Interfacial mechanisms of heterogeneous Fenton reactions catalyzed by iron-based materials: A review

Jie He⁎,1,2, Xiaofang Yang⁎⁎,1, Bin Men1, Dongsheng Wang⁎1

1. State Key Laboratory of Environmental Aquatic Chemistry, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China. E-mail: hejie10@mails.ucas.ac.cn
2. University of Chinese Academy of Sciences, Beijing 100049, China

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ABSTRACT

The heterogeneous Fenton reaction can generate highly reactive hydroxyl radicals (•OH) from reactions between recyclable solid catalysts and H2O2 at acidic or even circumneutral pH. Hence, it can effectively oxidize refractory organics in water or soils and has become a promising environmentally friendly treatment technology. Due to the complex reaction system, the mechanism behind heterogeneous Fenton reactions remains unresolved but fascinating, and is crucial for understanding Fenton chemistry and the development and application of efficient heterogeneous Fenton technologies. Iron-based materials usually possess high catalytic activity, low cost, negligible toxicity and easy recovery, and are a superior type of heterogeneous Fenton catalysts. Therefore, this article reviews the fundamental but important interfacial mechanisms of heterogeneous Fenton reactions catalyzed by iron-based materials. •OH, hydroperoxyl radicals/superoxide anions (HO2/•O2−) and high-valent iron are the three main types of reactive oxygen species (ROS), with different oxidation reactivity and selectivity. Based on the mechanisms of ROS generation, the interfacial mechanisms of heterogeneous Fenton systems can be classified as the homogeneous Fenton mechanism induced by surface-leached iron, the heterogeneous catalysis mechanism, and the heterogeneous reaction-induced homogeneous mechanism. Different heterogeneous Fenton systems catalyzed by characteristic iron-based materials are comprehensively reviewed. Finally, related future research directions are also suggested.

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Introduction

As one of the advanced oxidation processes (AOPs), heterogeneous Fenton reactions can effectively degrade refractory organics in water or soils (Andreozzi et al., 2002a; Kitis and Kaplan, 2007; Lücking et al., 1998; Melero et al., 2009; Mesquita et al., 2012; Pignatello et al., 2006; Zhang et al., 2011). Highly reactive hydroxyl radicals (•OH) are generated from reactions between recyclable solid catalysts and H2O2 at acidic or even circumneutral pH ranges (Pignatello et al., 2006; Seyed Dorraji et al., 2015; Xu and Wang, 2012b; Xue et al., 2009a). Hence, heterogeneous Fenton reactions have attracted wide attention.

The heterogeneous Fenton reaction was discovered about 100 years after the discovery of the classic homogeneous Fenton reaction (i.e., the reaction between Fe2+ and H2O2) in 1894 (Pignatello et al., 2006; Tyre et al., 1991). It can overcome the disadvantages of the homogeneous Fenton reaction, such
as decreasing reactivity due to catalyst consumption and the need for sludge treatment due to pH adjustments. However, unlike the well-known homogeneous Fenton mechanism, the mechanism behind heterogeneous Fenton reactions remains unresolved but fascinating, due to the complex interactions among solid catalysts, H₂O₂, parent organic compounds, generated reactive oxygen species (ROS), degradation byproducts and other co-existing substrates. To understand the reaction mechanisms is crucial for understanding Fenton chemistry and the development and application of efficient heterogeneous Fenton technologies.

Interface reactions include the generation and utilization of ROS, and are vital parts of heterogeneous Fenton mechanism. Different from other published reviews, which have focused on the preparation and performance of the catalysts (Dhakshinamoorthy et al., 2012; Garrido-Ramirez et al., 2010; Navalon et al., 2010a; Nidheesh, 2015; Perathoner and Centi, 2005), this article reviews the fundamental interfacial mechanisms of the heterogeneous Fenton reactions catalyzed by iron-based materials, which may also provide insights for the enhancement of heterogeneous Fenton reactions with additional energy, such as ultraviolet and visible light (UV-Vis), electricity, and ultrasound.

### 1. ROS in heterogeneous Fenton systems

In the heterogeneous Fenton systems catalyzed by iron-based materials, ROS are responsible for the degradation of organic contaminants, due to the limited adsorption capacity of catalysts and the weak oxidation potential of H₂O₂. Though the ROS generated remain controversial (Pham et al., 2009), ·OH, H₂O₂/O₂ and high-valent iron species are the three main types of ROS.

#### 1.1. ·OH

Hydroxyl radical (·OH) is the most commonly detected oxidant in heterogeneous Fenton systems. It can be generated from heterogeneous reactions between surface Fe^{II} (=Fe^{II}) and H₂O₂ (Eq. (1) (Lin and Gurol, 1998)) (detailed in Section 2.2), and might also be generated from the outer-sphere reaction between Fe^{2+} and H₂O₂ at acidic pH, which leads to homolytic O–O bond cleavage (Remucal and Sedlak, 2011), i.e., a homogeneous Fenton reaction induced by the leached iron (detailed in Section 2.1).

\[
\text{Fe^{II} + H}_2\text{O}_2 \rightarrow \text{Fe}^{III-}\text{OH} + \cdot \text{OH} \tag{1}
\]

With a high reduction potential (Table 1), ·OH is a strong and nonselective oxidant, and is able to react with various organic compounds at near-diffusion controlled rates (Keenan and Sedlak, 2008) (Table 2). Reactions between ·OH and organic compounds include abstraction of H atoms from C–H, N–H, or O–H bonds, and OH addition to unsaturated bonds like C=O bonds or aromatic rings (Pignatello et al., 2006; Xu and Wang, 2012a).

Since the half-life of ·OH radical is on the order of a few nanoseconds (BaČIĆ and MojiOVIĆ, 2005), and the ·OH migration distance is only micro-meters, ·OH radical can only be detected indirectly at present. (1) The reaction between ·OH and spin trap agents can form more stable adducts, which can be easily detected by electron spin resonance (ESR) spectroscopy. For example, ·OH reacts with 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) to form DMPO-OH adduct, which has a half-life of 12–156 min in neutral solutions (Faure et al., 2012) and exhibits a characteristic ESR spectrum for detection. (2) Inorganic ions like HCO₃⁻ and PO₄³⁻/HPO₄²⁻/H₂PO₄⁻, and alcohols like n-butanol, t-butanol, methanol and ethanol consume .OH quickly (Table 2).

### Table 1 - Physicochemical properties of three main reactive oxygen species (ROS).

| ROS          | Standard reduction potential | Half-life (sec) |
|--------------|------------------------------|----------------|
| ·OH          | E°(OH/H₂O₂) = 2.59 V         | 10⁻⁹⁴          |
| H₂O₂/O₂      | E°(H₂O₂/H₂O) = 1.50 V         | 10⁻⁵⁴          |
| Fe(IV)       | E°(Fe^{IV}/Fe^{III}) = 1.80 V | -0.35          |

• Remucal and Sedlak, 2011.
• Vanýsek, 2011.
• Bossmann et al., 1998.
• BaČIĆ and MojiOVIĆ, 2005.

