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Chapter 8

Fenton, Photo-Fenton, and Electro-Fenton systems for micro-pollutant treatment processes

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Abstract:

The existence of micropollutants in ground and surface water indicates the limitation of conventional wastewater treatment processes. Advanced oxidation process, particularly the Fenton process, could be a promising solution to get rid of these emerging contaminants. Fenton chemistry and related technologies, such as electro Fenton and the photo Fenton process, have demonstrated enormous potential for the future. In this chapter, we attempted to describe the complex mechanisms behind the Fenton and modified Fenton processes, as well as the critical parameters affecting their efficacy in removing organic micropollutants from wastewater. A considerable effort has been made to enlighten the reader on current state-of-the-art technology, the breadth of possible applications, and the remaining barriers to the commercialization of these processes for the elimination of emerging contaminants from water.

1. Introduction

Ubiquitous existence of micropollutants in the aquatic environment has become a matter of serious concern in the last few decades. These micropollutants include a wide variety of industrial chemicals, personal care products, pharmaceuticals, pesticides, UV filters, flame retardants, surfactants, and other endocrine-disrupting substances [1][2]. Most of these micropollutants are organic in nature and their existence in the environment is detected in the range of ng/l to μg/l [3]. Even though the detrimental impact of micropollutants on human health, aquatic life, and the ecosystem is still under investigation or completely unknown in some cases, their existence has been repeatedly attributed to several negative consequences, including short-term and long-term toxicity, endocrine disruption, and antibiotic resistance of microbes [2].

Most of the wastewater treatment plants operating currently are capable of reducing the concentrations of a wide range of micropollutants but they are not designed to eliminate them entirely. As a result, effluent from these wastewater treatment plants is one of the primary sources of micropollutants, which are typically discharged into surface waterways and eventually end up in soil, groundwater and the ocean [4]. The use of separation-based technologies, such as adsorption and membrane filtration (nanofiltration and reverse osmosis), due to their ease of operation and simplicity, are often adopted for the purpose of water purification. However, such technologies are merely phase transfer methods, which do not decompose or completely mineralize the micropollutants. As a result, micropollutants may persist in the system and ultimately reach the surrounding environment if the contaminated adsorbents or membrane concentrates are not adequately handled.

Advanced oxidation processes, on the other hand, are innovative treatment technologies intended to degrade and even totally mineralize refractory organic micropollutants in the aqueous phase by reacting with hydroxyl radicals (•OH). These radicals can be produced in situ by employing a primary oxidant (e.g., hydrogen peroxide and ozone), UV light, electrochemical techniques or a combination of these processes. The in situ generated •OH radicals have a very high oxidation potential (2.8 V) and are therefore capable of oxidizing a wide range of organic molecules in water. Over 1700 rate constants for •OH mediated reactions with organic and inorganic compounds in aqueous solution have been listed in the last few decades, recognizing their relevance in the natural environment, biological systems and beneficial chemical processes such as waste valorization.

A prominent example of a homogeneous AOP is Fenton's oxidation, in which Fe^{2+} ions act as the catalyst and H_2O_2 serves as the oxidant. The key benefits of the Fenton process over other oxidation techniques are the simplicity of equipment, ambient operating conditions and ease of integration with existing water treatment facilities. Unlike other common oxidants, Fenton reagents (Fe^{2+} and H_2O_2) are affordable, safe, and easy to handle, and do not pose any long-term environmental risks. Compared to all other AOPs, HO• production is relatively faster due to the rapid interaction between Fe^{2+} and H_2O_2. In this chapter, we endeavored to explain the complicated mechanisms of Fenton and modified Fenton processes, as well as the important factors that influence their effectiveness in removing organic micropollutants from the wastewater. A sincere attempt was made to provide the reader with information on state-of-the-art technology, the extent of potential applications and remaining obstacles to the development of these processes on a larger scale.

2. Classical Fenton Process

Fenton chemistry began in 1876, when Henry J. Fenton for first time observed the degradation of tartaric acid by hydrogen peroxide (H_2O_2) in the presence of ferrous ions (Fe^{2+}) [5][6]. Later in the 1930s, Haber and Weiss postulated that the catalytic breakdown of H_2O_2 by iron salt (Fe^{2+}) generates hydroxyl radicals (•OH), one of the most powerful oxidants known ($E° = 2.73V$) [7]'[8]. Since then, Fenton and related reactions have attracted a lot of attention because of their importance in synthesis and functionalization of materials, hazardous waste minimization, biomass treatment and biomedical application particularly in cancer treatment and dental care [9].

Generally, the mixture of H_2O_2 and Fe^{2+} is known as Fenton's reagent which generates •OH radical according to the following reaction [6][10][11]:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \bullet OH + OH^- \ (k = 63\text{-}76\ M^{-1}s^{-1}) \qquad (1)$$

The breakdown of H_2O_2 is initiated and catalyzed by Fe^{2+} ion in acidic media, which results in the formation of •OH. Chemical probes or spectroscopic techniques such as spin trapping can be used to confirm the formation of •OH in the Fenton process. The *in-situ* generated •OH interacts with the organic molecules via one of two mechanisms: hydroxyl addition or hydrogen abstraction [12]. Organic molecules with an aromatic system or numerous carbon-carbon bonds experience hydroxyl addition (Eq. 2), whereas unsaturated organic compounds undergo hydrogen abstraction (Eq. 3).

$\bullet OH + R \rightarrow R(OH)^{\cdot}$ (2)

$\bullet OH + RH \rightarrow R + H_2O$ (3)

In the absence of competitive scavenging of either •OH or $R^{\bullet}$, using a suitable concentration of Fe^{2+} and H_2O_2 should theoretically convert all organic molecules to carbon dioxide and water. However, the enhanced and non-specific reactivity of •OH towards both organic and inorganic molecules result in several undesired and competing reactions (Eq. 4-7) that can sabotage the oxidation efficiency of the Fenton process.

$Fe^{2+} + \bullet OH \rightarrow Fe^{3+} + OH^{-}$ ($k = 3.2 \times 10^{8}\ M^{-1}s^{-1}$) (4)

$H_2O_2 + \bullet OH \rightarrow \bullet O_2H + H_2O$ ($k = 3.3 \times 10^{7}\ M^{-1}s^{-1}$) (5)

$\bullet O_2H + \bullet OH \rightarrow + H_2O + O_2$ ($k = 6.6 \times 10^{11}\ M^{-1}s^{-1}$) (6)

$\bullet OH + \bullet OH \rightarrow H_2O_2$ ($k = 6 \times 10^{9}\ M^{-1}s^{-1}$) (7)

The regeneration of Fe^{2+} takes place by the reaction between H_2O_2 and the generated Fe^{3+} from the Fenton reaction. This reaction is known as Fenton like reaction and represented by the following reaction:

$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + \bullet O_2H + H^{+}$ ($k = 0.001\text{-}0.01\ M^{-1}s^{-1}$) (8)

As can be observed, the regeneration of Fe^{2+} by Fenton like reaction is much slower (~6000 times) than the Fenton reaction (Eq. 1). Fortunately, the reduction of Fe^{3+} with $\bullet O_2H$ from reaction (9), a superoxide ion ($O_2^{\bullet -}$) from reaction (10) or an organic radical $R^{\bullet}$ from reaction (11) can regenerate Fe^{2+} more rapidly.

$Fe^{3+} + \bullet O_2H \rightarrow Fe^{2+} + O_2 + H^{+}$ ($k = 2 \times 10^{3}\ M^{-1}s^{-1}$) (9)

$Fe^{3+} + O_2^{\bullet -} \rightarrow Fe^{2+} + O_2$ ($k = 5 \times 10^{7}\ M^{-1}s^{-1}$) (10)

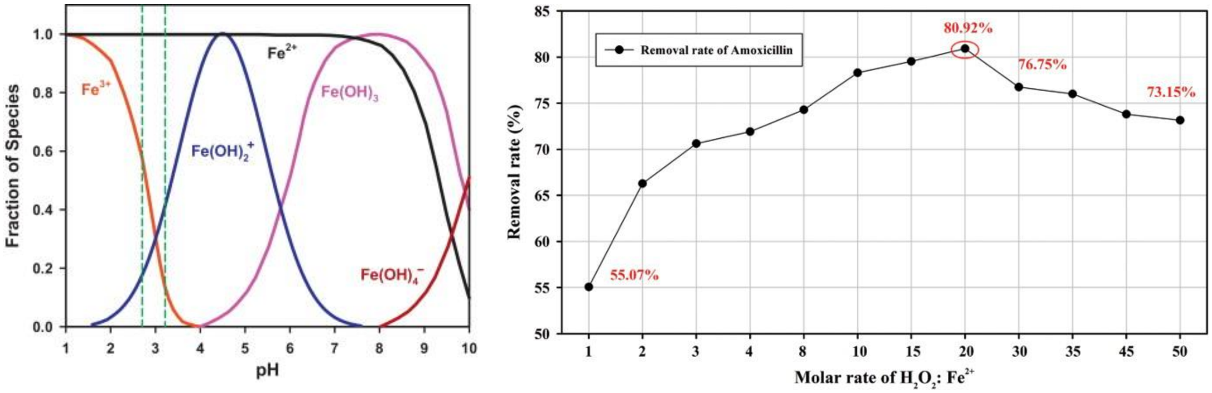
$Fe^{3+} + R^{\bullet} \rightarrow Fe^{2+} + R^{+}$ (11)

There are few rate constants available for reaction (11), however the most reactive species are tertiary alkyl radicals and radicals α to -OH, -OR or -CONH₂, which have k values of 10^7-10^8 $M^{-1}s^{-1}$.

