ iron oxide composites.

BARE ZVI NANOPARTICLES

Bare nZVI refers to zero-valent iron nanoparticles that are synthesized without any surface modification or coating. Bare nZVI is the most common type of nZVI used in Fenton processes for wastewater treatment. Under inert conditions, nZVI can be prepared by reducing iron salts in the presence of a reducing agent, such as sodium borohydride or hydrazine.

They have several advantages for use in Fenton processes. Firstly, it has a high reactivity due to its small size and high surface area, which allows for the efficient oxidation of pollutants in wastewater. Secondly, it is easy to prepare and can be synthesized using low-cost materials. Thirdly, bare nZVI can be used in various environmental conditions, including anaerobic conditions, making it suitable for use in various wastewater treatment applications [30].

However, there are also some challenges associated with the use of bare nZVI in Fenton processes. One of the main challenges is that the nanoparticles tend to aggregate and form larger particles, which can reduce their reactivity and hinder their ability to degrade pollutants efficiently. Additionally, bare nZVI is prone to oxidation and corrosion, which can reduce its effectiveness and lead to the formation of iron sludge [30].

Researchers have explored various surface modifications and coatings for nZVI to overcome these challenges to improve their stability and reactivity. These include coatings such as silica, starch, and polymers, and supports such as activated carbon and clay. However, despite the development of coated and supported nZVI, bare nZVI remains a popular and effective option for Fenton processes in wastewater treatment.

COATED nZVI

The coating on nZVI can be associated with various materials to improve their stability, reactivity, and selectivity in Fenton processes for wastewater treatment. Coatings can provide a protective layer on the surface of the nanoparticles, preventing oxidation, aggregation, and corrosion. Coatings can also improve the dispersibility of nZVI in water, making it easier to mix with other reagents and enhancing its reactivity.

Silica-coated nZVI (nZVI@SiO_2) is a commonly used coated nZVI in Fenton processes. Silica is an inert material that is resistant to oxidation, and its coating can provide a protective layer on the surface of the iron nanoparticles. The coating can also enhance the dispersibility of nZVI in water, allowing for better contact between the nanoparticles and the pollutants. Silica-coated nZVI has been shown to have improved stability and reactivity in Fenton processes, leading to more effective degradation of pollutants in wastewater [31].

Starch-coated nZVI (nZVI@starch) is another type of coated nZVI that has been used in Fenton processes. Starch is a natural polysaccharide that can be used as a stabilizing agent for nZVI. The coating can improve the dispersibility of nZVI in water and enhance its reactivity by providing a source of hydrogen peroxide through the decomposition of the starch. Starch-coated nZVI has been shown to be effective in the removal of organic pollutants, such as dyes and phenols, from wastewater [32].

Other materials that have been used as coatings for nZVI in Fenton processes include polymers, such as polyvinyl alcohol (PVA), and graphene oxide (GO) [33]. Polymer coatings can improve the stability and dispersibility of nZVI in water, while GO coatings can enhance the reactivity of nZVI through the generation of hydroxyl radicals. The choice of coating material depends on the specific application and the desired properties of the coated nZVI.

SUPPORTED nZVI

Supported nZVI refers to zero-valent iron nanoparticles that are supported on various materials to enhance their dispersion and stability in Fenton processes for wastewater treatment. The support material can improve the dispersibility of nZVI in water, prevent aggregation, and provide a protective layer to prevent oxidation and corrosion. The choice of support material depends on the specific application and the desired properties of the supported nZVI.

Activated carbon (AC) is a commonly used support material for nZVI in Fenton processes. AC has a high surface area and porosity, allowing for the adsorption of pollutants and the dispersion of nZVI in water. nZVI supported on AC (nZVI@AC) has been shown to be effective in the removal of various pollutants, including organic dyes, pharmaceuticals, and heavy metals from wastewater [34,35].

Clay is another material that can be used as a support for nZVI in Fenton processes. Clay has a layered structure and a high surface area, allowing for the adsorption of pollutants and the dispersion of nZVI in water. nZVI supported on clay (nZVI@clay) has been shown to have improved stability and reactivity in Fenton processes, leading to more effective removal of pollutants from wastewater [36].

Other materials that have been used as supports for nZVI in Fenton processes include magnetite, zeolites, and chitosan. Magnetite can enhance the magnetic properties of nZVI, allowing for easier separation and recovery of the nanoparticles [37]. Zeolites and chitosan can provide a source of hydrogen peroxide through the release of iron ions, enhancing the reactivity of nZVI in the Fenton processes [38].

Supported nZVI has several advantages over bare nZVI, including improved stability, dispersion, and reactivity. However, the use of support materials can also introduce additional complexity and cost to the synthesis and application of nZVI in Fenton processes. The choice of support material and synthesis method must be carefully considered to optimize the effectiveness and efficiency of supported nZVI in wastewater treatment.

OTHER COMPOSITES

Incorporating nZVI into various matrices enhances the performance and functionality of Fenton processes for wastewater treatment. The composites can provide additional functionalities such as improved stability, selectivity, and removal efficiency, or can enhance the properties of nZVI such as magnetic properties or catalytic activity. Polymer composites are one type of composite nZVI that has been used in Fenton processes. nZVI can be incorporated into polymer matrices such as polyvinyl alcohol, polyethylene glycol, and polyurethane to improve the dispersibility of the nanoparticles and prevent aggregation. Polymer composites have been shown to have improved stability and reactivity in Fenton processes compared to bare nZVI [39].

The nZVI can be further combined with semiconducting materials. Semiconductors have been identified as potential catalysts due to their high optical activity and low cost [40]. One such material is TiO_2, which has been used to form a nanoparticle layer on iron-based catalysts such as Fe_2O_3 nanograin [7]. The effectiveness of using TiO_2 nanostructures as catalysts depends on the amount of remaining compounds present. Studies have shown that the antimicrobial properties of the catalyst increased 2.5 times after using H_2O_2. In another study, researchers used a novel method to synthesize a catalyst for wastewater treatment. Specifically, they used porous $FeVO_4$ nanotubes decorated on CeO_2 nanotubes ($FeVO_4$ with CeO_2) and applied ultrasonic (US), ultraviolet (UV), and binary US/UV radiation [9]. This unique approach led to the formation of highly stable and efficient sonophotocatalysts, which retained their effectiveness even at high pH levels. The resulting catalyst was then used in a special three-way mechanism of Fenton's experiments, which relies on the trapped active species and the calculated energy of the forbidden gap. The study demonstrated the potential of this method in producing highly effective catalysts for wastewater treatment, which could have significant implications in the field of environmental remediation.

Other semiconductors that can be used as catalysts with iron include CdS [40,41], vanadate, $BiVO_4$ [42,43], noble metals (such as Ag), and metal-free semiconductors such as g-C_3N_4 [44]. In Fenton processes, nanoparticles of various sizes are used. For instance, $BiFeO_3$ having 100–150 nm [10], 20–40 and 100–200 nm magnetite-based nanostructures synthesized with plasma [6], magnetite nanostructures with dimensions of 22.7 and 15.1 nm [45], or 17–25 nm nanometric ball-milled magnetite [12]. Garrido-Ramirez *et al.* considered nanostructured allophane clays supported on iron oxide ($AlSi_2Fe_6$) as well as the graphite-modified glassy carbon (GC) and $AlSi_2Fe_6$ [11]. However, the most popular semiconductors are MOF, TiO_2, g-C_3N_4, and bismuth-like materials due to their potential interactions with various types of iron and optical properties [40]. Researchers have used various nanomaterials such as $BiFeO_3$, magnetite, and pyrite nanostructures, as well as nanostructured allophane clays supported on iron oxide and graphite-modified glassy carbon, to investigate the potential of combining different types of nanocatalysts. These studies suggest that combining different nanocatalysts can lead to synergistic effects that enhance the efficiency of the Fenton process for wastewater treatment.