#### 1.2. H₂O₂/O₂

Hydroperoxyl radical (H₂O₂⁻) and its conjugated base, superoxide anion (O₂⁻) (Eq. (2) (Pignatello et al., 2006)), are usually detected and accompanied by ·OH. They are generated from the reaction between superoxide-complexed Fe^{III} (=Fe^{III}OH) and H₂O₂ (detailed in Section 2.2), the reaction between ·OH and H₂O₂, and reactions between carbon-centered free radicals and O₂ (Eqs. (3)–(5) (Lin and Gurol, 1998; Pignatello et al., 2006)).

\[
\text{O}_2^- + \text{H}^+ \rightarrow \text{HO}_2 \cdot \quad \text{pK}_\alpha = 4.85 \pm 0.1 \tag{2}
\]

\[
\text{Fe}^{III-}\text{OH} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{III} + \text{H}_2\text{O} + \cdot \text{HO}_2 \tag{3}
\]

\[
\text{HO}_2^- + \text{H}_2\text{O}_2 \rightarrow \text{HO}_2^{-} + \text{H}_2\text{O} \tag{4}
\]

\[
\text{R}^- + \text{O}_2 \rightarrow \text{R}(\cdot \text{H})^+ + \text{HO}_2 \tag{5}
\]

H₂O₂/O₂ are less reactive than ·OH (Navalon et al., 2010a; Xue et al., 2009a) (Table 1). Some rate constants of O₂⁻ with selected substances are listed in Table 2. In free radical-dominated chain reactions, organic compounds are initially transformed to organic radicals by free radicals, and
Table 2 – Rate constants of ROS with selected substances.

| ROS | Substance       | Reaction formula | Rate constant (L/(mol·sec)) | pH | Reference                                      |
|-----|----------------|------------------|-----------------------------|----|-----------------------------------------------|
| •OH | Inorganic      | H₂PO₄⁻            | 2 × 10⁴                     | 7/8.5 | (Lipczynskakochany et al., 1995)              |
|      | compounds      | HPO₂⁻            | 6 × 10⁵                     | (Lipczynskakochany et al., 1995) | |
|      |                | PO₄²⁻            | 7 × 10⁵                     | (Lipczynskakochany et al., 1995) | |
|      |                | HCO₃⁻            | 5.7 × 10⁴                   | (Lipczynskakochany et al., 1995) | |
|      |                | CO₃²⁻            | 4 × 10⁴                     | (Lipczynskakochany et al., 1995) | |
|      |                | SO₄²⁻            | 2 × 10⁹                     | (Hanna et al., 2010) | |
|      |                | Cl⁻              | 1.2 × 10¹⁰                 | (Martin et al., 1995) | |
|      |                | I⁻               | 1.1 × 10¹⁰                 | (Martin et al., 1995) | |
|      |                | Cl⁰              | 8.9 × 10⁻²                 | (Lipczynskakochany et al., 1995) | |
|      |                | Cl²              | 6.4 × 10⁸                  | (Lipczynskakochany et al., 1995) | |
|      |                | Br⁻              | <1 × 10⁹                   | (Martin et al., 1995) | |
|      |                | NO₃⁻             | 3.9 × 10⁸                  | (Farhataziz and Ross, 1977) | |
|      |                | NO₂⁻             | 8.1 × 10⁸                  | (Farhataziz and Ross, 1977) | |
|      |                | H₂O₂             | 2.7 × 10⁷                  | (Buxton et al., 1988) | |
|      | Organic        | Methanol         | 6.02 × 10⁸                 | (Ravishankara and Davis, 1978) | |
|      | compounds      | Ethanol          | 1.58 × 10⁹                 | (Ravishankara and Davis, 1978) | |
|      |                | 2-Propanol       | 3 × 10⁹                   | (Hanna et al., 2010) | |
|      |                | n-Butanol        | 4.6 × 10⁹                  | (Andreozzi et al., 1999) | |
|      |                | t-Butanol        | 0.4 × 10⁹                  | (Andreozzi et al., 1999) | |
|      |                | Phenol           | 6.6 × 10⁹                  | (Buxton et al., 1988) | |
|      |                | 4-Chlorophenol   | 7.6 × 10⁹                  | (Lipczynskakochany et al., 1995) | |
|      |                | Dimethyl sulfoxide (DMSO) | 5.8 × 10⁶                  | (Farhataziz and Ross, 1977) | |
|      | O₂⁻            | Acetic acid      | 1.6 × 10⁹                  | (Keenan and Sedlak, 2008) | |
|      |                | Benzoic acid     | 5.9 × 10⁹                  | (Keenan and Sedlak, 2008) | |
|      |                | 2-Propanol       | 1 × 10⁹                   | (Lipczynskakochany et al., 1995) | |
|      |                | Benzoquinone     | 9.6 × 10⁸                  | (Farhataziz and Ross, 1977) | |
|      |                | Hydroquinone     | (1.6 ± 0.1) × 10⁷          | (Farhataziz and Ross, 1977) | |
|      |                | Superoxide dismutase (SOD) | 1.8 × 10⁹                  | (Farhataziz and Ross, 1977) | |
|      | FeO²⁺          | As(III)          | <10⁻⁶                     | 7   | (Hug and Leupin, 2003)                     |
|      | Inorganic      | Cl⁻              | 100                       | 1   | (Jacobsen et al., 1998)                     |
|      | compounds      | NO₃⁻             | ≤10⁻⁵                     | (Jacobsen et al., 1998) | |
|      |                | Methanol         | 5.74 × 10²                 | (Pestovsky and Bakac, 2008) | |
|      |                | Ethanol          | 2.5 × 10⁸                  | (Jacobsen et al., 1998) | |
|      |                | Phenol           | 1.5 × 10⁸                  | (Mártil et al., 2002) | |
|      |                | DMSO             | 1.26 × 10⁵                 | (Pestovsky and Bakac, 2006) | |
|      |                | Acetic acid      | 3.1                       | 0   | (Jacobsen et al., 1998)                     |
|      |                | Benzoic acid     | 80                        | 0   | (Jacobsen et al., 1998)                     |

a. OH⁺ represents surface OH⁻.
b. Means not mentioned in the literature.

The half-life of HO₂/O₂⁻ is four orders of magnitude longer than that of •OH (Table 1). The detection methods for HO₂/O₂⁻ are similar to that for •OH. (1) When using DMPO as the spin trap agent, stable ESR spectra of DMPO-OOH/DMPO-O₂⁻ adducts can only be obtained in the presence of DMSO (Kohno et al., 1994) or in organic-rich media (Wang et al., 2011). On one hand, the generation rate of DMPO-OOH/DMPO-O₂⁻ adducts is lower than that of DMPO-OH adduct. Alternatively, DMPO-OOH/DMPO-O₂⁻ adducts readily decompose to DMPO-OH adduct in aqueous medium (Kohno et al., 1994; Zhao et al., 1998). Hence, the interference from the co-existing •OH in solution should be eliminated before HO₂/O₂⁻ detection. (2) HO₂/O₂⁻ can also be deduced from the observed scavenging by characteristic quenchers like benzoquinone (Zhang et al., 2012) (Table 2). However, it is almost impossible to distinguish similar organic oxidation products generated by HO₂/O₂⁻ attack from •OH attack.