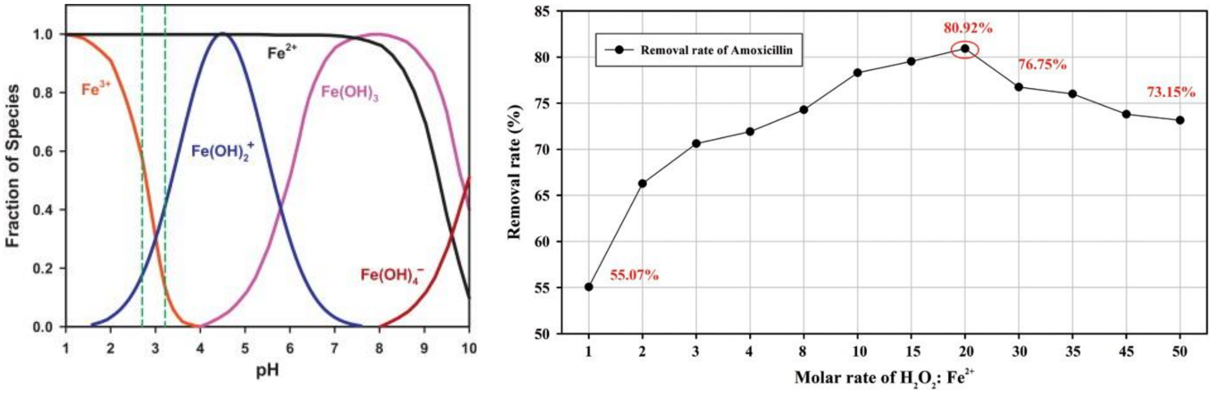
2.1. Factors affecting the efficiency of Fenton process

2.1.1. Operating pH

The pH of the reaction medium plays an essential role in the Fenton process as it affects the form of iron species and their catalytic activity to produce •OH. The speciation of iron species (Fe^{2+} and Fe^{3+}) as a function of pH is presented in Figure 1 (a).



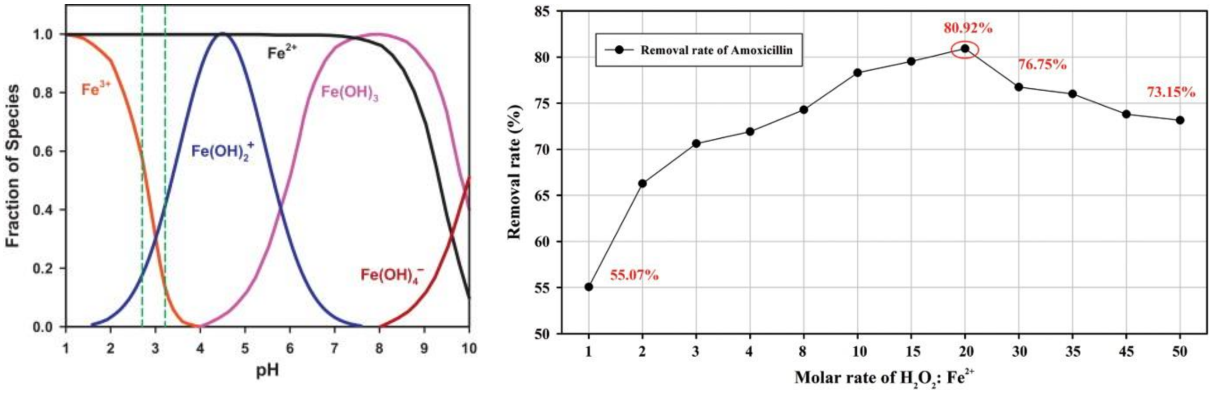
(a) (b)



(a) (b)

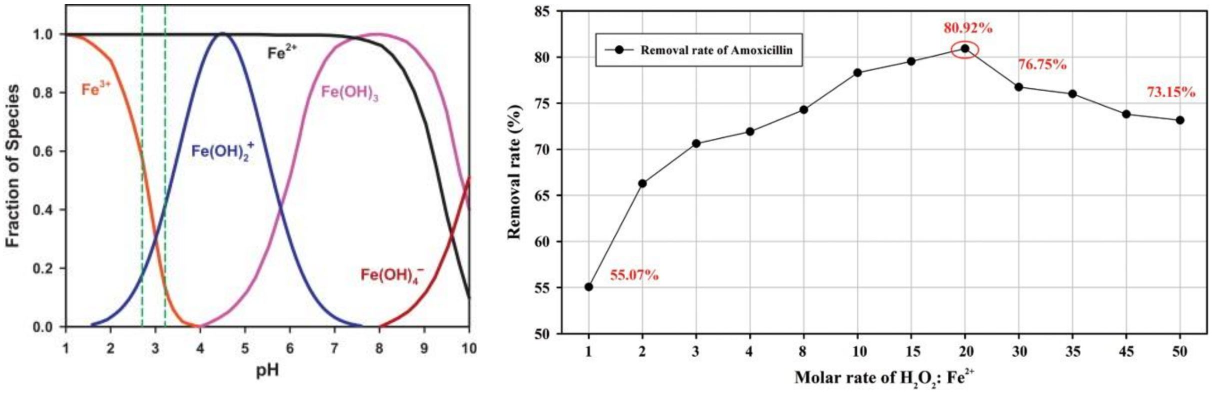
Figure 1: (a) Speciation of iron species as a function of solution pH. The optimum working range of pH for Fenton reaction is indicated by the dotted line, adapted from [13] with permission. (b) Effect of H_2O_2/Fe^{2+} molar ratio on amoxicillin removal, adapted from [14] with permission.

As can be seen in



(a) (b)

Figure 1 (a), Fe^{2+} remains in dissolved form up to neutral pH. Therefore, the fact why the optimum pH for Fenton reaction is 3 cannot be explained from Fe^{2+} speciation. During the Fenton process Fe^{3+} generates and it can be seen in



(a) (b)

Figure 1 that Fe^{3+} vanishes at pH 4 and begins to precipitate as $Fe(OH)_3$. When both ions (Fe^{2+} and Fe^{3+}) are present together and pH is raised above 3, the Fe^{2+} tends to coprecipitate with ferric oxyhydroxides, reducing the amount of active catalyst in the solution. In addition, with increasing pH, the oxidation potential of •OH diminishes. At pH 0, the oxidation potential of the redox couple $\bullet OH/H_2O$ is 2.59 V vs NHE, while at pH 14, it is 1.64 V vs NHE [15]. Moreover, auto decomposition of H_2O_2 into O_2 and H_2O takes place at higher pH. On the other hand, a reduction in the degradation efficiency of the organic contaminants by the Fenton process was observed below pH 3. This is because at lower pH, Fe (II) exists as the hexaquo complex, $[Fe(H_2O)_6]^{2+}$ and it interacts with H_2O_2 more slowly than other species. Furthermore, in the presence of excess H^+ ions, the peroxide is solubilized to produce the stable oxonium ion, $[H_3O_2]^+$, which is more stable and hinders the reactivity of Fe^{2+} with H_2O_2 [16]. Therefore, under a suitable pH, usually in the range of 2.8–3.2, the production of •OH and subsequent breakdown of pollutants via Fenton oxidation is efficient. To ensure that ferrous and ferric irons keep their catalytic activity, the pH of the solution must be kept within this range.

2.1.2. Fe^{2+} concentration

In the Fenton process, Fe^{2+} catalyzes the breakdown of H_2O_2 to create highly oxidative •OH, which may destroy even the most recalcitrant organic contaminants. The degradation efficiency of the organic contaminants usually improves as Fe^{2+} concentration rises; however, the excess amount of Fe^{2+} not only raises the operating expenses and iron sludge formation but it also raises the possibility of •OH scavenging, which results in a detrimental impact of Fenton reaction on organic contaminants degradation. Therefore, the determination of the optimum Fe^{2+} concentration is essential in order to achieve the maximum degradation of organic contaminants. For various organic compounds, the optimum concentration may differ and must be established experimentally. For example, Kavitha and Palanivelu studied Fenton process for nitrophenols degradation and observed that the optimum Fe^{2+} concentration for the maximum degradation of mono nitrophenol was 0.45 mM, while for di and tri-nitro phenol it was 0.36 mM [17].

2.1.3. H_2O_2 concentration

The initial concentration of H_2O_2, like that of Fe^{2+}, is a key factor in the degradation of organic contaminants by Fenton process. When the concentration of H_2O_2 increases, the degradation efficiency of organic contaminants usually improves. However, increasing the amount of H_2O_2 beyond the optimal limit has an adverse effect on the conversion efficiency, which might be due to the auto decomposition of H_2O_2 to O_2 and H_2O and the recombination of •OH and $•O_2H$ (Eq 6). Furthermore, an excess amount of H_2O_2 serves as a free radical scavenger, reducing the system's oxidation power (Eq. 5) [16].

2.1.4. Stoichiometric ratio of Fe^{2+}/H_2O_2

Besides the initial concentration of Fenton reagents (Fe^{2+} and H_2O_2), their stoichiometric ratio is also an important parameter that determines the degradation efficiency of organic micropollutants.

The optimal ratio of Fe^{2+} to H_2O_2 is usually determined from the laboratory scale study. A high Fe^{2+}/H_2O_2 ratio promotes the decomposition of H_2O_2 to •OH; however, it may not improve the mineralization degree due to scavenging reactions (Eq. 4, 7). Similarly, a lower ratio of Fe^{2+}/H_2O_2 means excess amount of H_2O_2 which can also promote the scavenging of •OH (Eq. 5) and reduce the efficiency of Fenton process. Guo et al. studied the amoxicillin removal using Fenton oxidation process and showed that the maximum removal was obtained at a molar ratio of $Fe^{2+}/H_2O_2 = 1/20$ (Figure 1 (b)) [14]. Beyond that optimum ratio up to 1/50 the removal efficiency of amoxicillin decreased from 80.92% to 73.15%.

2.1.5. Operating temperature

In Fenton process, increasing the temperature speeds up the reaction between H_2O_2 and Fe^{2+}, resulting in a high rate of •OH production. More •OH radicals could potentially encourage collisions with organic contaminants, improving degradation efficiency. For example, Zazo et al. [18] reported that when the reaction temperature raised from 25 °C to 90 °C in a homogeneous Fenton process, the mineralization efficiency of phenol increased from 28% to 80%. Further increase in temperature up to 130 °C did not improve the mineralization efficiency significantly. This is because at higher temperature the spontaneous breakdown of H_2O_2 and Fe^{2+} precipitation takes place. In another study it has been reported that the removal rate of amoxicillin improved from 74.02% to 80.02% as the temperature increased from 30 °C to 40 °C [14]. Therefore, maintaining an appropriate temperature should be evaluated based on the target pollutants to be treated.