PROCESS PARAMETERS

Some of the important process parameters in Fenton processes include pH, temperature, hydrogen peroxide (H_2O_2) concentration, nano-iron catalyst concentration, reaction time, or presence of contaminants. The pH of the solution can have a significant impact on the Fenton reaction rate and efficiency. Temperature can affect the rate of Fenton reactions, as higher temperatures can lead to faster reactions but can also increase the risk of catalyst deactivation. The concentration of H_2O_2 and iron catalyst concentration can affect the rate of Fenton reactions such as faster reactions but can also increase the risk of unwanted side reactions or catalyst deactivation. The presence of contaminants in the wastewater can affect the Fenton reaction rate and efficiency, as they may compete with the target contaminants for the available H_2O_2 and catalyst [46].

The pH of the solution is an important parameter in Fenton processes that use iron-based nanomaterials as catalysts. The optimal pH range for the Fenton process is typically between 2.5 and 4, which corresponds to the acidic range. At this pH range, the solubility of Fe^{3+} ions is higher, which leads to a higher concentration of Fe^{2+} ions in the presence of H_2O_2. The same relates to nanoparticulate iron-based catalysts. The increased concentration of Fe^{2+} ions enhances the Fenton reaction rate, resulting in more efficient degradation of pollutants in the wastewater. However, it is important to note that the pH can also influence the stability and reactivity of iron-based nanomaterials. For example, at low pH values, bare nZVI may experience rapid oxidation and passivation, leading to a decrease in its reactivity. Therefore, the pH of the solution should be carefully controlled and optimized to ensure that the iron-based nanomaterials exhibit the desired catalytic activity and stability [46].

Temperature is another important parameter that can affect the Fenton reaction rate in the context of iron-based nanomaterials used as catalysts. Higher temperatures can lead to faster reactions due to the increased kinetic energy of the reactants, but can also increase the risk of catalyst deactivation due to thermal degradation. For instance, bare nZVI can undergo thermal oxidation at high temperatures, resulting in a loss of its reactivity towards H_2O_2. Similarly, coated or supported nZVI may experience changes in their surface properties or structure at high temperatures, leading to a decrease in their catalytic activity. Therefore, it is important to carefully control the temperature during the Fenton processes to ensure that the iron-based nanomaterials exhibit the desired catalytic activity and stability. The optimal temperature range may vary depending on the type of nanomaterial used, the composition of the wastewater, and other process parameters. However, a temperature range of 20–40°C is typically used for Fenton processes employing iron-based nanomaterials as catalysts [47].

Reaction time affects Fenton reactions using iron-based nanomaterials. The duration of the Fenton reaction can affect the overall efficiency of the process by influencing the extent of pollutant degradation and the consumption of hydrogen peroxide. Shorter reaction times may not allow for the complete degradation of pollutants, resulting in incomplete treatment. On the other hand, longer reaction times may lead to excessive consumption of hydrogen peroxide and the formation of unwanted byproducts, which can decrease the efficiency of the process. Additionally, the optimal reaction time can depend on the specific type of iron-based nanomaterial being used, as well as other process parameters such as pH and hydrogen peroxide concentration. Therefore, the reaction time should be carefully optimized to balance the desired extent of pollutant degradation with the consumption of hydrogen peroxide and the formation of unwanted by-products [48].

The concentration of iron catalyst can affect the rate of the reaction, as higher concentrations can lead to faster reactions due to the availability of more active sites for the reaction. However, higher concentrations of iron catalysts can also increase the risk of catalyst deactivation due to the formation of iron oxide or other iron-containing species that can reduce the catalytic activity of the iron-based nanomaterials. The use of nano-iron can potentially shorten the Fenton reaction time compared to traditional Fenton processes using bulk iron or other iron-based catalysts. This is because nano-iron has a higher surface area to volume ratio, which can increase its reactivity and efficiency in the Fenton reaction. The increased surface area of nano-iron can provide more active sites for the reaction to occur, leading to faster reaction rates and shorter reaction times. Additionally, the small size of nano-iron particles can improve their dispersibility and accessibility to pollutants, further enhancing the efficiency of the process. However, it is important to note that the optimal reaction time can depend on various factors such as the specific type of nano-iron, pH, hydrogen peroxide concentration, and pollutant type and concentration. Additionally, the optimal concentration of iron catalyst can depend on the specific type of iron-based nanomaterial being used. For example, bare nZVI particles typically require higher concentrations of iron catalyst to achieve the effective catalytic activity, while coated or supported nZVI particles may require lower concentrations due to their improved stability and reactivity. Thus, the concentration of iron catalyst should be carefully optimized to balance the desired reaction rate and the risk of catalyst deactivation [49].

The H_2O_2 plays a crucial role in Fenton reactions by providing the hydroxyl radical ($^{\bullet}OH$) that is responsible for the oxidation of organic pollutants. The concentration of H_2O_2 can affect the reaction rate, with higher H_2O_2 concentrations generally leading to faster reactions. However, excessively high H_2O_2 concentrations can lead to unwanted side reactions, such as the generation of superoxide radicals ($^{\bullet}O_2^-$) and hydroperoxyl radicals ($HO_2^{\bullet}$) that can compete with the formation of $^{\bullet}OH$ radicals and reduce the efficiency of the Fenton reaction. Therefore, it is important to carefully optimize the H_2O_2 concentration in Fenton processes in relation to iron-based nanoparticle usage, to ensure that the desired level of $^{\bullet}OH$ radicals is generated without the production of unwanted side products. The optimal H_2O_2 concentration may depend on various factors, such as the type of iron-based nanomaterial used, the type and concentration of pollutants in the wastewater, and other process parameters. In general, the H_2O_2 concentration is typically maintained in the range of 1–10 mM in Fenton processes employing iron-based nanomaterials as catalysts. However, the optimal concentration may vary depending on the specific application and the desired reaction rate and selectivity [50].

The presence of other contaminants in the wastewater can have a significant impact on the efficiency of Fenton processes that use iron-based nanomaterials. For example, organic compounds, such as humic acid, can react with H_2O_2 and consume it before they can react with the target contaminant. This can reduce the efficiency of the Fenton process and result in incomplete removal of the target contaminant. Similarly, the presence of heavy metals in wastewater can affect the performance of iron-based catalysts, as they may bind to the active sites on the catalyst surface and reduce their reactivity. The presence of chloride ions can result in the oxidation of the catalyst and the formation of iron chloride, which reduces the reactivity of the catalyst. Therefore, it is crucial to evaluate the impact of other contaminants on the efficiency of Fenton processes using iron-based nanomaterials and optimize the process conditions accordingly [51].