1.3. High-valent iron species

Some researchers believe that high-valent iron species, i.e., ferryl(IV), are produced in heterogeneous Fenton systems, especially at neutral or basic pH or in the presence of ligands (Gonzalez-Ólmos et al., 2011; Hu et al., 2011; Katsoyiannis et al., 2008; Keenan and Sedlak, 2008; Luo et al., 2010), where high-valent iron is more stable (Diane and Virender, 2008). Though the generation mechanism of surface Fe(IV) (e.g., →Fe⁵⁺ = O) in heterogeneous Fenton systems remains unknown, Eq. (6) (Hu et al., 2011; Luo et al., 2010) is sometimes used for illustration. FeO²⁺ might also be generated from the leached iron-induced homogeneous Fenton reaction, most likely through heterolytic O–O bond cleavage by the inner-sphere reaction of FeOH⁺ and H₂O₂ (Buda et al., 2001; Remucal and Sedlak, 2011; Li et al., 2010).

\[
\text{Fe}^{II} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{IV} = \text{O} + \text{H}_2\text{O}
\]
High-valent iron is a weaker and more selective oxidant compared to \( \cdot \)OH (Table 1). It oxidizes organic compounds probably through one-electron (hydrogen atom transfer, electron transfer) and two-electron (hydroxide transfer, oxygen atom transfer) pathways, specifically by hydroxylation, methyleneketonization, olefin epoxidation, dehydrogenation, and \( \cdot \)S-oxidation etc. (Magario et al., 2012; Mártilde et al., 2002; Pestovskiy and Bakac, 2008; Pignatello et al., 2006). Some rate constants of \( \text{FeO}^{2+} \) with selected substances are listed in Table 2.

Though the half-life of ferryl(IV) in solution is about 0.35 sec (Table 1), calculated from its first-order decay rate constant (2/sec (Bossmann et al., 1998)) at pH 3–7, direct detection of ferryl(IV) is still difficult. (1) Since \( \text{FeO}^{2+} \) has a characteristic absorption band, e.g., in the 290–350 nm range at pH 0 (Mártilde et al., 2002), UV-Vis spectroscopy can be used for characterization, if the substrates do not interfere with the absorbance. (2) Resonance Raman spectroscopy and Mössbauer spectroscopy can also detect high-valent iron in solution directly, but only at extremely low temperatures (Nakamoto, 1997; Yuri and Virender, 2008). (3) Since ferryl(IV) can oxidize methanol or ethanol to the corresponding aldehydes, but does not oxidize 2-propanol or aromatic compounds to an appreciable extent (Pham et al., 2009, the respective reactivity with methanol, benzoic acid, and 2-propanol have been used for distinguishing between Fe(IV) and \( \cdot \)OH (Keenan and Sedlak, 2008). (4) The kinetic deuterium isotope effect (KDIE) (Gonzalez-Olmos et al., 2011; Pignatello et al., 1999), determined as the ratio of oxidation rates (KDIE = \( k_{\text{D}}/k_{\text{H}} \)) of the co-existing organic compounds with and without deuterium (like \( \cdot \)CH\(_2\)OH and CD\(_2\)OH), may behave differently with ferryl(IV) and \( \cdot \)OH, so it can be used as an indicator of ferryl(IV) (detailed below). (5) Olefin epoxidation is uncharacteristic of \( \cdot \)OH but is well-known for ferryl complexes (Gonzalez-Olmos et al., 2011). Therefore, it is used as the primary method for ferryl(IV) detection.

Gonzalez-Olmos et al. (2011) compared KDIE for methanol oxidation in an Fe-containing zeolite (Fe-ZSM5) catalyzed heterogeneous Fenton system (pH 7) with that in a homogeneous Fenton system (pH 3). They proposed that an additional oxidant besides \( \cdot \)OH in Fe-ZSM5/\( \text{H}_2\text{O}_2 \) system selectively attacked C-H bonds, and could react with t-butanol rather than HCO\(_3\). With the increasing concentration of HCO\(_3\), a ‘selective’ \( \cdot \)OH quencher, KDIE in the Fe-ZSM5/H\(_2\)O\(_2 \) system increased from 1.33 to 1.41, similar to that in a ferryl-involved photo-Fenton system, while KDIE decreased with increasing concentration of t-butanol. In a homogeneous Fenton system (the genuine \( \cdot \)OH reaction), KDIE was observed to be 1.07 and unaffected by the presence of scavengers. Moreover, Fe-zeolite catalyzed the epoxidation of cyclohexene by H\(_2\)O\(_2 \), suggesting Fe(IV) as the additional oxidant.

2. Interfacial mechanisms of heterogeneous Fenton systems

Ever since the discovery of heterogeneous Fenton reactions in 1991, Tyre et al. (1991) proposed two possible interfacial mechanisms, i.e., the homogeneous Fenton mechanism induced by surface-leached iron and heterogeneous catalysis on the mineral surface, as illustrated in Fig. 1. However, it is still difficult to distinguish the two mechanisms so far, and both mechanisms may even co-exist.

2.1. Homogeneous Fenton mechanism induced by surface-leached iron

In some heterogeneous Fenton systems, certain iron-based materials serve as the source of continuous dissolution of iron especially under acidic pH, which contribute to a homogeneous Fenton reaction-dominated mechanism (Lücking et al., 1998; Matta et al., 2007; Zeng and Lemley, 2009).

Zeng and Lemley (2009) found that about 20 mg/L ferrous ions desorbed from the prepared Fe\(^{2+}\)-substituted ion-exchange resins and played a major role in the degradation of 4,6-dinitro-o-cresol (DNOC) with H\(_2\)O\(_2 \). Addition of either HCl or Ca\(^{2+}\) promoted the desorption of Fe\(^{2+}\) by ion exchange, thus accelerating the homogeneous oxidation of DNOC. Accordingly, a first-order kinetic model of \( \text{Fe}^{2+} \) desorption and second-order oxidation kinetics with respect to \( \cdot \)OH and DNOC were proposed, both of which could simulate the experimental data well.