2.2. Catalysts for Fenton process

2.2.1. Homogeneous vs heterogeneous

In homogeneous Fenton process, both Fenton reagents (Fe^{2+} & H_2O_2) exist in the same phase. Therefore, the system shows negligible mass transfer restriction, which allows easily accessible iron ions in the reaction media to participate efficiently in the degradation process. However, there are some limitations in homogeneous Fenton process, which includes narrow pH range, loss of Fe^{2+} due to poor regeneration kinetics and generation of iron sludge which further increases the operating costs of Fenton process. These limitations can be overcome to some extent by employing heterogeneous iron catalysts, where iron is stabilized inside the interlayer space of the catalyst's structure and may efficiently generate •OH from H_2O_2 oxidation under non-controlled pH environments.

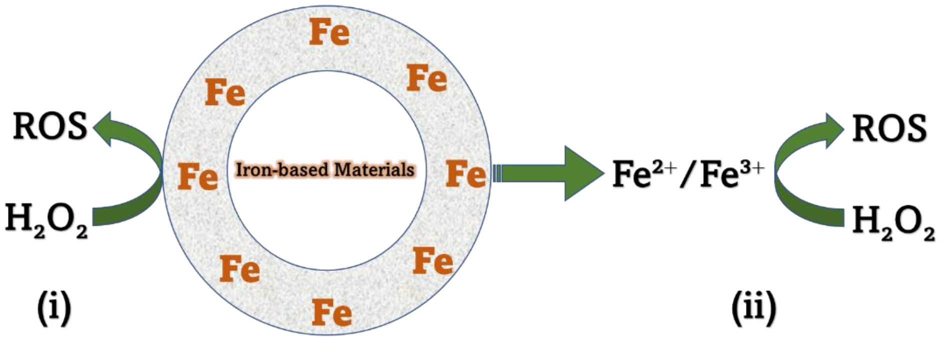


Figure 2: Schematic representation of the heterogeneous Fenton system: i. true heterogeneous catalytic reaction mechanism and ii. surface-leached iron mediated homogeneous reaction mechanism. ROS = reactive oxygen species.

Two possible reaction routes have been proposed to describe the reaction mechanism between heterogeneous Fe catalysts and H_2O_2 (Figure 2): i) the actual heterogeneous catalytic mechanism where the reactions take place at the catalytic surface bounded on a support and (ii) the homogeneous catalytic mechanism where Fe species leached out from the support material and the reaction takes place in the bulk solution. Heterogeneous Fenton reactions are generally regulated by kinetic processes such as reactant adsorption, surface chemical reaction and product desorption. On the other hand, especially at acidic pH, certain iron-based compounds can contribute to a homogeneous Fenton reaction dominated mechanism by serving as a source of continuous iron dissolution. However, leaching depletes the metal sites in the solid catalyst, resulting in the loss of catalytic activity over time. Lin and Gurol [19] studied the reaction of H_2O_2 on a solid iron oxide catalysts (goethite) in 1998 and proposed a widely accepted reaction mechanism for the heterogeneous catalytic breakdown of H_2O_2. In brief, H_2O_2 forms a primary surface complex, $(H_2O_2)_s$, with its interaction at goethite (≡Fe(III)) surface (Eq. 12). Within the complex, charge transfer from ligand to metal create a transitional state for the surface site (≡Fe(II)•O_2H), which is further deactivated by dissociation of the •O_2H (Eq. 13 & 14). Then, the formed ≡Fe(II) site catalyzes the formation of •OH (Eq. (15)) and the ≡Fe(III) surface regenerates.

$$\equiv Fe(III)\text{-}OH + H_2O_2 \leftrightarrow (H_2O_2)_s \quad (12)$$

$$(H_2O_2)_s \leftrightarrow \equiv Fe(II)\bullet O_2H + H_2O \quad (13)$$

$$\equiv Fe(II)\bullet O_2H \rightarrow \equiv Fe(II) + \bullet O_2H \quad (14)$$

$$\equiv Fe(II) + H_2O_2 \rightarrow \equiv Fe(III)\text{-}OH + \bullet OH \quad (15)$$

A two-step degradation process is observed in several heterogeneous Fenton systems, with an initial sluggish induction period followed by a fast oxidation period. The induction period, according to the researchers, is characterized by heterogeneous reactions such as surface iron leaching and heterogeneous catalysis, with the second kinetic stage characterized by homogeneous Fenton reactions caused by the leached iron [20][21].

One of the primary advantages of heterogeneous Fenton process over homogeneous Fenton process is the overall stability and reusability of the iron catalysts. The iron concentration in solution decreased with reaction time in case of homogeneous Fenton process owing to iron sludge formation. Furthermore, it is extremely difficult to separate the remaining ferrous ions since they are all homogeneously dissolved in water. On the other hand, all catalysts are solid in case of heterogeneous Fenton process, making separation from solution very simple.

2.2.2. Heterogeneous Fe catalysts

There are a wide variety of iron-based materials that are stable and only experience little iron leaching when subjected to reactions. Iron-based materials have the benefits of having a high Fenton activity, being inexpensive, having minimal toxicity, and being simple to recover.

2.2.2.1. Zero-valent Iron:

Zero-valent iron (ZVI) is a very effective reducing agent with a typical reduction potential of E^0 (Fe^{2+}/Fe^0) = -0.44V. In the presence of H_2O_2 or O_2, ZVI can release two electrons resulting in the formation of Fe^{2+} ions (Eq. 16 & 17). The generated Fe^{2+} ions are responsible for effective organic pollutant degradation either through a homogeneous Fenton mechanism (at pH 2-3) or via heterogeneous reaction-induced homogeneous process (at pH 4-6). ZVI continues to dissolve in the second stage of the heterogeneous reaction-induced homogeneous mechanism, largely by Fe^{3+} reduction (Eq. 18), which speeds up Fe^{2+} regeneration in the homogeneous Fenton reaction.

$Fe^0 + O_2 + 2H^+ \rightarrow Fe(II) + H_2O_2$ (16)

$Fe^0 + H_2O_2 + 2H^+ \rightarrow Fe(II) + 2H_2O$ (17)

$2Fe^{3+} + Fe^0 \rightarrow 3Fe^{2+}$ (18)

2.2.2.2. Magnetite:

Magnetite (Fe_3O_4) is a mixed-valence iron oxide that belongs to the spinel family and has special redox characteristics. Fe_3O_4 is the most magnetic of all the naturally occurring minerals on the planet. Fe_3O_4 has attracted a lot of attention in heterogeneous Fenton systems because of its structural ferrous ions, which are crucial in accelerating the production of •OH. Furthermore, magnetic separation may be used to rapidly remove Fe_3O_4 particles from an aqueous media after their catalytic purification application. pH, on the other hand, may influence the interfacial mechanism of Fe_3O_4-catalyzed heterogeneous Fenton systems as a result of Fe_3O_4 dissolution. Fe_3O_4 nanoparticles have high stability and reusability at neutral pH, owing to a heterogeneous catalytic reaction mechanism. However, at pH 3, organic pollutants are degraded by a heterogeneous reaction induced homogeneous mechanism. Furthermore, the activity of Fe_3O_4 nanoparticles reduce gradually over the duration of several runs, most likely because of the leached iron as well as other factors such as active catalytic sites poisoning by adsorbed organic species or surface oxidation.

2.2.2.3. Goethite:

Goethite is an iron (III) oxide mineral, with chemical formula Fe^{III}-O(OH), found abundantly in soil and other low-temperature environments. It is one of the commonly used iron oxides in Fenton process for the degradation of the organic contaminants. Goethite has received considerable interest as heterogeneous Fenton catalyst due to its i. ability to operate in a wide pH range, ii. higher thermodynamic stability, iii. positive performance under sunlight and iv. low cost and environmental friendliness. Based on the experimental evidence, a goethite catalyst appeared to be effective in the photo Fenton process in the presence of sun light [22].

2.2.2.4. Hematite:

Hematite (α-Fe_2O_3) is the most stable Fe(III) oxide ore and is found in a variety of forms, including kidney ore, iron rose, martite and specularite. It’s color ranges from black to steel or silver-grey, brown to reddish-brown [23]. In recent years, there has been considerable interest in hematite as a heterogeneous Fenton catalyst because it is (i) an inexpensive and readily available mineral (ii) non-toxic and environmentally benign. With its high surface area, distinct morphology and well-defined topology, hematite exhibits relatively high catalytic performance and stability. Huang and co-workers [24] showed that the {001} facet exposed hematite nanoplates had higher Fenton catalytic performance than the {002} exposed facet hematite nano cubes. The development of iron-ascorbate complexes on the facets of the hematite can considerably limit the dissolution of surface bound Fe^{2+} ions, resulting in greater stability and increased catalytic efficiency of hematite. Moreover, hematite can absorb light up to 560 nm and capture about 40% of the solar spectrum energy due to its small bandgap (2.2 eV), making it a potential material for photo-Fenton catalytic applications [25].

2.2.2.5. Ferrihydrite:

Ferrihydrite is a naturally occurring Fe (III) hydroxide with a large specific surface area (> 200 m^2/g) and numerous chemically active surface groups found in the earth crust, soils and sediments [26]. The large surface area of ferrihydrite results in more interaction between the catalyst, H_2O_2 and the contaminants when it is employed as a heterogeneous Fenton catalyst, improving the effectiveness of H_2O_2 activation and therefore the oxidation of organic micropollutants. Huang et al. [27] conducted a comparative investigation of catalytic effectiveness in the decomposition of H_2O_2 using various iron (III) oxides. The maximum activity was obtained with amorphous ferrihydrite, which had the largest surface area, followed by crystalline oxides needle-like goethite and plate-like hematite, which had the lowest surface area.