In heterogeneous Fenton processes, catalyst properties such as structure, size, and application are often adjusted to enhance their efficiency. Nanostructured coatings and materials with intermediate sizes between molecular and microscopic structures can also be used as catalysts. Nanostructures with various sizes and shapes influence the process. Iron nanoparticles, nanorods, nanotubes, and nanocrystals are the most commonly used nanocatalysts in HFP due to their electronic, magnetic, optoelectronic, biomaterials, and catalytic properties. The activity of solid catalysts is highly dependent on particle size and structure, as an increased surface area and active sites can enhance catalytic activity. However, the process is associated with some disadvantages, such as the high cost of catalyst generation and toxic organometallic precursors, which can damage cells mechanically. In some cases, nanostructures used as catalysts in heterogeneous Fenton processes have unique antibacterial, photocatalytic, and anti-accumulation properties.

SYNTHESIS

There are several methods that can be used to synthesize nanoparticulate iron-based nanocatalysts for use in Fenton processes, including:

- Coprecipitation: This method involves the simultaneous precipitation of Fe^{2+} and Fe^{3+} salts in the presence of a base or alkali under controlled pH and temperature conditions. The resulting precipitate can be further processed to obtain the desired nanoparticulate catalyst [52]. Coprecipitation is a widely used method for synthesizing nanoparticulate iron-based nanocatalysts for Fenton processes. In this method, Fe^{2+} and Fe^{3+} salts are simultaneously precipitated in the presence of a base or alkali at controlled pH and temperature conditions. The precipitate formed is then further processed to obtain the desired nanoparticulate catalyst. The coprecipitation process typically involves the addition of a base, such as ammonium hydroxide or sodium hydroxide, to a mixture of Fe^{2+} and Fe^{3+} salts, such as $FeCl_2$ and $FeCl_3$, under controlled pH and temperature conditions [53]. The pH and temperature are controlled to ensure the formation of the desired crystal structure and particle size distribution of the resulting nanoparticulate catalyst. After the coprecipitation step, the resulting precipitate is typically washed, dried, and calcined to remove any impurities and improve the catalytic activity of the catalyst. The calcination temperature and time can be adjusted to control the crystallinity and surface properties of the resulting catalyst. Coprecipitation is a relatively simple and cost-effective method for synthesizing iron-based nanoparticulate catalysts for Fenton processes. The resulting catalysts typically have high surface area, high reactivity, and good stability, making them suitable for a wide range of environmental applications.

- Sol-gel method: It is based on the formation of a sol or solution of metal salts, followed by gelation to form a solid material. The resulting gel can then be dried and calcined to obtain the desired nanoparticulate catalyst. The sol-gel method is a widely used method for the synthesis of nanoparticles, including iron-based nanocatalysts for Fenton processes. The process involves several steps, including the formation of a sol, gelation, drying, and calcination. Sol is a stable colloidal suspension of nanoparticles in a liquid medium. In the case of iron-based nanocatalysts, a sol can be formed by dissolving Fe^{2+} and Fe^{3+} salts in a suitable solvent, such as water or alcohol. The sol may also contain a stabilizing agent, such as a surfactant, to prevent particle aggregation. Gelation is the process of converting the sol into a gel or solid material. This can be achieved by various methods, such as adding a cross-linking agent or changing the temperature and pH of the sol. The resulting gel contains a network of nanoparticles. The gel is then dried to remove the solvent and obtain a solid material. This can be done by various methods, such as air-drying or freeze-drying. Calcination is the process of heating the dried material to a high temperature to remove any remaining organic compounds and to induce particle growth and crystallization. The resulting material is a nanoparticulate catalyst that can be used in Fenton processes. The sol-gel method offers several advantages for the synthesis of iron-based nanocatalysts. It allows for precise control over the size and shape of the nanoparticles, as well as the ability to incorporate other materials or dopants into the catalyst. Additionally, the resulting catalyst has a high surface area and porosity, which can enhance its catalytic activity [54].
- Hydrothermal method: This method involves the synthesis of nanoparticles under high pressure and high temperature conditions in a closed vessel. The resulting nanoparticles are usually highly crystalline and have a narrow size distribution. The hydrothermal method is a popular method for synthesizing nanoparticulate iron-based nanocatalysts for use in Fenton processes. The process involves the use of high pressure and high temperature conditions in a closed vessel, which allows for the precise control of the reaction conditions and the resulting nanoparticle properties. In this method, iron salts are typically dissolved in water or another solvent, and a reducing agent or a hydroxide is added to the solution to promote the formation of the desired nanoparticle morphology. The solution is then sealed in a high-pressure reaction vessel and heated to the desired temperature and pressure. During the hydrothermal reaction, the precursors undergo nucleation and growth, leading to the formation of nanoscale particles with controlled size, shape, and composition. The process is often carried out under alkaline conditions to promote the formation of iron oxides or hydroxides, which are commonly used as Fenton catalysts. The resulting nanoparticles are usually highly crystalline and have a narrow size distribution, making them ideal for use as Fenton catalysts. Additionally, the

hydrothermal method can be used to synthesize a wide range of iron-based nanomaterials, including iron oxides, iron hydroxides, and iron sulfides, which can be tailored to specific applications in environmental remediation and water treatment [55,56].

- Reduction method: Reduction of iron salts or oxides using a reducing agent such as sodium borohydride or hydrazine is applied to form nanoparticles. The resulting nanoparticles can be further processed to obtain the desired catalyst. The reduction method is a simple and effective way to prepare iron-based nanoparticles for use in Fenton processes. In this method, iron salts or oxides are typically used as precursors and a reducing agent, such as sodium borohydride or hydrazine, is added to the solution. The reducing agent causes the iron ions to undergo a reduction reaction, resulting in the formation of zero-valent iron (Fe^0) nanoparticles [57]. The size and morphology of the resulting nanoparticles can be controlled by adjusting various reaction parameters such as the concentration of the precursor, the type and concentration of the reducing agent, the reaction temperature, and the reaction time. In general, smaller nanoparticles can be obtained by using higher concentrations of the reducing agent and by reducing the reaction time. The reduction method has several advantages over other synthesis methods, including its simplicity, low cost, and the ability to prepare a wide range of nanoparticle sizes and shapes. However, the method requires careful control of reaction conditions to ensure reproducibility and prevent the formation of unwanted by-products. Once the nanoparticles are synthesized, they can be further processed to obtain the desired catalyst by washing and drying the nanoparticles, and then calcining them at a high temperature. The resulting catalyst can be characterized using various techniques, such as X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and Fourier-transform infrared spectroscopy (FTIR), to ensure that the nanoparticles have the desired size, morphology, and chemical composition.
- Microwave-assisted method: It is based on the use of microwaves to rapidly heat a reaction mixture containing iron salts or precursors. The resulting nanoparticles are typically smaller in size and more uniform than those obtained using conventional methods. The microwave-assisted method is a relatively new technique for the synthesis of iron-based nanoparticles, which has gained popularity due to its several advantages over conventional methods. In this method, a reaction mixture containing iron salts or precursors is subjected to microwave irradiation, which rapidly heats the mixture, leading to the formation of nanoparticles [58]. The microwave-assisted method is an attractive approach because it provides a fast and energy-efficient way of synthesizing nanoparticles. Additionally, this method enables better control over the reaction conditions, such as temperature, pressure, and reaction time, which can result in more uniform nanoparticles with desired properties. The microwave-assisted method can also be used for the synthesis of different types of iron-based nanoparticles, including iron oxide, iron sulfide [59], and iron carbide.