Lücking et al. (1998) attributed the catalytic activity of iron powder and iron-impregnated activated carbon to leached iron ions. Over 200 mg/L iron ions leached from iron powder through surface corrosion (Eqs. (7)–(9)) (Chu et al., 2012; Joo et al., 2005; Xu and Wang, 2011) during the oxidation of 4-chlorophenol (4-CP) at initial pH 5. Iron leaching increased as pH decreased, accelerating both H\(_2\)O\(_2 \) activation and 4-CP degradation.

\[
\text{Fe}^0 + \text{H}_2\text{O}_2 + 2\text{H}^+ \rightarrow \text{Fe}^{2+} + 2\text{H}_2\text{O} \\
\text{Fe}^0 + \text{O}_2 + 2\text{H}^+ \rightarrow \text{Fe}^{2+} + \text{H}_2\text{O}_2 \\
\text{Fe}^0 + 2\text{H}^+ \rightarrow \text{Fe}^{2+} + \text{H}_2
\]

\(pH\) influences not only the surface iron leaching process, but also iron speciation and reactivity in the induced homogeneous Fenton reactions. In homogeneous Fenton systems, the reactions between \( \cdot \)OH and organic compounds are usually very fast (\( k \approx 10^7–10^8 \text{L/(mol·sec)} \)). Hence, the generation of \( \cdot \)OH (Eq. (10)) (Pignatello et al., 2006), where H\(_2\)O\(_2 \) ligands on Fe are omitted) becomes the slowest step (Lipczynskakochany et al., 1995), i.e., rate-determining step (RDS). \( \text{Fe}^{2+} \) exists predominantly as \( \text{Fe}^{2+} \) at \( pH \) below 3 and changes to \( \text{Fe(OH)}^- \) and \( \text{Fe(OH)}_2 \) as \( pH \) increases to 4 (Pignatello et al., 2006). Due to the formation of \( \text{Fe(OH)}_2 \), which is about 10 times more reactive than \( \text{Fe}^{2+} \), the generation rate of \( \cdot \)OH increases and reaches a plateau at \( pH \) 4 corresponding to a value about 7 times greater than at \( pH \) 3 (Pignatello et al., 2006). In addition, \( \text{Fe}^{2+} \) also tends to coprecipitate with less Fenton-reactive Fe(III) oxyhydroxides (Eq. (11)) (Pignatello et al., 2006) at \( pH \) above 3. Therefore, the optimum \( pH \) of homogeneous Fenton systems is usually 3.

\[
\text{Fe}^{(II)} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{(III)} + \cdot \text{OH} + \text{HO}^- \\
k = 40–80 \text{L/(mol·sec)}
\]

\[
\text{Fe}^{(III)} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{(II)} + \text{HO}_2^- + \cdot \text{H}^+ \\
k = 2 \times 10^{-3}–2.6 \times 10^{-3} \text{L/(mol·sec)}
\]
Moreover, iron-complexing ligands can increase Fe(III) solubility (Remucal and Sedlak, 2011) and broaden the Fenton pH range. A chelating agent may influence the reactivity of iron in at least three ways (He et al., 2015): (i) changing the redox potential of Fe²⁺/Fe³⁺; (ii) creating a labile coordination position on iron ions for complexation with H₂O₂, since the complex between Fe²⁺ and H₂O₂ may be a precursor of ROS generation (Pignatello et al., 2006; Remucal and Sedlak, 2011); and (iii) scavenging. OH or generating high-valent iron species (Pignatello et al., 2006).

Admittedly, the proportion of iron leaching-induced homogeneous Fenton mechanism varies for different reaction systems, and cannot be simply determined by the amount of leached iron. For example, Hartmann et al. (2010) suggested that as much as 50–80 mg/L iron ions could start a homogeneous Fenton reaction. However, the research of Kwan and Voelker (2002) showed that 0.34 mg/L leached Fe³⁺ already contributed to the overall oxidation of formic acid in the ferrihydrite/H₂O₂ system at pH 3.

2.2. Heterogeneous catalysis mechanism

A large number of iron-based materials are stable and undergo limited iron leaching during reactions (Lin and Gurol, 1998; Xue et al., 2009a). Hence, organic compounds are mainly oxidized by the ROS generated from heterogeneous catalysis. Besides, Andreozzi et al. (2002a, 2002b) once proposed a mechanism of non-radical oxidation between adsorbed H₂O₂ and adsorbed 3,4-dihydroxybenzoic acid on goethite, probably due to the low goethite loading.

Heterogeneous Fenton reactions are usually controlled by kinetic processes (Lin and Gurol, 1998; Xue and Wang, 2012a) including reactant adsorption, surface chemical reaction and product desorption, due to the fast diffusion process. The kinetic expressions vary according to different RDS.

The rate of catalytic H₂O₂ decomposition on the goethite surface is found to be proportional to the surface area of goethite and the concentration of H₂O₂ (Huang et al., 2001; Kwan and Voelker, 2003; Lin and Gurol, 1998). Therefore, a mechanism of H₂O₂ decomposition based on surface complexation chemistry was proposed by Lin and Gurol (1998) and is widely accepted. Briefly, H₂O₂ complexes with the goethite surface (≡FeIII–OH) to form a precursor surface complex, (H₂O₂)ₖ (Eq. (12)). The electron transfer from ligand-to-metal within the complex produces a transitional state for the surface site (≡FeII·O₂H⁻) (Eq. (13)), which is deactivated through the dissociation of the peroxy radical (Eq. (14)). Then the produced surface ≡FeII catalyzes the generation of ·OH (Eq. (1)). Free radicals may be consumed by surface sites (Eqs. (15)–(16)) and by adsorbed H₂O₂ (Eqs. (17)–(18)), and even be terminated by reacting with each other (Eqs. (19)–(20)). Since ≡FeIII·OH⁻ and ≡FeII cycle on the surface, goethite acts as a heterogeneous catalyst. Based on the above elementary reaction steps, a decomposition rate model that resembles the classic Langmuir–Hinshelwood (i.e., the reaction between adsorbed H₂O₂ and surface sites) rate expression (Eq. (21)) (Lin and Gurol, 1998), where r₁ (mol/(L·min)) represents H₂O₂ decomposition rate, [H₂O₂] (mol/L) and [FeOOH] (mol/L) represent the concentration of H₂O₂ and FeOOH, respectively, t (min) represents time, k (L/(mol·min)) and Kₘ (L/mol) represent the rate and binding constants, respectively) was obtained and could fit the experimental data well. Hence, the proposed mechanism of H₂O₂ surface decomposition was confirmed. However, more direct and conclusive interface evidence is still needed.