2.2.2.6. Pyrite:

Pyrite (FeS_2), being one of the most common sulfide minerals with a high ferrous content, can be considered as an ideal heterogeneous Fenton reagent for decomposing H_2O_2 to oxidize organic pollutants [28]. The use of FeS_2, being a natural source of Fe^{2+} and H^+ ions, brings several benefits to the Fenton process. In fact, dissolved oxygen in aqueous solutions oxidizes FeS_2, resulting in the formation of Fe^{2+} and H^+ ions (Eq. 19). The *in situ* generated Fe^{2+} reacts with H_2O_2 according to classic Fenton reaction. Meanwhile, FeS_2 interacts with H_2O_2 to form Fe^{3+} through reaction (Eq. 20), which is subsequently reduced to Fe^{2+} by reaction (Eq. 21). As a result, both the production and regeneration of Fe^{2+} by FeS_2 result in a Fenton process that is self-regulatory [29][30].

$2FeS_2 + 7O_2 + 2H_2O \rightarrow 2Fe^{2+} + 4SO_4^{2-} + 4H^+$ (19)

$2FeS_2 + 15H_2O_2 \rightarrow 2Fe^{3+} + 14H_2O + 4SO_4^{2-} + 2H^+$ (20)

$2FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 2Fe^{2+} + 2SO_4^{2-} + 16H^+$ (21)

2.2.2.7. Ferrite

The interaction of iron oxides with other transition metals result in the formation of ferrites, which are recognized as ceramic compounds. Ferrites are categorized as spinel, garnet or hexagonal ferrites depending on their crystal forms. Spinel ferrites, in particular, have attracted a considerable attention as a heterogeneous Fenton catalyst for the elimination of different organic contaminants [23]. It has a face-centered cubic lattice with the general formula $M_xFe_{3-x}O_4$ (where M denotes bivalent metal ions such as Cu, Mn, Co, Zn etc.), in which oxide ions are organized in a face-centered cubic fashion, while metal ions are distributed in tetrahedral and octahedral positions. Wang et al. [31] developed mesoporous copper ferrite ($CuFe_2O_4$) for the degradation of imidacloprid using the heterogeneous Fenton process. Template assisted fabrication of $CuFeS_2$ exhibited high surface area and porosity, which contributed to the high number of catalytically active sites and enhanced production of OH radicals. Moreover, the thermodynamic suitability of Fe^{3+} reduction by Cu^+ promoted the redox recycle of Fe^{2+}/Fe^{3+} and Cu^+/Cu^{2+} in mesoporous $CuFe_2O_4$.

2.2.3. Non-ferrous heterogeneous catalysts

Besides the heterogeneous Fe catalysts, several other materials with multiple oxidation states and redox stability are employed to decompose H_2O_2 via Fenton like reaction mechanisms. Zero-valent aluminum (ZVAl), cerium, chromium, manganese, copper and ruthenium have recently gained significant interest as Fenton catalysts due to their ability to operate over a wider pH range and the high chemical stability. Although the specific method of activation is significantly reliant on the type of catalyst, it is largely controlled by the pH of the solution or the presence of metal-ligand complexes. Apart from that, the pH-dependent dual function of H_2O_2 as both oxidant and reductant makes redox transformation of these non-ferrous metal species simple [13].

2.2.3.1. Aluminum

Aqueous solution of aluminum contains just one oxidation state, Al^{3+}. Consequently, unlike in the case of iron, which can exist in both the Fe^{2+} and Fe^{3+} forms, there is no possibility of an electron transfer process between Al^{3+} and H_2O_2. However, zero-valent aluminum (ZVAl or Al^o), a strong reducing agent with a reduction potential of E^o (Al^{3+}/Al^o) = -1.66V, offers a considerably higher thermodynamic driving force for the decomposition of H_2O_2. In 2009, Bokare and Choi[32] for the first time demonstrated the generation of •OH by zero-valent aluminum (ZVAl) in a Fenton-like process. Under acidic conditions, the native surface Al_2O_3 layer on ZVAl was dissolved to expose the bare Al^o surface (Eq. 19). In the presence of dissolved O_2, electron transfer from ZVAl resulted in the *in-situ* production of H_2O_2 (Eq. 20 & 21) and the subsequent breakdown into •OH (Eq. 22), which further triggered the oxidative mineralization of organic contaminants like phenol, 4-chlorophenol, nitrobenzene and dichloroacetate.

$$Al^o \rightarrow Al^{3+} + 3e^- \qquad (22)$$

$$O_2 + H^+ + e^- \rightarrow \bullet O_2H \qquad (23)$$

$$2(\bullet O_2H) \rightarrow H_2O_2 + O_2 \qquad (24)$$

$$Al^o + 3H_2O_2 \rightarrow Al^{3+} + 3HO\bullet + 3OH^- \qquad (25)$$

Several noteworthy features of ZVAl's usage to decompose H_2O_2 into •OH and subsequent contaminants oxidation include its high natural availability and low weight. In addition, higher reduction potential and enhanced water solubility of Al^{3+}-species result in a considerably higher oxidative ability of ZVAl aerobic system compared to Fe-based one [32]. However, it is not feasible to employ ZVAl-based AOP systems to treat the organic contaminants in non-acidic environment due to the inefficient removal of Al_2O_3 surface layer under neutral or near neutral pH environment.

2.2.3.2. Cerium

Cerium is the only metal in the lanthanide or rare-earth group that exhibits both +3 and +4 oxidation states in solution. In alkaline conditions, the cerous (Ce^{3+}) form is a powerful reducing agent, whereas in acidic conditions, the ceric (Ce^{4+}) form is a powerful oxidant. Therefore, under appropriate redox environment, cerium can effectively cycle between Ce^{3+} and Ce^{4+} oxidation states and capable of activating H_2O_2 via a Fenton-like mechanism [33].

$Ce^{3+} + H_2O_2 \rightarrow Ce^{4+} + \bullet OH + OH^-$ (26)

$Ce^{4+} + H_2O_2 \rightarrow Ce^{3+} + \bullet O_2H + H^+$ (27)

Among all cerium compounds, ceria (CeO_2) is the most studied material. Research has shown that the generation of •OH radicals as well as the overall oxidation process are inextricably linked to the surface characteristics of the CeO_2. A study Wang and co-workers [34] showed that the interaction of H_2O_2 and bare CeO_2 leads to the production of persistent peroxide like species ($\equiv Ce^{III}\text{-}O_2H^-$), which do not readily degrade into •OH. However, the surface functionalization of CeO_2 with sulfuric acid accelerated the decomposition of peroxide species to •OH radicals via acid-catalyzed intra-molecular electron transfer mechanism.

2.2.3.3. Chromium

Chromium (Cr) is a poisonous metal that may exist in a variety of oxidation states, ranging from -2 to +6. However only trivalent [Cr(III)] and hexavalent [Cr(VI)] species are widely found in water and both react strongly with H_2O_2 to produce •OH in a sequence of Fenton-like reactions. The reaction between the Cr(III) and H_2O_2 strongly relies on the solution pH. Cr (III) exists in the form of $[Cr(H_2O)_6]^{3+}$ at $pH \leq 3$ and entirely unreactive towards H_2O_2, while at neutral pH it exhibits the highest reactivity and yield of •OH generation [35]. A Fenton-like route leads to the formation of •OH (Eq. 28, 29 and 30):

$Cr(III) + H_2O_2 \rightarrow Cr(IV) + \bullet OH + OH^-$ (28)

$Cr(IV) + H_2O_2 \rightarrow Cr(V) + \bullet OH + OH^-$ (29)

$Cr(V) + H_2O_2 \rightarrow Cr(VI) + \bullet OH + OH^-$ (30)

On the other hand, the interaction between Cr(VI) (exists as $Cr^{VI}O_4^-$) and H_2O_2 causes the replacement of oxo ligands by peroxo groups as well as one electron reduction of metal center, resulting in the formation of a $[Cr^V(O_2)_4]^{3-}$ complex, which decomposes at acidic pH to produce •OH and regenerates Cr(VI) [36].

$[Cr^{VI}O_4]^{2-} + nH_2O_2 \rightarrow [Cr^V(O_2)_4]^{3-}$ (31)

$[Cr^V(O_2)_4]^{3-} + H^+ \rightarrow [Cr^{VI}(O_2)_3(O)]^{2-} + \bullet OH$ (32)

Despite the fact that dissociation of Cr (V) complex into •OH is significantly preferred at acidic pH, the formation of Cr (V) intermediate occurs throughout a wide pH range (3.0 – 9.0), which is a key benefit of employing Cr(VI) for Fenton like activation of H_2O_2. Moreover the aqueous solubility of Cr (VI) over the entire pH range is another advantage of employing Cr(VI)/H_2O_2 as a homogeneous AOP. Despite these realistic beneficial reaction conditions, the toxicity of Cr (VI) precludes its intentional inclusion in wastewater treatment. However, it is possible to treat all Cr-contaminated wastewater using H_2O_2 as both oxidant and reductant. Precise control of solution pH will allow the oxidation of Cr (III) to Cr(VI) and subsequent regeneration via Cr(VI) reduction [35].

2.2.3.4. Manganese

Manganese (Mn) may exist in a wide range of oxidation states, from 0 to +7; however, only the +2 and +4 oxidation states have significant environmental and catalytic implications. Generally, under aerobic condition Mn^{2+} is oxidized to Mn^{4+}, resulting in colloidal intermediates of Mn^{3+}-oxyhydroxides which further converted to MnO_2. Simultaneously, chemical redox reactions readily convert the Mn^{4+} species to Mn^{2+} (Eq. 33).

$$MnO_2 + \text{organic substrate} \rightarrow Mn^{2+} + \text{oxidized products} \qquad (33)$$

To illustrate manganese's possibility as a Fenton-like catalyst, a homogeneous Mn^{2+}/H_2O_2 system for the degradation of 1-hexanol was studied by Watts and co-workers and revealed that the system was capable of 99% degradation of 1-hexanol in acidic pH [37]. Moreover, several oxide polymorphs of Mn (MnO_2, MnOOH and Mn_3O_4) can react effectively with H_2O_2 and generate various kinds of reactive oxygen species including •OH and $O_2^{\cdot -}$ in the pH range 3.5-7.0.