The resulting nanoparticles can have different sizes and shapes depending on the reaction conditions, such as the concentration of reactants and the duration of microwave irradiation. Furthermore, this method can be easily scaled up for the large-scale production of nanoparticles. The microwave-assisted method is a promising approach for the synthesis of iron-based nanoparticles, which can be utilized in various applications, including Fenton processes.

- Electrochemical method: It involves the electrochemical reduction of iron salts or precursors in a suitable electrolyte solution to form nanoparticles. The resulting nanoparticles are typically highly crystalline and have a narrow size distribution. The electrochemical method is a technique that can be used to synthesize nanoparticles of various metals, including iron. The process involves the application of an electric current to a solution containing iron salts or precursors, which leads to the reduction of the metal ions and the formation of nanoparticles. The reaction takes place at the surface of the electrode, which can be made of a variety of materials, such as platinum or carbon. The electrochemical method offers several advantages over other synthesis methods. For example, it allows for precise control of the size and shape of the nanoparticles by adjusting the reaction conditions, such as the current density, temperature, and pH of the electrolyte solution. Additionally, the process can be easily scaled up for industrial production. One variation of the electrochemical method is the template-assisted approach, in which a template is used to control the size and shape of the nanoparticles. The template can be a solid substrate, such as a glass slide or silicon wafer, or a porous membrane. The electrochemical deposition of the metal occurs in the pores of the template, resulting in nanoparticles with uniform size and shape. In summary, the electrochemical method is a powerful technique for synthesizing iron-based nanoparticles for use in Fenton processes, offering precise control over the size and shape of the nanoparticles and the ability to scale up for industrial production [60].

Biological synthesis methods have gained popularity due to their environmentally-friendly nature, as they do not involve the use of toxic substances. Microorganisms play a key role in these methods as their activity leads to the release of metabolites into the solution, which can react with ions or compounds deposited on their surface, leading to the formation of mineral particles. One such method involves the biosynthesis of Fe^{3+} by ferric-reducing bacteria (FRB) through the reduction of Fe^{3+} ions into hydroxide form under anaerobic conditions [61–65]. The Fe^{2+} ions released are then adsorbed with greater excess and are converted to magnetite through sulfate-reducing bacteria (SRB) like *Desulfomonas*. Another biological method is biologically controlled biomineralization (BCM), where microorganisms control the intracellular process of the formation of magnetite crystals. This process is controlled by ligands with stereochemical properties that stimulate the initial layer and induce crystal growth. Magnetotactic bacteria can also be used in biosynthesis [66–68]. Plant extracts like *Camellia sinensis*, *Peumus boldus*, and

Terminalia catappa have also been used as a source of secondary metabolites to mediate the redox and stabilize particles in the synthesis process [69–71].

The process of synthesizing nanoparticles for use as catalysts is a critical step that can greatly influence the resulting properties and performance of the catalyst. There are several factors that should be taken into consideration when selecting a synthesis method, including the desired properties of the catalyst, the scale of synthesis, and the intended application.

The properties of the nanoparticulate catalyst that may be influenced by the synthesis method include the size of the particles, their distribution, morphology, purity, quantity, and process quality with regards to environmental and economic considerations. For instance, a specific size range and distribution may be necessary for optimal catalytic activity, while high purity may be required to avoid unwanted side reactions or toxicity issues. Additionally, the quantity of catalyst produced must be sufficient to meet the demands of the intended application.

The scale of synthesis is another important consideration, as some synthesis methods may be more suitable for large-scale production, while others may be more suitable for small-scale or laboratory-scale synthesis. For example, some methods may require specialized equipment or facilities that are not available on a small scale or may not be economically viable for large-scale production.

Finally, the intended application of the nanoparticulate catalyst should also be taken into account when selecting a synthesis method. Different applications may require different properties, such as high stability, selectivity, or activity, which may be better achieved using specific synthesis methods. Moreover, the synthesis method may also impact the environmental and economic sustainability of the overall process, such as by generating harmful by-products or requiring expensive reagents.

In summary, the choice of synthesis method for nanoparticulate catalysts is a crucial step that should be carefully considered to ensure optimal performance, scalability, and sustainability for the intended application.

NANOCATALYST CHARACTERIZATION

There is a long list of techniques that can be used to characterize iron-based nanocatalysts prior to their use in Fenton processes. These are SEM, TEM, XRD, FTIR, X-ray photoelectron spectroscopy (XPS), Brunauer–Emmett–Teller (BET) analysis, and Zeta potential analysis. These characterization techniques can provide important information about the structure, morphology, surface chemistry, and stability of the nanocatalyst, which can help optimize its performance in Fenton processes [3,72].

SEM is a powerful tool for the characterization of nanocatalysts in Fenton processes. SEM is a type of electron microscopy that uses a beam of high-energy electrons to scan the surface of a sample and generate an image. The electrons interact with the atoms in the sample, producing signals that can be detected and used to create a detailed image of the surface topography and morphology. SEM is particularly useful for determining the morphology and size distribution of the nanocatalyst. The images generated by SEM can reveal the shape and size of the nanoparticles, as well as any surface features or defects. The size distribution of the nanoparticles can be determined by analyzing the SEM images, which can provide information on the average particle size and the size distribution range. In addition to providing information on the morphology and size of the nanocatalyst, SEM can also be used to investigate the surface chemistry of the nanoparticles. By using energy-dispersive X-ray spectroscopy (EDX) or X-ray photoelectron spectroscopy (XPS) in conjunction with SEM, researchers can determine the elemental composition and chemical state of the nanoparticles. This can be useful in identifying any surface modifications or coatings that may be present on the nanoparticles, which can have a significant impact on their reactivity and stability in Fenton processes [9].

TEM is a powerful imaging technique that can provide detailed information about the morphology, size distribution, and crystallinity of nanocatalysts. In TEM, a focused beam of electrons is transmitted through a thin sample, which interacts with the electrons to form an image. TEM can be used to determine the size and shape of individual nanoparticles and their aggregates, as well as the size distribution of the particles in a sample. The resolution of TEM can reach sub-nanometer scale, allowing the observation of the atomic structure of nanoparticles. TEM can also be used to determine the crystal structure of the nanoparticles and their degree of crystallinity, which can affect their catalytic activity. In addition, TEM can be used in combination with other techniques such as energy-dispersive X-ray spectroscopy (EDS) to determine the elemental composition and distribution of the nanocatalysts. This information is important for understanding the chemical nature and activity of the catalysts. Overall, TEM is a valuable tool for characterizing nanocatalysts and understanding their properties and behavior in Fenton processes.

XRD is a technique that is commonly used to identify the crystal structure and crystallinity of nanocatalysts. In XRD analysis, a beam of X-rays is directed at the sample, and the interaction of the X-rays with the atoms in the sample produces a diffraction pattern. The diffraction pattern provides information about the crystal structure of the sample, including the spacing and orientation of the atoms in the crystal lattice. In the context of nano-catalysts for Fenton processes, XRD can be used to identify the crystal structure of the iron-based nanocatalysts, such as bare or coated nZVI, supported nZVI, and composite nZVI. The XRD pattern of the nanocatalyst can help to confirm the presence of iron-based nanoparticles and their crystal structure, which is important for understanding their reactivity and efficiency in Fenton processes. Moreover, XRD can also be used to detect any changes in the crystal structure of the nanocatalyst after being used in the Fenton processes, which may indicate changes in the catalytic activity or stability of the nanocatalyst.