\[
\text{Fe}^{III} - \text{OH} + \text{H}_2\text{O}_2 \rightarrow (\text{H}_2\text{O}_2)_k \quad (12)
\]

\[
(\text{H}_2\text{O}_2)_k \rightarrow (\equiv \text{Fe}^{II} \cdot \text{O}_2\text{H}) + \text{H}_2\text{O} \quad (13)
\]

\[
(\equiv \text{Fe}^{II} \cdot \text{O}_2\text{H}) \rightarrow \text{Fe}^{II} + \text{HO}_2\cdot \quad (14)
\]

\[
\text{HO}_2\cdot + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{III} \cdot \text{OH} + \text{OH}^{-} \quad (1)
\]

\[
\text{HO}_2\cdot + \text{H}_2\text{O}_2 \rightarrow \text{OH}^{-} + \text{O}_2 \quad \text{pK}_a = 4.85 \pm 0.1 \quad (2)
\]

\[
\text{Fe}^{III} \cdot \text{OH} + \text{HO}_2\cdot \rightarrow \text{Fe}^{II} + \text{H}_2\text{O}/\text{OH}^{-} + \text{O}_2^2 \quad (15)
\]

\[
\text{OH}^{-} + \equiv \text{Fe}^{II} \rightarrow \text{Fe}^{III} \cdot \text{OH}^{-} \quad (16)
\]

\[
\text{OH}^{-} + (\text{H}_2\text{O}_2)_k \rightarrow \text{Fe}^{III} \cdot \text{OH} + \text{H}_2\text{O} \cdot + \text{H}_2\text{O} \quad (17)
\]

\[
(\text{H}_2\text{O}_2)_k + \text{HO}_2\cdot \rightarrow \text{Fe}^{III} \cdot \text{OH} + \text{H}_2\text{O}/\text{OH}^{-} + \text{OH}^{-} + \text{O}_2 \quad (18)
\]

\[
\text{HO}_2\cdot + \text{HO}_2\cdot \rightarrow (\text{H}_2\text{O}_2)_k + \text{O}_2 \quad (19)
\]

\[
\text{OH}^{-} + \text{H}_2\text{O}_2 \rightarrow \text{HO}_2\cdot + \text{H}_2\text{O} + \text{O}_2 \quad (20)
\]

\[
-r_1 = -\frac{d[H_2O_2]}{dt} = k[\text{FeOOH}[H_2O_2]/1 + K_m[H_2O_2]] \quad (21)
\]
compounds may also compete with H$_2$O$_2$ for surface active sites (Lücking et al., 1998; Oliveira et al., 2007), inhibiting H$_2$O$_2$ surface decomposition.

However, mechanisms of ROS utilization by organic compounds vary. Some researchers hypothesize that the surface-generated ROS mainly attack the adsorbed organic compounds, i.e., a Langmuir–Hinshelwood mechanism. They ascribe the enhanced degradation of organic compounds by iron-based materials to the enrichment of the organic compounds at the surface (Hu et al., 2011; Liang et al., 2012; Yang et al., 2009). Xue et al. (2009a) found that excess adsorbed PCP might compete with H$_2$O$_2$ for magnetite surface sites, leading to a decreased generation of ROS and thus a decreased oxidation rate. The Langmuir–Hinshelwood model (Eq. (22) (Xue et al., 2009a), where $k_{app}$ ($1/hr$) is the initial pseudo-first-order rate constant, $k_{int}$ (mmol/(L·hr)) and $K_s$ (L/mmol) are the intrinsic reaction rate constant and the adsorption constant of PCP over Fe$_3$O$_4$ surface respectively, $[\text{PCP}]_i$ (mmol/L) is the initial PCP concentration) could simulate experimental data. Fluoride (F$^-$) adsorbed on Fe$_3$O$_4$ and inhibited both H$_2$O$_2$ decomposition and PCP oxidation, also suggesting the surface reaction mechanism. Moreover, the Raman spectra of the suspension showed the removal of adsorbed PCP during oxidation. Nevertheless, other researchers propose that the surface-generated ROS mainly oxidize the organic compounds in solution, especially for unadsorbed organic compounds (Furman et al., 2009; Liang et al., 2012), i.e., an Eley–Rideal mechanism. He et al. (2014) directly observed that adsorbed catechol or 4-chlorocatechol remained on the nano-Fe$_3$O$_4$ surface during the oxidation by in-situ flow-cell ATR-FTIR experiments. Hence, ROS was hypothesized to predominantly attack the unadsorbed parent compounds near the interface region. In addition, the generated organic intermediates were also adsorbed on the nano-Fe$_3$O$_4$ surface, and might affect the catalytic reactivity of Fe$_3$O$_4$.

\[
k_{app} = \frac{k_{int}K_s}{1 + [\text{PCP}]_i}
\]  

(22)

Because electrostatic attractions between charged organic compounds and charged iron oxide surfaces are reported to affect organic oxidation reactions (Kwan and Voelker, 2004; Zhang et al., 2010), pH and ion strength may influence the oxidation rates (Kwan and Voelker, 2004). Moreover, both H$^+$ and ligands can promote the dissolution of some iron-based materials, including a homogeneous Fenton mechanism (He et al., 2015; Sun et al., 2014; Xue et al., 2009c).

2.3. Heterogeneous reaction-induced homogeneous mechanism

Some heterogeneous Fenton systems are characterized by a two-stage degradation kinetic process, i.e., an initial slow induction period and a subsequent rapid oxidation period. Researchers postulate the induction period as heterogeneous reactions including surface iron leaching and heterogeneous catalysis, and the second kinetic stage as homogeneous Fenton reactions induced by the leached iron (Xu and Wang, 2011, 2012a; Zhou et al., 2008).

Xu and Wang (2012a) found that the degradation curve of 2,4-dichlorophenol (2,4-DCP) with Fe$_3$O$_4$ magnetic nanoparticles (MNPs)/H$_2$O$_2$ exhibited two-stage first-order kinetics at pH 2 and 3. During the whole oxidation process, H$_2$O$_2$ was decomposed gradually. In the first stage, iron was dissolved slowly, indicating slow iron leaching and heterogeneous catalysis. Both the activated surface sites of Fe$_3$O$_4$ MNPs and the concentrated H$_2$O$_2$ near the surface may scavenge the surface-generated ROS (Eqs. (4), (15)–(16)), leading to the observed slow oxidation. And the activation energy ($E_a$) was higher than that of a homogeneous Fenton reaction. In the second stage, iron leached more rapidly. Both the oxidation rate constant and $E_a$ were similar to that of a homogeneous Fenton system. The radical scavenging experiments confirmed that the primary ROS was free·OH in the bulk solution rather than surface-bound ·OH. Therefore, two-stage degradation kinetics may suggest a heterogeneous reaction-induced homogeneous mechanism.

3. Different heterogeneous Fenton systems catalyzed by characteristic iron-based materials

Iron-based materials possess the advantages of high Fenton activity, low cost, negligible toxicity, and easy recovery (Pereira et al., 2012; Rahim Pouran et al., 2014). Hence, they become a superior type of heterogeneous Fenton catalysts, which can degrade phenolic compounds, dyes, insecticides, etc. efficiently. According to the reactive content and physicochemical properties, iron-based heterogeneous Fenton catalysts are divided into five primary categories, i.e., zero-valent iron, iron minerals and iron (hydro)oxides, multimetallic iron-based materials, supported-iron-based materials, and horseradish peroxidase (HRP)-based materials (Table 3).