2.2.3.5. Copper

Copper (Cu) is another metal that has been utilized effectively as a Fenton-like catalyst. It exists in two states of oxidation: monovalent (Cu^+) and divalent (Cu^{2+}). The redox reaction of Cu with H_2O_2 is analogous to that of the Fe^{2+}/Fe^{3+} Fenton system:

$$Cu^+ + H_2O_2 \rightarrow Cu^{2+} + {\bullet}OH + OH^- \ (k = 1.0\text{x}10^4\ M^{-1}s^{-1}) \qquad (34)$$

$$Cu^{2+} + H_2O_2 \rightarrow Cu^+ + {\bullet}O_2H + OH^- \ (k = 4.6\text{x}10^2\ M^{-1}s^{-1}) \qquad (35)$$

Although the more stable hydrolyzed complex of Cu ($Cu(OH)_2$ or Cu^{2+}) is a Fenton active catalysts similar to iron Fenton system, the aqueous solubility of Cu^{2+} and Fe^{3+} are rather different. While the iron aquo complex $[Fe(H_2O)_6]^{3+}$ is insoluble above pH 5, the copper aquo complex $[Cu(H_2O)_6]^{2+}$ is soluble at neutral pH, allowing Cu^{2+}/H_2O_2 system to operate across a wider pH range than the Fe^{3+}/H_2O_2 redox system [38].

2.2.3.6. Ruthenium

Ruthenium (Ru) is the sole member of the platinum group metals that shows Fenton-like activity in the presence of H_2O_2. Hu et al. performed the oxidation of bisphenol A utilizing the Ru^{3+}/Ru^{2+} ($E°(Ru^{3+}/Ru^{2+}) = 1.29V$) redox couple. In the pH range 4.0-8.0, the interaction between Ru^{2+} and H_2O_2 effectively produced •OH and higher pH showed increasing oxidation efficiency [39]. The optimal degradation efficiency at neutral or near-alkaline pH is advantageous for Ru catalysts in practical application. Moreover, high stability of Ru catalysts prevents metal leaching which is beneficial for multiple catalytic cycle.

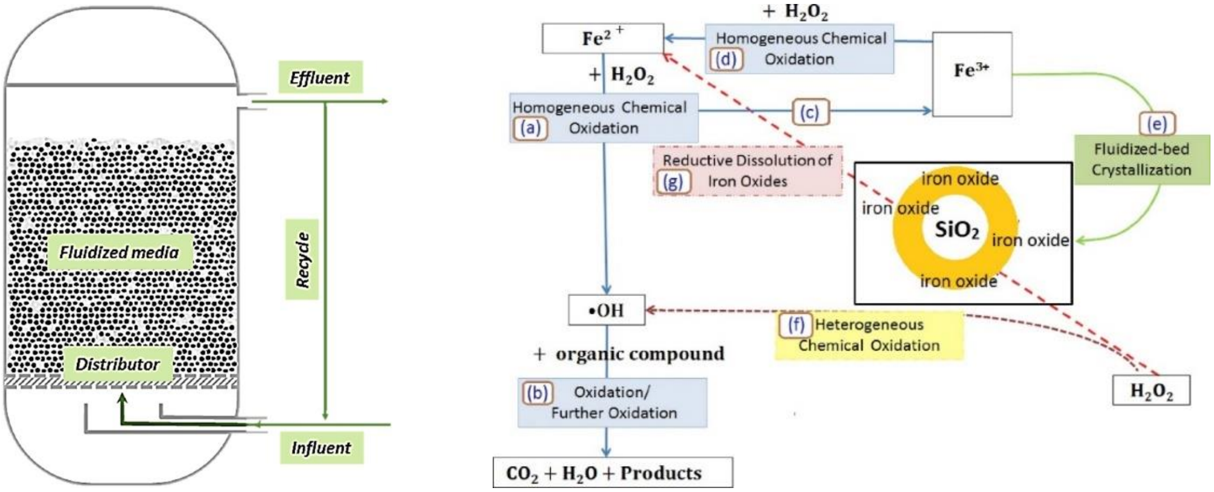
2.3. Fluidized bed Fenton process

A Fluidized bed Fenton (FBF) process is an innovative technology where a fluidized bed reactor is coupled with Fenton process to increase the overall process performance and minimize iron sludge formation. The fluidized materials, specified as carriers in the FBF process, can be an inert solid or an iron-based material. Fe^{3+} ions generated from the Fenton reaction can precipitate and crystallize on the surface of the carriers. Fe-O(OH) is the most common form of crystallized iron oxide and it can further function as a heterogeneous catalyst for the decomposition of H_2O_2. The crystallization of ferric ion, however, might be hampered by the pH of the reaction medium. The Fe (III) species are insoluble above pH 5.0 and precipitate in the hydroxide form ($Fe(OH)_3$), which can prevent Fe-O(OH) crystallization onto the carriers. A heterogeneous iron catalyst, such as goethite or iron oxide wastes, can be employed directly as a fluidization carrier to solve this problem.

It is possible to have several reactions occurring simultaneously in the fluidized bed Fenton process. These reactions include [40]:

i. Homogeneous chemical oxidation (H_2O_2/Fe^{2+})
ii. Heterogeneous chemical oxidation (H_2O_2/iron oxide)

iii. Fluidized-bed crystallization and
iv. Reductive dissolution of iron oxides



(a) (b)

Figure 3: Schematics of (a) basic fluidized bed reactor (b) reactions that take place in the fluidized-bed Fenton process. Adapted from Ref [41] with permission.

The schematic representation of basic fluidized bed reactor and the possible reaction mechanism in a fluidized-bed Fenton process is depicted in Figure 3. The homogeneous reactions occur in both the fluidized-bed and conventional Fenton processes, and they include: (a) homogeneous •OH production from Fe^{2+} and H_2O_2, (b) reaction of organic matter with the •OH, (c) conversion of Fe^{2+} to Fe^{3+}, and (d) slower conversion of Fe^{3+} back to Fe^{2+}. Additionally, the presence of a carrier causes the following heterogeneous reactions in the fluidized-bed Fenton process: (e) crystallization of Fe^{3+} in iron oxide forms, which is initiated by the carrier, (f) production of •OH from H_2O_2, which is catalyzed by iron oxides, and (g) redissolution of iron oxide to Fe^{2+}.

During the FBF process, the carrier materials, as well as their surface properties and size distribution, all play an important role, with the following effects in (i) fluid velocity for the starting fluidization of carrier material, (ii) crystallization thermodynamics by modifying the Gibbs energy of iron oxide nucleation and crystal growth, (iii) iron oxide crystallization kinetics and (iv) final weight of the carrier. As a result, the choice of carriers is an essential part that impacts the efficiency of the FBF process. In this context, a variety of carriers, including pure SiO_2, Al_2O_3, goethite, iron oxide waste, chitosan nanoparticles, quartz sand, and even activated-fly ash containing Fe_2O_3, have been utilized in the FBF process.

3. Photo-Fenton

During the classical Fenton process Fe^{3+} generates and accumulates in the system due to slow reaction kinetics of Fenton like reaction (Eq. 7), through which the regeneration of Fe^{2+} takes place from Fe^{3+}. As a result, the oxidation efficiency of the Fenton process decreases gradually, and the system generates iron sludges. It has been reported that the organic compounds mineralization efficiency of Fenton process ranges from 40-60% depending on the materials used. The oxidation efficiency of the traditional Fenton process can be improved by combining it with a light source, such as UV or visible light, and this is known as the Photo-Fenton process.

Fenton process generates Fe^{3+}, which mainly exists in the process as $[Fe(OH)]^{2+}$ at pH 2.8-3.5 [42]. Under light irradiation (λ<580nm) $[Fe(OH)]^{2+}$ undergoes photoreduction, regenerating Fe^{2+} and creating more •OH. The regenerated Fe^{2+} recombine with H_2O_2 to produce •OH radicals and Fe^{3+}, and the cycle continues:

$$Fe(OH)^{2+} + h\nu \rightarrow Fe^{2+} + \bullet OH \qquad (36)$$

In addition, direct photolysis of H_2O_2 takes place upon light irradiation (λ<310 nm) which generates additional •OH in the system according to eq:

$$H_2O_2 + h\nu \rightarrow 2\ \bullet OH \qquad (37)$$

Therefore, in comparison to the Fenton reaction, the photo-Fenton reaction has a much lower total iron consumption and sludge production. Apart from that, photo-Fenton process allows to use Fe(III) compounds instead of Fe(II) to initiate the Fenton reaction. A schematic reaction mechanism of photo-Fenton process for the decomposition of organic micropollutants is depicted in Figure 4.

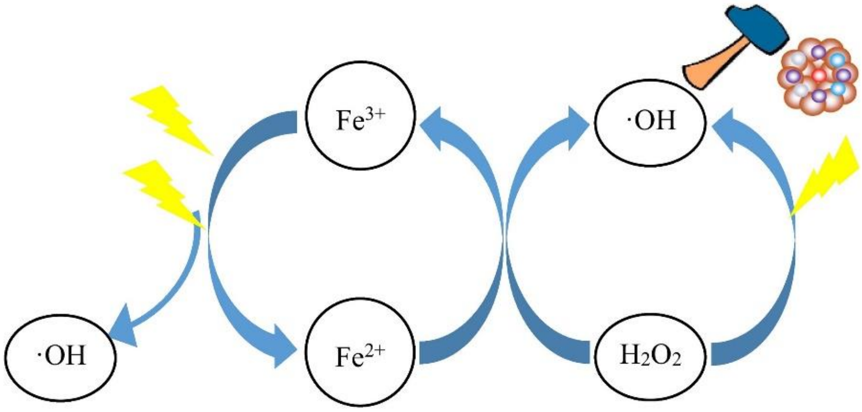


Figure 4: Reaction mechanism for the photo-Fenton process. Adapted from [43] with permission.