FTIR is a technique used to identify the functional groups present on the surface of nanocatalysts. It works by measuring the absorption or transmission of infrared radiation by the sample. The infrared spectrum produced provides information about the chemical bonds present in the sample. In the case of nanocatalysts for Fenton processes, FTIR can be used to identify functional groups such as hydroxyl groups, carboxylic acid groups, and amine groups on the surface of the catalyst. These functional groups can play a role in the catalytic activity of the nanoparticles by facilitating electron transfer reactions between the catalyst and the reactants. FTIR is a useful technique for characterizing nanocatalysts because it is non-destructive, requires very little sample preparation, and provides detailed information about the chemical composition of the sample. It is often used in combination with other characterization techniques such as SEM and TEM to provide a comprehensive understanding of the properties of the nanocatalyst.

XPS is a surface-sensitive technique that can provide information about the chemical composition and oxidation state of the nanocatalyst. In XPS, X-rays are used to excite electrons from the surface of the nanocatalyst, and the energy of the emitted electrons is measured. The energy of the emitted electrons can be used to identify the elements present in the nanocatalyst and to determine their oxidation state. XPS is particularly useful for studying the surface chemistry of nanocatalysts, as it can provide information about the chemical species present on the surface and the interactions between the nanocatalyst and the surrounding environment. For example, XPS can be used to determine the oxidation state of iron in iron-based nanocatalysts before and after the Fenton process, providing insights into the mechanism of the reaction and the role of the nanocatalyst in the process. Finally, XPS is a powerful tool for the characterization of nanocatalysts, providing valuable information about the chemical composition, oxidation state, and surface chemistry of the material.

BET analysis is a technique used to measure the surface area and porosity of materials, including nanocatalysts. The method is based on the measurement of the adsorption and desorption of a gas, typically nitrogen, on the surface of the material. The amount of gas adsorbed is proportional to the surface area of the material. BET analysis provides information about the specific surface area, pore size distribution, and total pore volume of the nanocatalyst. In the context of nano-catalysts for Fenton processes, BET analysis can be used to determine the available surface area for catalytic reactions. A higher surface area generally means more available sites for reactions to occur, which can increase the efficiency of the Fenton process. Additionally, BET analysis can provide information on the pore size distribution and porosity of the nanocatalyst, which can impact the transport of reactants and products to and from the catalytic sites.

Zeta potential analysis is a technique that can be used to measure the surface charge and stability of nanoparticles. When nanoparticles are dispersed in a liquid medium, they acquire a surface charge due to the adsorption of ions from the medium. The zeta potential is the electric potential difference between the surface of the nanoparticle and the surrounding liquid medium, which indicates the magnitude of the surface charge. Zeta potential analysis involves measuring the movement of the nanoparticles under the influence of an electric field. The magnitude and direction of the movement of the nanoparticles is related to the zeta potential. Nanoparticles with a high zeta potential are more stable in solution because the electrostatic repulsion between particles prevents them from aggregating or settling out of solution. In contrast, nanoparticles with a low zeta potential are more likely to aggregate or form clumps, which can reduce their effectiveness as catalysts. For nano-catalysts used in Fenton processes, zeta potential analysis can be useful in determining the stability of the nanoparticles in the wastewater matrix. The presence of other contaminants in the wastewater can affect the surface charge and stability of the nanoparticles, which can in turn affect their catalytic activity. By measuring the zeta potential of the nanoparticles before and after exposure to wastewater, researchers can evaluate the stability of the nanoparticles and the effectiveness of their surface modification strategies.

Nanocatalysts are complex materials that require a range of characterization techniques to fully understand their structure and properties. These techniques provide information about the morphology, size, composition, surface chemistry, and surface charge of the nanocatalyst, which are all important factors that can influence its performance in Fenton processes [3]. An important aspect of nanocatalysts is to identify and test a plethora of various parameters. For this purpose, some techniques SEM, XRD, XPS, TEM, scanning transmission electron microscopy mapping (STEM), energy-dispersive X-ray spectroscopy (EDX), or atomic force microscopy (AFM) are used, as shown in Figure 4.1.

Altogether, the combination of mentioned techniques provides a comprehensive understanding of the structure and properties of nanocatalysts, which is critical for optimizing their performance in Fenton processes. However, an in-operando techniques can provide real-time monitoring of the Fenton reaction, allowing for a more accurate understanding of the reaction mechanisms and the behavior of the catalyst under actual reaction conditions [73]. This can provide insight into the dynamic changes that occur during the Fenton reaction, such as changes in the surface structure, oxidation state, and composition of the catalyst. For example, in-operando spectroscopic techniques such as in-operando X-ray absorption spectroscopy (XAS) and in-operando Fourier-transform infrared spectroscopy (FTIR) can be used to

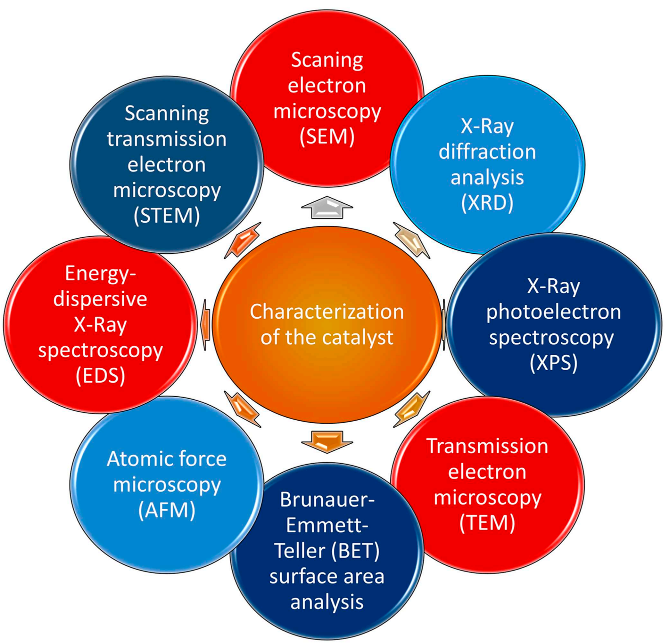

FIGURE 4.1 Techniques used for the characterization of Fenton nano-catalysts.

Source: Own work.

monitor the oxidation state of the catalyst and the evolution of reactive intermediates, such as hydroxyl radicals. In-operando transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM) can provide information on the changes in the catalyst morphology and structure during the reaction. Finally, in-operando techniques can provide a more complete understanding of the Fenton reaction mechanisms and the behavior of the catalyst, which can help to optimize the process and design more efficient catalysts.

SUMMARY

Iron-based Fenton processes have been demonstrated to be effective in removing a wide range of pollutants from wastewater. However, the use of traditional Fenton processes has limitations such as high operational costs and the need for large amounts of chemicals. Nanomaterials, due to their unique properties, offer great potential in enhancing the efficiency of Fenton processes. Nanomaterials can provide a higher surface area and increased reactivity compared to their bulk counterparts, leading to improved catalytic performance. Additionally, the controlled size and morphology of nanocatalysts can also play a significant role in their catalytic activity. Furthermore, the magnetic properties of some iron-based nanoparticles enable them to be easily separated from the treated water using a magnetic field, which makes them highly suitable for wastewater treatment applications. Despite the potential benefits, there are still challenges that need to be addressed in the use of nanomaterials for Fenton processes. These include the potential release of nanoparticles into the environment, the potential toxicity of certain nanoparticles to human health, and the need for cost-effective and scalable synthesis methods.