3.1. Zero-valent iron (ZVI or Fe$^{0}$)

Though ZVI is commonly used as a reductant ($E^0_{ZVI}$(Fe$^{2+}$/Fe$^{0}$) = −0.447 V (Vanýsek, 2011)) in permeable reactive barriers, it has been proved to be a highly efficient heterogeneous Fenton catalyst (Lücking et al., 1998; Tang and Chen, 1996; Xu and Wang, 2011; Zhou et al., 2008). Specifically, nanoparticulate ZVI (nZVI) possesses high surface reactivity and has easy access to contaminated zones, even though aggregation may occur. A heterogeneous Fenton system consisting of 0.5 g/L nZVI and 0.003 mol/L H$_2$O$_2$ could completely remove 100 mg/L of the biocide 4-chloro-3-methyl phenol (CMP) within 15 min and 63% of the corresponding total organic carbon (TOC) in 1 hr at pH 6 (Xu and Wang, 2011).

Reductive ZVI is usually corroded through two-electron transfer in the presence of H$_2$O$_2$ under acidic conditions (Eqs. (7)–(9)). Even dissolved oxygen (DO) can lead to ZVI corrosion and in-situ H$_2$O$_2$ generation as well (Eq. (8)), which may lead to a Fenton-like reaction (Keenan and Sedlak, 2008). The released Fe$^{2+}$ ions in ZVI/H$_2$O$_2$ systems are responsible for the efficient degradation of organic contaminants through a homogeneous Fenton mechanism at acidic pH, such as pH 2 or 3 (Lücking et al., 1998; Tang and Chen, 1996; Xu and Wang, 2011; Zhou et al., 2008), or a heterogeneous reaction-induced homogeneous mechanism at higher pH, such as pH 4 or 6 (Xu and Wang, 2013; Zhou et al., 2008). In the second stage of the heterogeneous reaction-induced homogeneous mechanism, ZVI continues to dissolve, mostly...
through the reduction of Fe\(^{3+}\) (Zhou et al., 2008) (Eq. (23)), which accelerates the regeneration of Fe\(^{2+}\) in the homogeneous Fenton reaction. Meanwhile, a layer of iron oxides, probably lepidocrocite (\(\gamma\)-FeOOH) and magnetite (Fe\(_3\)O\(_4\)), is formed in the presence of oxygen and covers the ZVI surface (Zhou et al., 2008). Though \(\gamma\)-FeOOH alone (Chou and Huang, 1999) or Fe\(_3\)O\(_4\) alone (Xu and Wang, 2012a) has lower catalytic activity than ZVI, the surface pre-oxidized ZVI by H\(_2\)SO\(_4\) showed higher reactivity than fresh ZVI (Xu and Wang, 2011). Therefore, the stability and reusability of ZVI need to be further evaluated.

\[
2\text{Fe}^{3+} + \text{Fe}^0 \rightarrow 3\text{Fe}^{2+}. \tag{23}
\]

\(\cdot\text{OH}\) is the dominant ROS in ZVI-catalyzed heterogeneous Fenton systems, while high-valent iron (Eq. (24)) and DO may also play a role (Keenan and Sedlak, 2008; Xu and Wang, 2011; Zhou et al., 2008). Xu and Wang (2011) found that \(\text{Fe}^0\) was responsible for 79% of CMP removal, and surface-bound \(\cdot\text{OH}\) accounted for 57%, according to radical-scavenging experiments. They also speculated the remaining 21% of CMP removal by \(\text{Fe}(IV)\) attack. Zhou et al. (2008) found that the low concentration of 4-chlorocatechol, which was the oxidation product by \(\cdot\text{OH}\) attack, could not explain the rapid 4-CP degradation, and thus proposed another DO-involved organic radical mechanism.

\[
\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}(IV) + \text{H}_2\text{O}. \tag{24}
\]

### Table 3 – Efficient iron-based heterogeneous Fenton catalysts.

| Category | Iron-based heterogeneous Fenton catalysts |
|----------|------------------------------------------|
| Zero-valent iron | Iron powder (Lücking et al., 1998; Tang and Chen, 1996), zero-valent iron (ZVI or Fe\(^0\)) (Zhou et al., 2008), nanoparticulate zero-valent iron (nZVI) (Xu and Wang, 2011). |
| Iron minerals and iron (hydr)oxide | Magnetite (Fe\(_3\)O\(_4\)) (Gao et al., 2007; Xu and Wang, 2012a; Xue et al., 2009a, 2009b; Zhang et al., 2009), goethite (\(\gamma\)-FeOOH) (Lin and Gurol, 1996; Lu et al., 2002; Ortiz de la Plata et al., 2010), green rust (GR(CF\(_3\)), GR(CO\(_2\))\(_3\)), (Hanna et al., 2010), ferrous hydroxide colloids (Yan et al., 2012), pyrite (Fe\(_3\)S\(_2\)) (Matta et al., 2007; Zhang et al., 2014), Fe\(_3\)O\(_4\)/HA (Niu et al., 2011), prussian blue modified \(\gamma\)-Fe\(_2\)O\(_3\) (PB MNPs) (Wang and Huang, 2011; Zhang et al., 2010), Fe\(_3\)/Fe\(_3\)O\(_4\) (Costa et al., 2008), Fe\(_3\)O\(_4\)/HA (Nie et al., 2007), iron oxide/Fe\(_0\) (Nie et al., 2008, 2010). |
| Multimetallic iron-based materials | Supported iron-based materials as support | Fe-activated carbon (Fe/AC) (Duarte et al., 2012), ordered mesoporous carbon supported iron (Fe/OMC) (Duan et al., 2014), magnetite-loaded mesocellular carbonaceous material (Fe\(_3\)O\(_4\)/MSU-F-C) (Chun et al., 2012), iron-doped carbon aerogel (Duarte et al., 2009), iron-impregnated carbon aerogel (Duarte et al., 2009), Fe\(_3\)O\(_4\)/multi-walled carbon nanotube (Fe\(_3\)O\(_4\)/MWCNTs) (Hu et al., 2011), Fe\(_3\)O\(_4\)/MWCNTs (Liao et al., 2009), Fe\(_3\)O\(_4\) decorated reduced graphene oxide (Fe\(_3\)O\(_4\)/rGO) (Li et al., 2013), graphene oxide–Fe\(_3\)O\(_4\) (GO–Fe\(_3\)O\(_4\)) (Zubir et al., 2015, 2014). |
| | Carbon-based materials as support | Quartz/magnetite (Hanna et al., 2008), quartz/amorphous iron (III) (Hanna et al., 2008), quartz/magnemite (Hanna et al., 2008), quartz/goethite (Hanna et al., 2008), iron oxide nanoparticles immobilized in alumina coated mesoporous SBA-15 silica (FeALSIs) (Lim et al., 2006), FeALSIs–ox (Pham et al., 2009), FeS–ox (Pham et al., 2009), Fe–zeolite (Fe-ZSM5 (Gonzalez-Olmos et al., 2011; Kuznetsova et al., 2004; Makhotkina et al., 2006), Fe–Beta (Gonzalez-Olmos et al., 2011)), natural vanadium–titanium magnetite (Liang et al., 2010). |
| | Silicate-based materials as support | Fe–MCM-41 mesoporous materials (Gokulakrishnan et al., 2009), pillared saponite clay impregnated with Fe(II) acetylacetonate (Herney-Ramirez et al., 2011), Fe-Al pillared clay (Luo et al., 2009), \(\gamma\)-FeOOH on a brick grain support (Chou and Huang, 1999), natural containing Fe-clay (Djeffal et al., 2014). |
| | Organic compound as support | Fe\(^{2+}\)-substituted ion-exchange resin (Zeng and Lemley, 2009) (detailed in Section 1.1). |
| | HRP-based materials | HRP immobilized on aluminum-pillared interlayered clay (Al-PILC) (Cheng et al., 2006). |