Similar to Fenton process, photo-Fenton reactions can be categorized as homogeneous and heterogeneous process depending on the catalysts employed in the system (free Fe-ions or Fe-based solid catalysts). As compared to homogeneous system, the heterogeneous Fenton process with light irradiation may generate more •OH. Combining iron oxides with semiconductors make it easier to create a heterojunction structure that separates photogenerated carriers, resulting in an increased photo-Fenton degradation efficiency. Hernández-Uresti and coworkers [44] developed a Fe impregnated $BiVO_4$ catalyst by directly hydrolyzing the Fe salt onto $BiVO_4$ nanoparticles. The synergistic impact of photocatalysis and photo-Fenton was shown to be responsible for the enhanced and complete degradation of 10 mg/L ciprofloxacin (CIP) by 1wt% Fe doped $BiVO_4$ catalysts under UV-Vis irradiation for 30 min. Based on the experimental results it was found that the photogenerated hole (h^+) and H_2O_2 played an important role for CIP degradation. The following reactions took place in the 1wt% Fe-$BiVO_4$ catalyzed photo-Fenton system:

$$\text{Fe-BiVO}_4 + h\nu \rightarrow \text{Fe-BiVO}_4(e^-) + \text{Fe-BiVO}_4(h^+) \quad (38)$$

$$\text{Fe-BiVO}_4(e^-) + H_2O_2 \rightarrow \bullet OH + OH^- \quad (39)$$

$$\text{Fe-BiVO}_4(e^-) + Fe^{3+} \rightarrow Fe^{2+} \quad (40)$$

$$\text{Fe-BiVO}_4(h^+) + Fe^{2+} \rightarrow Fe^{3+} \quad (41)$$

$$\text{Fe-BiVO}_4(h^+) + \text{CIP} \rightarrow \text{Oxidized products} \quad (42)$$

$$\bullet OH + \text{CIP} \rightarrow \text{Oxidized products} \quad (43)$$

Upon light irradiation, photogenerated charge carriers (Fe-$BiVO_4$(e^-) and Fe-$BiVO_4$(h^+)) are developed due to an excitation of electron from the valence band to the conduction band of Fe-$BiVO_4$. Reduction of H_2O_2 with the photogenerated electrons leads to the generation of •OH (Eq. 34) which can degrade the CIP. Simultaneously, H_2O_2 interacts with the surface bound Fe according to the Fenton reaction and generates •OH. Apart from that, the redox conversion of Fe^{3+}/Fe^{2+} takes place on the catalysts surface with the photogenerated charge carriers (Eq. 35 and 36) which also inhibit the recombination of charge carriers.

4. Electro-Fenton

The efficiency of a Fenton process can be improved by coupling the Fenton reaction with electrochemical processes, known as Electro-Fenton (EF) process. In the EF process, at least one of the Fenton reagents are either in situ generated (H_2O_2 and Fe^{2+}) or regenerated (Fe^{2+}) electrochemically. The earliest investigations on EF like reactions took place in the late 1970s and early 1980s, when hydroxylation reactions of organic molecules such as cyclohexane, benzene, toluene, phenol and others were carried out in acidic conditions with the addition of various catalysts, including Fe^{2+} [45][46]. However, in 1986 Sudoh et al. for the first time studied the EF process for water treatment. Using platinum and graphite electrode in the presence of Fe^{2+} catalysts, they investigated the degradation of phenol at a cathodic potential of -0.6V [47].

H_2O_2 can be generated continuously at the cathode of an electrochemical cell by directly injecting pure O_2 gas or air in acidic aqueous solution. Injected O_2 gas is first dissolved in the aqueous phase and then transported from the bulk to the cathodic surface, where it is converted to H_2O_2 by a two-electron oxygen reduction reaction according to the Eq. 14.

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \qquad E^\circ = 0.695\ \text{V/SHE} \qquad (44)$$

In the same acidic condition, dissolved oxygen can convert into H_2O by four-electron oxygen reduction reaction (Eq. 15) and can compete with the reaction Eq. 14.

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \qquad E^\circ = 1.23\ \text{V/SHE} \qquad (45)$$

On the other hand, Fe^{2+} can be generated electrochemically either by oxidative dissolution of sacrificial iron anode (Eq. 16) or cathodic reduction of Fe^{3+} (Eq. 17)

$Fe^\circ \rightarrow Fe^{2+} + 2e^-$ (46)

$Fe^{3+} + e^- \rightarrow Fe^{2+}$ (47)

The generation and stability of H_2O_2 are affected by the cell configuration, cathode materials and operating environment. For example, in an undivided cell, H_2O_2 can undergo anodic oxidation via the formation of hydroperoxyl radical as intermediates according to the following equations:

$H_2O_2 \rightarrow {\bullet}O_2H + H^+ + e^-$ (48)

${\bullet}O_2H \rightarrow O_2 + H^+ + e^-$ (49)

In addition, electrogenerated H_2O_2 can be reduced further at the cathode surface or disproportioned to O_2 gas and H_2O according to the following reactions:

$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$ (50)

$2\,H_2O_2 \rightarrow O_2 + 2H_2O$ (51)

Depending on the addition or in situ electro-generation of Fenton reagents, the EF process can be divided into four types as shown in Table 1 [46][43]. In type I, Fe^{2+} is supplied externally while H_2O_2 is produced in situ by electrochemical reduction of O_2 at the cathode, avoiding the costs and dangers of handling, shipping and storage of H_2O_2. In type II, both Fenton reagents, Fe^{2+} and H_2O_2, are supplied externally and then Fe^{2+} is regenerated at the cathode from Fe^{3+}, which is generated from Fenton reaction (Eq. 1). This type of process can reduce the initial Fe^{2+} input and iron sludge production. In type III, H_2O_2 is supplied externally but Fe^{2+} is electro-generated using a sacrificial anode. This method has certain drawbacks such as high anode consumption rate and a considerable amount of iron sludge generation. In type IV, both Fenton reagents, H_2O_2 and Fe^{2+}, are in situ generated electrochemically using an air sparging cathode and sacrificial anode, respectively.

Table 1: Different strategies of EF process and their corresponding electrochemical reactions.

Type	Fe^{2+}	H_2O_2	Electrochemical Reactions
I.	External addition	Cathodic in situ electro-generation	Anode: $2H_2O \rightarrow 4H^+ + O_2 + 2e^-$ Cathode: $O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$

Type	Fe^{2+}	H_2O_2	Electrochemical Reactions
II.	Cathodic in situ electro-regeneration	External addition	Anode: $2H_2O \rightarrow 4H^+ + O_2 + 2e^-$ Cathode: $Fe^{3+} + e^- \rightarrow Fe^{2+}$
III.	Anodic in situ electro-generation	External addition	Anode: $Fe^0 \rightarrow Fe^{2+} + 2e^-$ Cathode: $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$
IV.	Anodic in situ electro-generation	Cathodic in situ electro-generation	Anode: $Fe^0 \rightarrow Fe^{2+} + 2e^-$ Cathode: $O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$; $Fe^{3+} + e^- \rightarrow Fe^{2+}$

EF process offers several advantages over the classical Fenton process, such as

i. The ability to generate Fenton's reagents in situ eliminates the need for storage and dosing facilities for those compounds.
ii. Cathodic regeneration of Fe^{3+} to Fe^{2+} accelerates the Fenton reaction and minimizes iron sludge production.
iii. Because of additional electro-generation of •OH at the anode, organic contaminants mineralization rates are higher than with the traditional Fenton process.

4.1. Factors affecting the EF process

4.1.1. Cell configuration

Fenton's reagent can be electrogenerated in either a divided or an undivided cell using two- or three-electrode systems. Divided cell systems consist of two solutions, anolyte and catholyte, which are generally divided by an ion exchange membrane or salt bridge that enables ions to flow between the cells in order to maintain electroneutrality in both solutions. H_2O_2 is electrogenerated in the catholyte from the reduction of dissolved oxygen (Eq. 39) and participate in the pollutant degradation via Fenton process. Depending on whether a reference electrode is used or not, the system can function with three or two electrodes. Three-electrode systems typically work under potentiostatic conditions while two-electrode systems operate under galvanostatic conditions. In potentiostatic condition, a constant potential is applied to the cathode against a reference electrode (usually Ag/AgCl or SCE) resulting in a current flow between the anode and cathode while in galvanostatic condition a constant current or current density is directly applied to the cell.

On the other hand, in undivided cell there is no separator between the anode and cathode which provides an advantage of lower cell voltage requirement for electrolysis. However, this type of system is not appropriate for obtaining large amount of H_2O_2 due to the anodic oxidation of H_2O_2 to O_2 (Eq. 43 and 44). A schematic representation of divided and undivided EF cell configurations with their corresponding electrode reactions are depicted in Figure 5.