The potential release of nanoparticles into the environment is a major concern associated with the use of nanotechnology in various applications, including wastewater treatment using iron-based Fenton processes. The release of nanoparticles can occur at various stages of the process, such as during the synthesis, application, and disposal of the nanocatalysts. Once released into the environment, nanoparticles can interact with various environmental matrices, including water, soil, and air, and potentially affect the ecology and health of organisms. The small size and high surface area of nanoparticles can result in increased reactivity and toxicity compared to their bulk counterparts. Additionally, the physicochemical properties of nanoparticles can change depending on the environmental conditions, such as pH, temperature, and ionic strength, which can further affect their behavior and potential toxicity. Therefore, it is important to ensure that the release of nanoparticles is minimized and that the potential risks associated with their use are carefully evaluated. This includes implementing appropriate safety measures during the synthesis, handling, and disposal of nanoparticles, as well as conducting comprehensive environmental risk assessments to evaluate the potential impacts of their use on the environment [74].

The potential toxicity of certain nanoparticles to human health is an important concern in the field of nanotechnology. Nanoparticles have unique physicochemical properties, including a high surface area to volume ratio and increased reactivity, which can make them more toxic than their bulk counterparts. In particular, nanoparticles may have the ability to enter and accumulate in living cells, leading to potentially harmful interactions with cellular components and processes. Studies have shown that some nanoparticles, such as those made of certain metals or metal oxides, can cause oxidative stress and inflammation in cells, which may contribute to a range of adverse health effects. Other potential health concerns include genotoxicity, immunotoxicity, and carcinogenicity. However, it is important to note that not all nanoparticles are equally toxic, and the toxicity of a nanoparticle can depend on factors such as its size, shape, surface chemistry, and the specific biological system it is interacting with. In addition, advances in nanotoxicology research are helping to identify safe exposure levels and to develop strategies for mitigating potential health risks associated with nanoparticle exposure. Therefore, in terms of future directions, it is important to carefully evaluate the potential toxicity of nanoparticles and to implement appropriate safety measures to minimize the risk of harm to the environment and human health. Furthermore, studies could be conducted on the long-term effects of nanoparticles on the environment and human health to ensure their safe and sustainable use in wastewater treatment applications [34].

The cost-effective and scalable synthesis methods are crucial for the industrial-scale production of nanoparticulate iron-based catalysts for Fenton processes. While there are several methods available for the synthesis of these materials, some of them may not be suitable for large-scale production due to high cost or low scalability. Therefore, there is a need for the development of synthesis methods that can produce large quantities of catalysts at low cost. In addition to the cost and scalability, the synthesis methods should also be environmentally friendly, avoiding the use of hazardous chemicals or the generation of toxic waste. This would not only reduce the overall cost of production but also minimize the potential impact on the environment. Another important factor to consider is the reproducibility and consistency of the synthesis methods. The nanoparticulate iron-based catalysts should be produced with a high degree of uniformity in terms of particle size, morphology, and composition to ensure consistent performance in Fenton processes. Therefore, researchers are actively exploring new synthesis methods that are cost-effective, scalable, environmentally friendly, and produce nanoparticles with high reproducibility and consistency. These efforts would help to overcome the challenges associated with the industrial-scale production of nanoparticulate iron-based catalysts for Fenton processes and advance the application of these materials in wastewater treatment.

Research efforts could focus on developing environmentally friendly synthesis methods for nanocatalysts, as well as investigating the potential synergistic effects of combining different types of nanocatalysts. Investigating the potential synergistic effects of combining different types of nanocatalysts involves exploring the possibility of creating a nanocatalyst with enhanced efficiency for Fenton processes. This approach takes advantage of the unique properties of different nanocatalysts to create a composite nanocatalyst with superior catalytic activity, stability, and selectivity. For example, combining iron-based nanocatalysts with other nanomaterials such as carbon nanotubes or graphene oxide can lead to improved catalytic performance due to the synergistic effects between the two materials. Carbon nanotubes and graphene oxide have a high surface area, excellent conductivity, and strong adsorption capabilities, which can enhance the catalytic activity and stability of the iron-based nanocatalyst.

Combining different types of iron-based nanocatalysts with different crystal structures, sizes, and surface properties can lead to improved catalytic performance; for example, combining hematite and magnetite nanoparticles can lead to enhanced Fenton oxidation of pollutants due to the synergistic effects of the two materials. Hematite nanoparticles have a high surface area and strong adsorption capability, while magnetite nanoparticles have magnetic properties that allow for easy separation and recovery. However, investigating the potential synergistic effects of combining different types of nanocatalysts also requires careful consideration of the compatibility and stability of the different materials in the composite nanocatalyst. It is important to ensure that the different nanocatalysts do not interfere with each other's catalytic activity or stability and that they are compatible with the wastewater matrix. Furthermore, optimizing the synthesis process and the ratio of different nanocatalysts is necessary to obtain the maximum catalytic efficiency and stability of the composite nanocatalyst. Overall, investigating the potential synergistic effects of combining different types of nanocatalysts has the potential to significantly enhance the efficiency of iron-based Fenton processes for wastewater treatment and advance the field toward sustainable and cost-effective treatment solutions.

REFERENCES

1. Aghdasinia, H., et al., Pilot plant fluidized-bed reactor for degradation of basic blue 3 in heterogeneous fenton process in the presence of natural magnetite. *Environmental Progress & Sustainable Energy*, 2017. **36**(4): p. 1039–1048.
2. Guo, S., et al., Graphene modified iron sludge derived from homogeneous Fenton process as an efficient heterogeneous Fenton catalyst for degradation of organic pollutants. *Microporous and Mesoporous Materials*, 2017. **238**: p. 62–68.
3. Luo, T., et al., Efficient degradation of tetracycline by heterogeneous electro-Fenton process using Cu-doped Fe@Fe2O3: Mechanism and degradation pathway. *Chemical Engineering Journal*, 2020. **382**: p. 122970.
4. Zhao, X., et al., Removing organic contaminants with bifunctional iron modified rectorite as efficient adsorbent and visible light photo-Fenton catalyst. *J Hazard Mater*, 2012. **215–216**: p. 57–64.
5. Benzaquén, T.B., et al., Heterogeneous Fenton reaction for the treatment of ACE in residual waters of pharmacological origin using Fe-SBA-15 nanocomposites. *Molecular Catalysis*, 2020. **481**: p. 110239.
6. Khataee, A., et al., Preparation of nanostructured magnetite with plasma for degradation of a cationic textile dye by the heterogeneous Fenton process. *Journal of the Taiwan Institute of Chemical Engineers*, 2015. **53**: p. 132–139.
7. Akhavan, O. and R. Azimirad, Photocatalytic property of Fe2O3 nanograin chains coated by TiO2 nanolayer in visible light irradiation. *Applied Catalysis A: General*, 2009. **369**(1): p. 77–82.
8. Khataee, A.R., et al., Combined heterogeneous and homogeneous photodegradation of a dye using immobilized TiO2 nanophotocatalyst and modified graphite electrode with carbon nanotubes. *Journal of Molecular Catalysis A: Chemical*, 2012. **363–364**: p. 58–68.
9. Eshaq, G., et al., Superior performance of FeVO(4)@CeO(2) uniform core-shell nanostructures in heterogeneous Fenton-sonophotocatalytic degradation of 4-nitrophenol. *J Hazard Mater*, 2020. **382**: p. 121059.