### 3.2. Iron minerals and iron (hydr)oxides

#### 3.2.1. Magnetite (Fe\(_3\)O\(_4\))

Fe\(_3\)O\(_4\) is the only pure iron oxide having mixed valences. Surface structural Fe(II) is crucial for \(\cdot\text{OH}\) generation as discussed in Section 2.2. Fe\(_3\)O\(_4\) is usually represented by the formula (Fe\(^{3+}\))\(_{1-x}\)(Fe\(^{2+}\))\(_{x}\)O\(_4\), i.e., with Fe(III) in tetrahedral sites and both Fe(II) and Fe(III) in octahedral sites, which can be characterized by Mössbauer spectroscopy. The two valence states on octahedral sites are not distinguishable due to fast electron hopping (Xue et al., 2009a), which may accelerate the cycling of structural Fe(II)/Fe(III). Therefore, Gao et al. (2007) first reported the intrinsic peroxidase-like activity of ferromagnetic Fe\(_3\)O\(_4\), which was then applied as an efficient heterogeneous Fenton catalyst, mainly catalyzing the generation of \(\cdot\text{OH}\) (Eq. (1)).

Compared to ZVI, Fe\(_3\)O\(_4\) undergoes less iron leaching but requires more H\(_2\)O\(_2\) and longer reaction time. Even the highly efficient Fe\(_3\)O\(_4\) MNPs, which exhibit superparamagnetism and uniform dispersion, consume ten times more H\(_2\)O\(_2\) than nZVI (Xu and Wang, 2011, 2012a). In addition, it commonly needs hours to remove the parent organics.

\(\text{pH}\) may influence the interfacial mechanism of Fe\(_3\)O\(_4\)-catalyzed heterogeneous Fenton systems due to Fe\(_3\)O\(_4\) dissolution. At neutral pH, Fe\(_3\)O\(_4\) (MNPs) exhibit excellent stability and reusability (Xue et al., 2009a; Zhang et al., 2009), following a heterogeneous catalysis mechanism as discussed in Section 2.2. At the acidic pH of 3, the two-stage degradation kinetics of
2,4-DCP suggested a heterogeneous reaction-induced homogeneous mechanism (detailed in Section 2.3) (Xu and Wang, 2012a). Meanwhile, the activity of Fe3O4 MNPs decreased gradually during consecutive runs, probably due to the leached iron and other factors, like the poisoning of the active catalytic sites by adsorbed organic species or oxidation of the surface (He et al., 2014) etc.

3.2.2. Goethite (α-FeOOH)

Goethite is one of the most thermodynamically stable iron oxides at ambient temperature, with large surface area (100–200 m²/g), and was the primary iron oxide studied as an efficient heterogeneous Fenton catalyst.

In the heterogeneous Fenton systems, goethite usually undergoes iron leaching through surface reactions. The oxidation of 2-chlorophenol (2-CP) in goethite/H2O2 at pH 3 followed the heterogeneous reaction-induced homogeneous mechanism (Lu et al., 2002; Ortiz de la Plata et al., 2010). Proton-promoted dissolution of goethite (Eq. (25) (Lu et al., 2002)) initiated a Fe3+-induced homogeneous Fenton-like reaction. As the degradation of organic compounds proceeded, some reductive byproducts, such as catechol, ascorbate, and chlorohydroquinone, promoted a reductive dissolution of goethite, producing more reactive Fe2+. Meanwhile, they could also enhance the regeneration of Fe3+ by reducing Fe2+ in solution, accelerating the homogeneous Fenton reaction. Even after the removal of 2-CP, Fe3+ may continue to leach by non-reductive dissolution with byproducts like oxalic acid.

$$\alpha$$-FeOOH + 3H⁺ → Fe3+ + 2H₂O  

(25)

However, goethite shows low solubility in other cases. For example, no dissolved iron was detected in the oxidation of n-butyl chloride at pH 7.5, and the oxidation rate was independent of pH (5–9) and alkalinity conditions. Hence, a heterogeneous catalysis mechanism was suggested (Lin and Gurol, 1996).

3.2.2.3. Other iron minerals and iron (hydr)oxides

Other iron minerals and iron (hydr)oxides including naturally existing pyrite (Matta et al., 2007), green rust (Hanna et al., 2010), limonite (Souza et al., 2009) and synthesized ferrous hydroxide colloids (Yan et al., 2012), nano α-FeOOH (Pinto et al., 2012), Fe₃O₄/HA (Niu et al., 2011), PBMNPs (Wang and Huang, 2011; Zhang et al., 2010), Fe₅/iron oxide (Costa et al., 2008; Nie et al., 2008, 2010), etc., are effective heterogeneous Fenton catalysts. Due to the low iron leaching and the limited reactivity of the reaction filtrate, most of the reaction systems follow the heterogeneous catalysis mechanism. Pyrite (FeS₂), however, can react with H₂O₂ and leaches Fe²⁺, which is then reduced to Fe²⁺ by FeS₂, leading to the homogeneous Fenton mechanism.

Structural Fe(II) has been found to have higher reactivity towards H₂O₂ decomposition than structural Fe(III), which contributes to the accelerated oxidation of organic compounds (Costa et al., 2006; Hanna et al., 2010; Xue et al., 2009b; Yan et al., 2012), similar to the situation of a homogeneous Fenton system (Eqs. (10)–(11)). Hanna et al. (2010) found that the reactivity of GR(Cl-) was higher than that of GR(SO₄²⁻) or GR(CO₃²⁻) due to the higher structural Fe(II)/Fe(III) ratio.