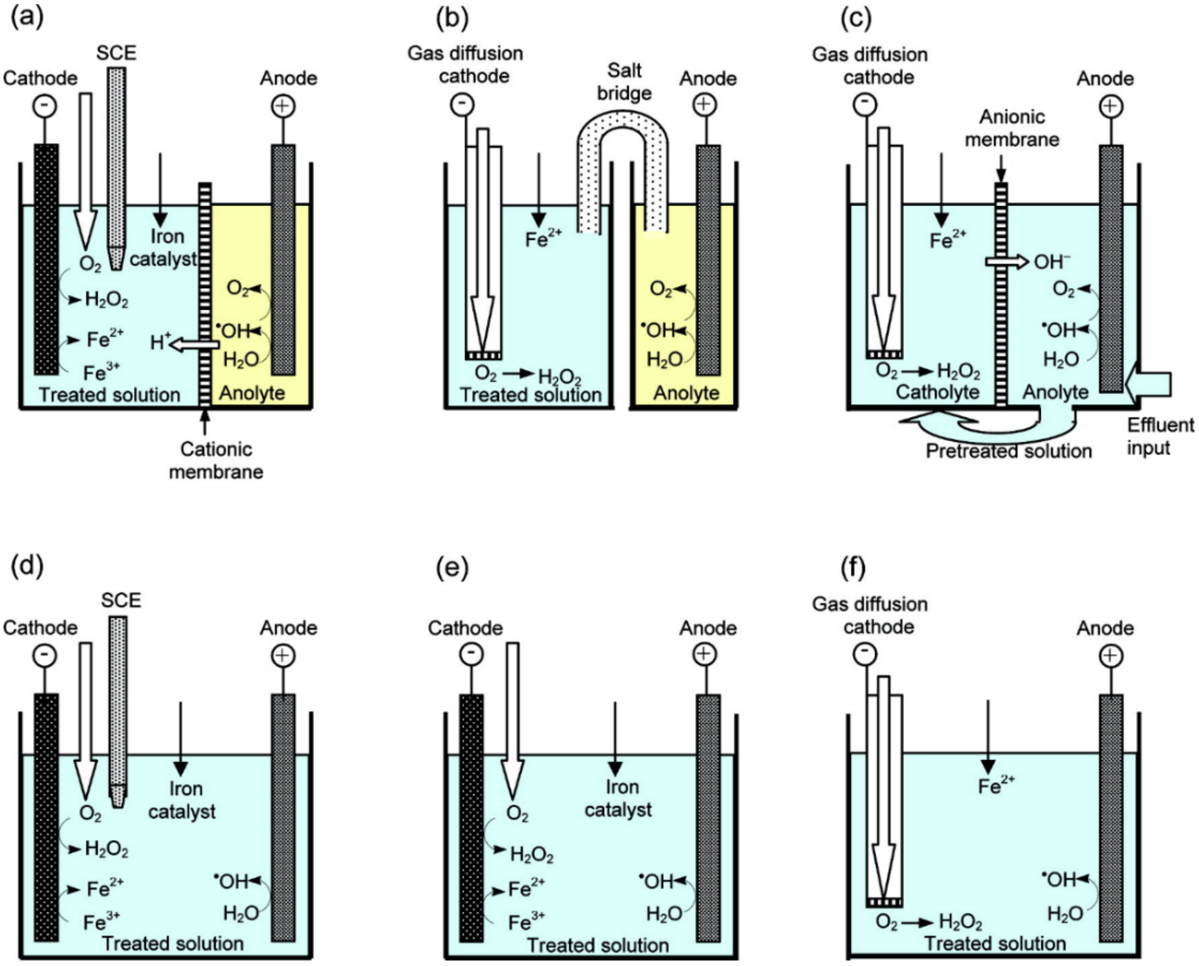


Figure 5: Schematic representation of divided (a-c) and undivided cell (d-f) configurations used in EF treatment of organic micropollutants with their corresponding electrode reactions. Adapted from ref [11] with permission.

4.1.2. Current density

Current density, which is the driving force of H_2O_2 electro-generation, plays a significant role in the efficiency of the EF process. Higher current density increases the production of H_2O_2, which in turn enhances the production of •OH. A higher current density also leads to rapid Fe^{2+} regeneration (Eq. 42) and improves the Fenton process efficiency. However, higher current density may hasten the development of side reactions such as anodic oxygen evolution (Eq. 47), cathodic hydrogen reduction (Eq. 48) and parasitic reactions of •OH (Eq. 49). Apart from that, higher current density necessitates increased energy usage.

$$2H_2O \rightarrow 4H^+ + O_2 + 4e^- \qquad (52)$$

$$2H^+ + 2e^- \rightarrow H_2 \qquad (53)$$

$$2HO\bullet \rightarrow O_2 + 2H^+ + 2e^- \qquad (54)$$

Therefore, increasing current density has the advantages of faster pollutant degradation rates and shorter reaction times, but it also has the disadvantages of higher energy consumption with worse current efficiency. Therefore, it is important to adjust the applied current density in order to achieve a satisfactory balance between the intended process efficiency and the associated energy expenditures [48][49].

4.1.3. Electrode materials

Selecting the appropriate electrode materials is an essential step in electro-Fenton process. Proper anode materials are essential in preventing electrode corrosion and high oxygen overvoltage anodes can generate •OH to increase treatment efficiency [50]. Platinum's high conductivity and excellent stability make it a good choice for functioning as an anode in electrochemical operations [49][48]. Extensively studied platinum anodes include Pt flake, Pt gauze, Pt grid, Pt mesh, Pt plate and Pt sheet. However, the high costs of Pt reduce its economic feasibility. A better strategy for dealing with this issue is to utilize platinized anode, which are anodes that have a layer of Pt plating applied on a suitable metal, and similar results to Pt anodes have been achieved. Apart from Pt, other noble metals like gold and silver can also work as an anode material but their exorbitant prices do not make them viable for practical use.

Boron doped diamond (BDD) is another expensive but efficient and suitable electrode material for the EF process. In many electrochemical processes BDD has been used as either an anode or both an anode and cathode. Because of broader potential window and smaller background currents in aqueous solutions, BDD provide a stronger response and lower detection limit. When compared to Pt electrodes BDD aids in the production of significantly higher amount of •OH and may fully eliminated unsaturated and aromatic contaminants [51]. The performance of BDD electrode compared with Pt electrode was monitored by studying the degradation of 2-(2,4-dichlorophenoxy)-propionic acid and the findings revealed that BDD electrode provided higher degradation efficiency due to its higher electrochemical activity and enhanced production of •OH on the surface [52]. Dimensionally stable anodes (for example, Ti rod coated with RuO_2/IrO_2), carbon felt, graphite and carbon nanotubes (CNTs) are other forms of anodes utilized in EF processes.

Carbon-based materials are commonly employed as cathodes for EF system due to their effectiveness in DO reduction, lower H_2O_2 decomposition capability and enhanced hydrogen evolution overpotential. The most common carbon-based cathode materials used for H_2O_2 electro-generation are graphite rods, felts, paper and plates, carbon felts, carbon sponge, CNTs, activated carbon fiber and reticulated vitreous carbon. A further improvement of H_2O_2 electro-generation can be achieved by modifying the cathode materials to generate more active sites at the cathode surface. Porous carbon, porous CNT sponge and carbon aerogel are some prominent example of modified carbon cathodes [11].

4.1.4. Electrolytes

Electrolytes play an important role in the efficiency of an electro-Fenton process by improving the solution conductivity. Sodium sulphate (Na_2SO_4) is the most widely used electrolyte due its high ionic strength and little interference with aqueous solutions in EF process. Other electrolytes have been used as well, including NaCl, KCl, $NaClO_4$ and $NaNO_3$. When chloro-salts are utilized as the electrolyte, the presence of Cl^- is expected to improve degradation efficiency and reduce reaction time by generating chlorine ($Cl_2(aq)$) or hypochlorous acid (HClO), both of which are powerful oxidizing agents in aqueous solutions. However, the presence of these active Cl species might lead to the generation of toxic organochlorinated compounds as intermediates. For example, electrochemical oxidation of phenol generated nonvolatile chlorinated aliphatic acids and volatile trichloromethane, when NaCl was used as electrolyte. The formation of toxic intermediate compounds can be prevented only when organic molecules are fully mineralized.

4.1.5. Oxygen sparging rate

The rate of oxygen sparging is a key limiting factor in EF process efficiency. A higher oxygen sparging rate can increase the DO level and mass transfer rate in the system, promoting H_2O_2 generation on which the removal efficiency of the organic contaminants is dependent [49]. However, the generation of H_2O_2 is not proportional to the amount of oxygen flowing through the system. In fact, the increasing O_2 sparging rate does not increase the DO concentration in the system once the DO concentration of the system reaches saturation (8.28 mg/L at 25°C) and therefore, H_2O_2 production remains steady.

5. Application of Fenton and modified Fenton processes for micropollutant treatment

Fenton and modified Fenton processes have been extensively studied for the degradation and mineralization of various emerging micropollutants. In a study, Höfl et al. [53] evaluated the effectiveness of three AOPs (UV/H_2O_2, UV/O_3 and Fenton process) for the degradation of adsorbable organic halogen (AOX) and COD from a pharmaceutical wastewater and pointed out the benefits of the Fenton process over other AOPs. The findings revealed that all three techniques are effective at degrading AOX and COD. When comparing AOX degradation to COD degradation, UV irradiation showed a strong selectivity for AOX. Processes relying on •OH radicals, on the other hand, were less selective but more efficient in COD removal. Both COD and AOX could be eliminate almost entirely using Fenton process, with a very short reaction time compared to other two AOPs.

Zhu et al. [54] studied the degradation of bisphenol A (BPA) using a composite material of oxidized multi-walled carbon nanotubes and ferrihydrite (CNTs/Fh) as a heterogeneous Fenton catalyst. They synthesized a series of CNTs/Fh composites by simply swirling CNTs and Fh together. When compared to simple Fh, a 3% CNTs/Fh system degraded the pollutant seven times faster. Furthermore, after four cycles of reuse CNTs/Fh maintained strong Fenton activity and XPS findings revealed that the graphitic structure of the used CNTs is highly robust. DFT calculations and cyclic voltammetry characterization of the CNTs/Fh composite were useful to reveal the catalytic mechanism of possible degradation process (Figure 6). The increased electron conductivity of CNTs/Fh composites facilitated Fe(III)/Fe(II) redox cycling, promoting the breakdown of H_2O_2 and the formation of •OH.