10. Luo, W., et al., Efficient removal of organic pollutants with magnetic nanoscaled BiFeO3 as a reusable heterogeneous Fenton-like catalyst. *Environmental Science & Technology*, 2010. **44**(5): p. 1786–1791.
11. Garrido-Ramírez, E.G., et al., Characterization of nanostructured allophane clays and their use as support of iron species in a heterogeneous electro-Fenton system. *Applied Clay Science*, 2013. **86**: p. 153–161.
12. Hassani, A., et al., Preparation of magnetite nanoparticles by high-energy planetary ball mill and its application for ciprofloxacin degradation through heterogeneous Fenton process. *J Environ Manage*, 2018. **211**: p. 53–62.
13. Guo, H., et al., Degradation of chloramphenicol by pulsed discharge plasma with heterogeneous Fenton process using Fe3O4 nanocomposites. *Separation and Purification Technology*, 2020. **253**: p. 117540.
14. Wang, L., et al., Removal of chlorpheniramine in a nanoscale zero-valent iron induced heterogeneous Fenton system: Influencing factors and degradation intermediates. *Chemical Engineering Journal*, 2016. **284**: p. 1058–1067.
15. Wang, J. and J. Tang, Fe-based Fenton-like catalysts for water treatment: Preparation, characterization and modification. *Chemosphere*, 2021. **276**: p. 130177.
16. Taghizadeh, S.-M., et al., New perspectives on iron-based nanostructures. *Processes*, 2020. **8**(9): p. 1128.
17. Minella, M., et al., Photo-Fenton oxidation of phenol with magnetite as iron source. *Applied Catalysis B: Environmental*, 2014. **154–155**: p. 102–109.
18. Hussain, S., et al., Removal of organics from landfill leachate by heterogeneous Fenton-like oxidation over copper-based catalyst. *Catalysts*, 2022. **12**(3): p. 338.
19. Gholizadeh, A.M., et al., Phenazopyridine degradation by electro-Fenton process with magnetite nanoparticles-activated carbon cathode, artificial neural networks modeling. *Journal of Environmental Chemical Engineering*, 2021. **9**(1): p. 104999.
20. Wang, Y., et al., Goethite as an efficient heterogeneous Fenton catalyst for the degradation of methyl orange. *Catalysis Today*, 2015. **252**: p. 107–112.
21. Jaiswal, A., et al., Synthesis, characterization and application of goethite mineral as an adsorbent. *Journal of Environmental Chemical Engineering*, 2013. **1**(3): p. 281–289.
22. Mohapatra, M., et al., Removal of As(V) by Cu(II)-, Ni(II)-, or Co(II)-doped goethite samples. *Journal of Colloid and Interface Science*, 2006. **298**(1): p. 6–12.
23. Lai, J., S. Xuan, and K.C.-F. Leung, Tunable synthesis of hematite structures with nanoscale subunits for the heterogeneous photo-Fenton degradation of azo dyes. *ACS Applied Nano Materials*, 2022. **5**(10): p. 13768–13778.
24. Twinkle, et al., Graphene oxide (GO)/Copper doped Hematite (α-Fe2O3) nanoparticles for organic pollutants degradation applications at room temperature and neutral pH. *Materials Research Express*, 2019. **6**(11): p. 115026.
25. Zhu, Y., et al., Hydrothermal carbons/ferrihydrite heterogeneous Fenton catalysts with low H2O2 consumption and the effect of graphitization degrees. *Chemosphere*, 2022. **287**: p. 131933.
26. Fang, D., et al., Enhanced catalytic performance of β-FeOOH by coupling with single-walled carbon nanotubes in a visible-light-Fenton-like process. *Science and Engineering of Composite Materials*, 2018. **25**(1): p. 9–15.
27. Shi, X., et al., Stoichiometry-controlled synthesis of pyrite and greigite particles for photo-Fenton degradation catalysis. *New Journal of Chemistry*, 2022. **46**(29): p. 14205–14213.
28. Suryawanshi, P.L., et al., *Chapter 27 - Fenton with zero-valent iron nanoparticles (nZVI) processes: Role of nanomaterials*, in Handbook of Nanomaterials for Wastewater Treatment, B. Bhanvase, et al., Editors. 2021, Elsevier. p. 847–866.
29. Pasinszki, T. and M. Krebsz, Synthesis and application of zero-valent iron nanoparticles in water treatment, environmental remediation, catalysis, and their biological effects. *Nanomaterials*, 2020. **10**(5): p. 917.

30. Lefevre, E., et al., A review of the environmental implications of in situ remediation by nanoscale zero valent iron (nZVI): Behavior, transport and impacts on microbial communities. *Science of The Total Environment*, 2016. **565**: p. 889–901.
31. Guan, Z., et al., Application of novel amino-functionalized nzvi@sio2 nanoparticles to enhance anaerobic granular sludge removal of 2,4, 6-Trichlorophenol. *Bioinorganic Chemistry and Applications*, 2015. **2015**: p. 548961.
32. Yang, C., et al., Does soluble starch improve the removal of Cr(VI) by nZVI loaded on biochar? *Ecotoxicology and Environmental Safety*, 2021. **208**: p. 111552.
33. Chen, X., et al., Review on nano zerovalent iron (nZVI): from modification to environmental applications. *IOP Conference Series: Earth and Environmental Science*, 2017. **51**(1): p. 012004.
34. Duarte, F., et al., Treatment of textile effluents by the heterogeneous Fenton process in a continuous packed-bed reactor using Fe/activated carbon as catalyst. *Chemical Engineering Journal*, 2013. **232**: p. 34–41.
35. Stenzel, M.H., Remove organics by activated carbon adsorption. *Chemical Engineering Progress; (United States)*, 1993. **89**: 4.
36. De León, M.A., et al., Application of a montmorillonite clay modified with iron in photo-Fenton process. Comparison with goethite and nZVI. *Environmental Science and Pollution Research*, 2015. **22**(2): p. 864–869.
37. Yang, B., et al., Enhanced heterogeneous Fenton degradation of Methylene Blue by nanoscale zero valent iron (nZVI) assembled on magnetic Fe3O4/reduced graphene oxide. *Journal of Water Process Engineering*, 2015. **5**: p. 101–111.
38. Raji, M., et al., Nano zero-valent iron on activated carbon cloth support as Fenton-like catalyst for efficient color and COD removal from melanoidin wastewater. *Chemosphere*, 2021. **263**: p. 127945.
39. González-Bahamón, L.F., et al., Photo-Fenton degradation of resorcinol mediated by catalysts based on iron species supported on polymers. *Journal of Photochemistry and Photobiology A: Chemistry*, 2011. **217**(1): p. 201–206.
40. Wang, X., et al., Nanostructured semiconductor supported iron catalysts for heterogeneous photo-Fenton oxidation: a review. *Journal of Materials Chemistry A*, 2020. **8**(31): p. 15513–15546.
41. Shi, J., Z. Ai, and L. Zhang, Fe@Fe2O3 core-shell nanowires enhanced Fenton oxidation by accelerating the Fe(III)/Fe(II) cycles. *Water Res*, 2014. **59**: p. 145–153.
42. Huang, S., et al., Constructing magnetic catalysts with in-situ solid-liquid interfacial photo-Fenton-like reaction over Ag3PO4@NiFe2O4 composites. *Applied Catalysis B: Environmental*, 2018. **225**: p. 40–50.
43. Liu, Y., et al., Active magnetic Fe3+-doped BiOBr micromotors as efficient solar photo-fenton catalyst. *Journal of Cleaner Production*, 2020. **252**: p. 119573.
44. Oh, Y., et al., Divalent Fe atom coordination in two-dimensional microporous graphitic carbon nitride. *ACS Applied Materials & Interfaces*, 2016. **8**(38): p. 25438–25443.
45. Acisli, O., et al., Combination of ultrasonic and Fenton processes in the presence of magnetite nanostructures prepared by high energy planetary ball mill. *Ultrasonics Sonochemistry*, 2017. **34**: p. 754–762.
46. Yu, R.-F., et al., Monitoring of ORP, pH and DO in heterogeneous Fenton oxidation using nZVI as a catalyst for the treatment of azo-dye textile wastewater. *Journal of the Taiwan Institute of Chemical Engineers*, 2014. **45**(3): p. 947–954.
47. Zazo, J.A., et al., Intensification of the Fenton process by increasing the temperature. *Industrial & Engineering Chemistry Research*, 2011. **50**(2): p. 866–870.
48. Mohammad Reza, S., L. Mehdi Ghanbarzadeh, and O. Rabbani, Evaluation of the main parameters affecting the Fenton oxidation process in municipal landfill leachate treatment. *Waste Management & Research*, 2010. **29**(4): p. 397–405.

49. Litter, M.I. and M. Slodowicz, An overview on heterogeneous Fenton and photoFenton reactions using zerovalent iron materials. *Journal of Advanced Oxidation Technologies*, 2017. **20**(1).
50. Wibowo, A., et al., The influence of hydrogen peroxide concentration on catalytic activity of fenton catalyst@bacterial cellulose. *IOP Conference Series: Materials Science and Engineering*, 2019. **509**(1): p. 012020.
51. Chen, Q., et al., Where should Fenton go for the degradation of refractory organic contaminants in wastewater? *Water Research*, 2023. **229**: p. 119479.
52. Jinasan, A., et al., Highly active sustainable ferrocenated iron oxide nanocatalysts for the decolorization of methylene blue. *RSC Advances*, 2015. **5**(40): p. 31324–31328.
53. Zhao, Y., Z. Qiu, and J. Huang, Preparation and analysis of Fe_3O_4 magnetic nanoparticles used as targeted-drug carriers* *Supported by the technology project of Jiangxi Provincial education department and Jiangxi Provincial Science Department. *Chinese Journal of Chemical Engineering*, 2008. **16**(3): p. 451–455.
54. Yoshimura, M. and S. Somiya, Hydrothermal synthesis of crystallized nano-particles of rare earth-doped zirconia and hafnia. *Materials Chemistry and Physics*, 1999. **61**(1): p. 1–8.
55. Lester, E., et al., Reaction engineering: The supercritical water hydrothermal synthesis of nano-particles. *Journal of Supercritical Fluids*, 2006. **37**(2): p. 209–214.
56. Huber, D.L., Synthesis, properties, and applications of iron nanoparticles. *Small*, 2005. **1**(5): p. 482–501.
57. Qin, L., et al., Spherical Zvi/Mn-C bimetallic catalysts for efficient Fenton-like reaction under mild conditions. *Catalysts*, 2022. **12**(4): p. 444.
58. Zanchettin, G., et al., High performance magnetically recoverable Fe3O4 nanocatalysts: fast microwave synthesis and photo-fenton catalysis under visible-light. *Chemical Engineering and Processing - Process Intensification*, 2021. **166**: p. 108438.
59. Yuan, Y., L. Wang, and L. Gao, Nano-sized iron sulfide: structure, synthesis, properties, and biomedical applications. *Frontiers in Chemistry*, 2020. **8**.
60. Bañ Uelos, J., et al., Electrochemically prepared iron-modified activated carbon electrodes for their application in electro-Fenton and photoelectro-Fenton processes. *Journal of The Electrochemical Society*, 2015. **162**: p. E154–E159.
61. Bhatti, H.N., et al., Biocomposite application for the phosphate ions removal in aqueous medium. *Journal of Materials Research and Technology*, 2018. **7**(3): p. 300–307.
62. Kausar, A., et al., Preparation and characterization of chitosan/clay composite for direct Rose FRN dye removal from aqueous media: comparison of linear and non-linear regression methods. *Journal of Materials Research and Technology*, 2019. **8**(1): p. 1161–1174.
63. Remya, V.R., et al., Silver nanoparticles green synthesis: A mini review. *Chemistry International*, 2017. **2**: p. 165–171.
64. Roh, Y., et al., Microbial synthesis and the characterization of metal-substituted magnetites. *Solid State Communications*, 2001. **118**(10): p. 529–534.
65. Mandal, D., et al., The use of microorganisms for the formation of metal nanoparticles and their application. *Appl Microbiol Biotechnol*, 2006. **69**(5): p. 485–492.
66. Bibi, I., et al., Nickel nanoparticle synthesis using Camellia Sinensis as reducing and capping agent: Growth mechanism and photo-catalytic activity evaluation. *Int J Biol Macromol*, 2017. **103**: p. 783–790.
67. Recio Sánchez, G., et al., Leaf extract from the endemic plant Peumus boldus as an effective bioproduct for the green synthesis of silver nanoparticles. *Materials Letters*, 2016. **183**.
68. Muthulakshmi, L., et al., Preparation and properties of cellulose nanocomposite films with in situ generated copper nanoparticles using Terminalia catappa leaf extract. *International Journal of Biological Macromolecules*, 2017. **95**: p. 1064–1071.

69. Truskewycz, A., R. Shukla, and A.S. Ball, Iron nanoparticles synthesized using green tea extracts for the fenton-like degradation of concentrated dye mixtures at elevated temperatures. *Journal of Environmental Chemical Engineering*, 2016. **4**(4, Part A): p. 4409–4417.
70. Kajani, A.A., et al., Anticancer effects of silver nanoparticles encapsulated by Taxus baccata extracts. *Journal of Molecular Liquids*, 2016. **223**: p. 549–556.
71. Bibi, I., et al., Green synthesis of iron oxide nanoparticles using pomegranate seeds extract and photocatalytic activity evaluation for the degradation of textile dye. *Journal of Materials Research and Technology*, 2019. **8**(6): p. 6115–6124.
72. Bury, D., et al., Photocatalytic activity of the oxidation stabilized $Ti_3C_2T_x$ MXene in decomposing methylene blue, bromocresol green and commercial textile dye. *Small Methods*, 2023. **7**: p. 2201252.
73. Yang, Z., et al., Identification and understanding of active sites of non-noble iron-nitrogen-carbon catalysts for oxygen reduction electrocatalysis. *Advanced Functional Materials*. **n/a**(n/a): p. 2215185.
74. Barnes, R.J., et al., The impact of zero-valent iron nanoparticles on a river water bacterial community. *Journal of Hazardous Materials*, 2010. **184**(1): p. 73–80.