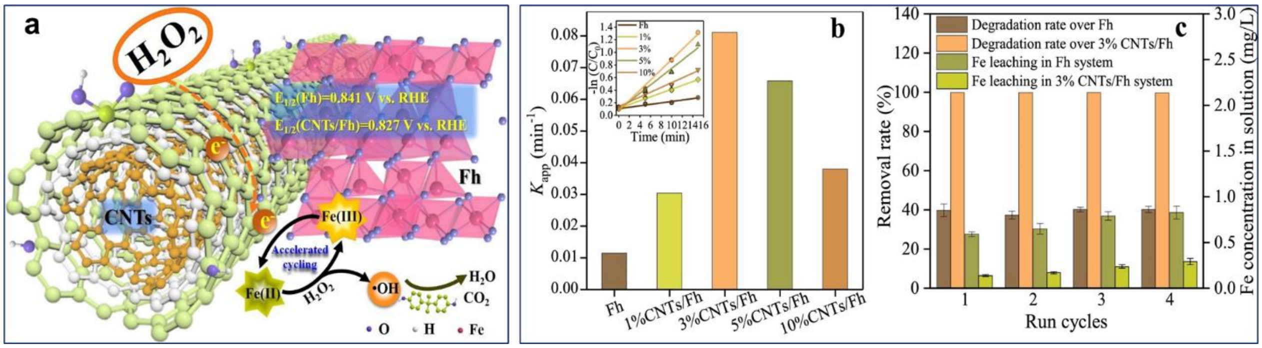


Figure 6: Degradation of bisphenol-A by CNT/Fh composite catalysts: (a) reaction mechanism, (b) apparent degradation rate constants (c) stability test of CNT/Fh catalysts. Adapted with permission from Ref. [54]

Zhong et al. [55] used a heterogeneous photo-Fenton process catalyzed by titanomagnetite to study the degradation of tetrabromobisphenol A (TBBPA), a brominated flame retardant. Within 240 minutes of UV irradiation, almost complete breakdown of TBBPA was accomplished using the optimal conditions of 0.125g/L catalyst dosage, 10 mmol/L H_2O_2 and pH 6.5. The addition of Ti^{4+} to the magnetite significantly enhanced its catalytic activity. TBBPA degradation was triggered by debromination and the ß-scission reaction. The produced intermediates, which mostly comprise mono-, di- and tri-BBPA, were identified by gas chromatography-mass spectrometry (GC-MS) and their concentration approached undetectable levels during the experiment. In another research, Ayoub et al. [56] studied the heterogeneous photo-Fenton process for the removal of 21 micropollutants from the water samples collected from the Meurthe river located in France. The identified micropollutants belong to the pharmaceuticals, personal care products, endocrine disruptors and per fluorinated compounds with different initial concentrations ranging from 0.8-88 ng/L. The heterogeneous catalysts used for the photo-Fenton process was iron (III) impregnated zeolite. Under optimized reaction conditions (20wt% Fe (III) impregnated zeolite dosage, 0.007 mol/L H_2O_2 concentration, pH 5.5 and UV light irradiation), 19 out of 21 micropollutant's concentration reached below the detection limit within 30 min to 6 hours depending on their initial concentration.

Barhoumi et al. [57] studied the degradation of levofloxacin using heterogeneous pyrite catalyzed electro-Fenton process using BDD/carbon felt cell. Pyrite serves as a source of Fe^{2+} ions and regulates the solution pH. Another Fenton reagent, H_2O_2, was *in-situ* electrogenerated withing the system under oxygen bubbling. The major oxidizing agent •OH was produced from anodic oxidation of water and Fenton process. A 95% elimination of total organic carbon was possible when a levofloxacin solution with a 0.23mM concentration was degraded at 300 mA for 8 hours. Analysis of mineralization of levofloxacin by ion chromatography revealed the presence of F^-, NO_3^- and NH_4^+ in the solution.

Zhao et al. [58] investigated the electro-Fenton degradation of emerging pesticide, imidacloprid, using iron oxide modified activated carbon aerogel (Fe_3O_4@Fe_2O_3/ACA) composite cathode. The system operated within a wide pH range, from 3 to 9, without compromising the ability to degrade 90% of imidacloprid and TOC within 30 and 60 minutes, respectively. A comprehensive analysis of surface characteristics and produced oxidants was used to suggest the oxidation process of the E-Fenton process with the new composite cathode at varied pH ranges. In acidic pH, electro-generated H_2O_2 interacts with dissolved iron ions and surface Fe (II) sites to produce •OH through a Haber-Weiss process, while in basic pH it interacts with Fe (II) and Fe (III) sites on the surface and produce superoxide anion (•O_2^-/•O_2H) and •OH.

5.1. Mineralization study of Phenol by Fenton Process:

Among the various toxic and persistent organic micropollutants, phenol and phenolic compounds are found in high concentrations in wastewater discharge of various industries including pharmaceuticals, foods, resins, dyes, papermaking and petrochemicals. The existence of phenol in waterbodies causes severe pollution and both human and aquatic life are severely affected by its carcinogenic and mutagenic consequences [59]. Brillas and Gracia-Segura proposed a Fenton-based reaction mechanism (Figure 7) for phenol degradation and mineralization in water based on experimental evidences [60][61][62]. The information on the production of various oxidation products can be obtained using high-performance liquid chromatography (HPLC) and GC-MS analysis of treated wastewater. Hydroxylation and charge transfer processes between the oxidation derivatives are involved in the mineralization process of Phenol. When phenol is first hydroxylated, it produces hydroquinone (HQ), catechol (CT) and resorcinol (RC) as intermediate products. The activation energies (E_a) for the formation of HQ, CT and RC by phenol hydroxylation are 0.855, 1.174 and 2.534 kcal/mol, respectively [61]. As a result, the detection of HQ is prevalent over other hydroxylated phenol intermediates. It is worth noting that HQ and CT have redox equilibrium with their respective quinones (4-Benzoquinone and 2-Benzoquinone), even though these species are also classified as intermediates. Simultaneously, 1,2,3-

trihydroxybenzene is produced by further hydroxylation of CT and RC. Following the ring opening of these aromatic intermediates, a mixture of carboxylic acids is produced, which is then converted to oxalic and formic acids. The final transformations of these two acids are end up with CO_2 and H_2O.

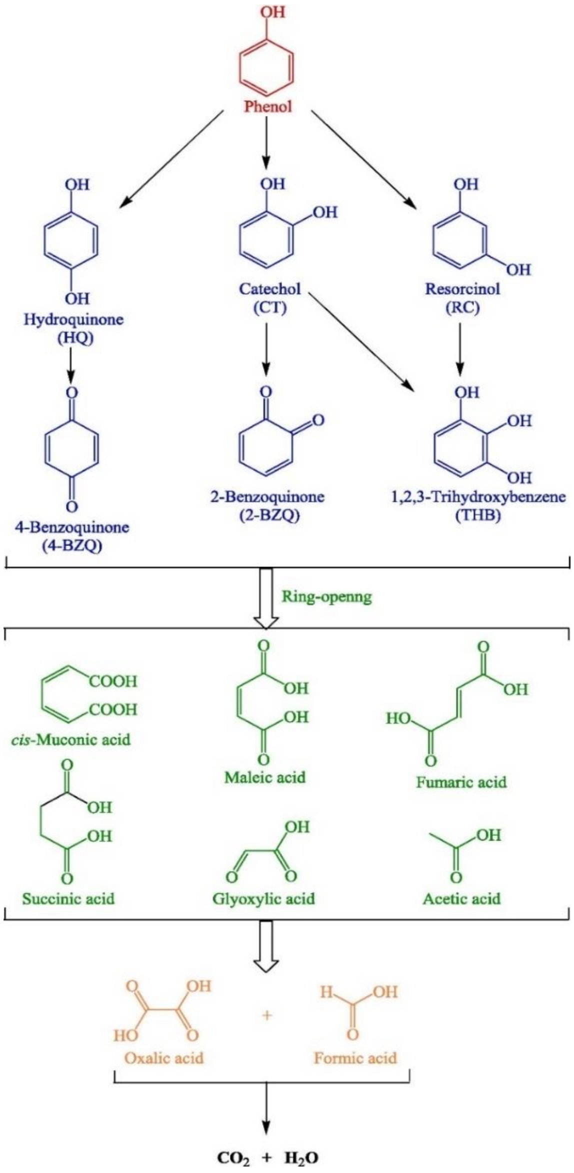


Figure 7: Degradation and mineralization pathway of Phenol by •OH generated from Fenton process. Adapted with permission from Ref. [60].

Although the mineralization pathway illustrated in Figure 7 is apparently simpler, the complete mineralization of phenol may be impeded by several species in the aqueous matrix. The presence of iron ions, which either naturally occurs in water or is introduced as Fenton's catalyst is one of the most unwanted consequences. For example, Fe^{3+}, generated by the Fenton reaction, is well recognized to form very stable complexes with final carboxylic acids. These complexes of Fe (III)-carboxylate are seldom degraded by the •OH and induce a poor degree of mineralization. This situation can be overcome by introducing EF or PF process.

In EF, Fe^{3+} ions are effectively reduced to Fe^{2+} and generates Fe (II) carboxylate complexes by their interaction with carboxylic acids. Fe (II) carboxylate complexes are more easily degraded than Fe (III)-carboxylate complexes and more phenol mineralization is obtained. In case of PF process, photolysis of Fe (III) carboxylate complexes improves the mineralization efficiency.

6. Concluding remarks and future perspective

Fenton oxidation is a promising advanced oxidation process to overcome the challenges related to the treatment of emerging and persistent micropollutants in aqueous environment. Both Fenton reagents (Fe^{2+} and H_2O_2) are easily available, inexpensive and environment friendly. Homogeneous Fenton process exhibits minimal limitation on mass transfer and therefore exhibit faster reaction kinetics. However, limited working pH range and enormous amount of iron sludge production limits its application on industrial scale. The development of heterogeneous Fenton catalysts is a promising solution to overcome the limitations of conventional Fenton process. Recent studies on various kinds of Ferrous and non-ferrous heterogeneous Fenton catalysts showed enormous potential for large scale application of Fenton process. The commercial use of heterogeneous Fenton processes may be hindered primarily by the deactivation of catalyst's active sites in long run. Therefore, more research devoted to the development of novel catalysts with wider workable pH range, high stability, minimal deactivation and leaching is necessary.

FBF process is a promising strategy to implement the Fenton process on a larger scale. A synergistic combination of homogeneous and heterogeneous Fenton processes can be achieved in a FBF process which further promotes the removal efficiency of emerging contaminants. Moreover, the development of modified Fenton processes, such as photo-Fenton and electro-Fenton, shows enormous potential for application on a broader scale. Several research groups around the world are currently working on the development of the photo-Fenton and electro-Fenton processes, particularly on the development of novel reactor configurations, electrode materials and operational parameters. Integrating the FBF process with light irradiation or an electric field may provide an excellent solution for large scale applications.

Finally, there should be a lot more focus on identifying reaction intermediates, developing rate expression for complex contaminants transformation and mineralization, identifying scale-up factors and establishing cost-effectiveness criteria.

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