Hence, accelerating the electron transfer from Fe(III) to Fe(II) on iron (hydr)oxides surfaces can greatly enhance the catalytic activity (Costa et al., 2008; Nie et al., 2007, 2008, 2010; Niu et al., 2011; Zhang et al., 2010). For example, Fe₃O₄/HA showed better catalytic activity than Fe₃O₄, probably due to the higher reduction potential of complexed Fe(III)–HA/Fe(II)–HA, which could contribute to the rapid regeneration of Fe(II) (Niu et al., 2011). Fe⁵/Fe₃O₄ possessed higher activity than pure Fe⁵ or Fe₃O₄, due to the electron transfer from Fe⁵ to magnetite Fe(III) (Eq. (26)) (Costa et al., 2008), which was also proved by the oxidation of 2-chlorophenol (2-CP) in goethite/H₂O₂ at pH 3. The Fe⁵/Fe₃O₄ exhibited high reactivity, probably due to the enhanced regeneration of Fe(II) by reducing Fe³⁺ in solution, accelerating the homogeneous Fenton reaction. Even after the removal of 2-CP, Fe³⁺ may continue to leach by non-reductive dissolution with byproducts like oxalic acid.

$$\text{Fe}^5 + 2\text{Fe}^{\text{III}}_{\text{magnetite}} \rightarrow 3\text{Fe}^{\text{II}}_{\text{magnetite}}$$  

(26)

Aside from the redox action of surface Fe(II)/Fe(III), porous ferrous hydroxide colloid (Fe-colloid I) may generate OH· from direct homolysis of the adsorbed H₂O₂ at caged active sites on the surface, since Fe-colloid II with no pores exhibited lower activity (Yan et al., 2012). Though some researchers (Luo et al., 2010) agreed with this hypothesis, more experimental evidence is still needed.

3.3. Multimetallic iron-based materials

Incorporating other metals into iron-based materials can effectively enhance the reactivity towards the productive decomposition of H₂O₂ and the oxidation of organic compounds (Costa et al., 2006; Deng et al., 2008; Xu and Wang, 2012b), through varied mechanisms.

Though the interfacial electron transfers between the added metals and iron are very fast and hard to observe, they are believed to cause the observed high catalytic reactivity. The oxidation of Fe(II) can be accelerated by thermodynamically favorable coupling reactions with metals like Ce(IV), Co(III), Mn (III) or V(V) (Costa et al., 2006; Xu and Wang, 2012b). Meanwhile, the corresponding reduced metals (i.e., Ce(III), Co(II), Mn (II) or V(IV)) can also activate H₂O₂ decomposition (Costa et al., 2006; Deng et al., 2008; Xu and Wang, 2012b), contributing to an enhanced interfacial OH· generation (Fig. 2). Xu and Wang (2012b) confirmed the generation of Ce(III) from Ce(IV) and the oxidation of Fe(II) to Fe(III) on the surface of Fe₃O₄/CeO₂ from XPS spectra. They also found that CeO₂ facilitated the dissolution of iron, inducing a homogeneous Fenton reaction. Hence, the high reactivity of Fe₃O₄/CeO₂ was attributed to both the enhanced heterogeneous catalysis and homogeneous reactions.

On the other hand, Fe₃₋₅Cr₃₋₅O₄ exhibited high reactivity, probably due to the enhanced regeneration of Fe(II) by the coupled oxidation of Cr(II) (Eq. (27)) (Magalhaes et al., 2007). In addition, similar to the substitution of octahedral Fe(II) by Co(II) or Mn (II) (Costa et al., 2006), Cr(III) substituted for octahedral Fe(III) of Fe₃O₄ for valence balance. The increased surface area and surface hydroxyl groups might also contribute to the high efficiency of Fe₃₋₅Cr₃₋₅O₄.

$$\text{Fe}^{\text{III}} + \text{Cr(II)} \rightarrow \text{Fe}^{\text{II}} + \text{Cr(III)}$$  

(27)

When Nb⁵⁺ was inserted into goethite, oxygen vacancy sites were formed in the goethite structure, according to the Mössbauer spectra (Oliveira et al., 2008). Since none of the OH scavengers could inhibit H₂O₂ decomposition, H₂O₂ probably reacted with the surface oxygen vacancies (O3surf), generating...
adsorbed oxygen \([O_{\text{ads}}]\), which eventually produced \(O_2\) (Eqs. (28)-(29) (Oliveira et al., 2008)). Electrospray ionization coupled with mass spectrometry (ESI-MS) and density functional theory (DFT) calculations also detected other intermediates besides hydroxylation products. Therefore, oxygen vacancy sites participated in the Nb-substituted goethite/H\(_2\)O\(_2\) system.

\[
\text{[surf] + } \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{[O}_{\text{ads}}]
\]

(28)

\[
2\text{[O}_{\text{ads}}] \rightarrow \text{O}_2
\]

(29)

3.4. Supported iron-based materials

More and more researchers choose carbon materials, like AC, MWCNTs and (r)GO, and silicate materials, like mesoporous silica, quartz, zeolite, and saponite, as the support for efficient heterogeneous Fenton catalysts due to the good chemical stability, high mechanical strength and low cost. Some supports even have large specific surface area (100–1000 m\(^2\)/g) and a hydrophobic surface (Hu et al., 2011). Though graphite, AC, and MWCNTs can also catalyze the active decomposition of H\(_2\)O\(_2\) to a much lower degree (Hu et al., 2011; Lucking et al., 1998), the iron-based material is still the active component of the catalysts.

Some supports can concentrate the organic compounds near the catalytic active center of iron oxides by enhanced adsorption, and thus increase the degradation efficiency (Chun et al., 2012; Hana et al., 2008; Hu et al., 2011; Liao et al., 2009; Liu et al., 2013; Zubir et al., 2014). Hu et al. (2011) found that more 17α-methyltestosterone (MT) was oxidized in the Fe\(_3\)O\(_4\)/MWCNTs-H\(_2\)O\(_2\) system than in the Fe\(_3\)O\(_4\)-H\(_2\)O\(_2\) system, due to the observed high adsorption of MT on Fe\(_3\)O\(_4\)/MWCNTs through hydrophobic interactions. The observed insignificant iron leaching suggested the heterogeneous catalysis mechanism.

Well-dispersed iron oxides on a support can increase the number of active sites for the heterogeneous Fenton reaction, contributing to the high reactivity, though this may lead to iron leaching at acidic pHs as well (Duarte et al., 2009, 2012; Pham et al., 2009). Lim et al. (2006) found higher reactivity for a catalyst prepared by impregnating iron oxide nanoparticles on alumina-coated SBA-15 (FeAlSi) than that of FeSi. TEM images showed iron oxide nanoparticle aggregates on FeSi but not on FeAlSi, and the porosity of FeAlSi was lower than that of the original SBA-15. Both evidences suggested the presence of homogeneously dispersed iron oxide on the pore wall of FeAlSi, which may contribute to the higher reactivity. In addition, the function of Al on the high reactivity needs further research (Lim et al., 2006; Pham et al., 2009).

![Fig. 2 – Proposed mechanism for the participation of M in heterogeneous Fenton systems: M(y) represents Mn(II) or Co(II) for Fe\(_3\) \(_\text{M}_x\)O\(_4\), and Ce(III) for Fe\(_3\)O\(_4\)/CeO\(_2\).](image)

3.5. HRP-based materials

Horseradish peroxidase (HRP) is a heme peroxidase and contains a single protoporphyrin IX heme group with Fe(III) at the active center in the inactive form (Allen et al., 2009). HRP has good solubility and can effectively catalyze the oxidation of organic compounds, such as phenol (Cooper and Nicell, 1996), bisphenol A (Escalona et al., 2014), 3,3',5,5'-tetramethylbenzidine (Gao et al., 2007), and dyes (de Souza et al., 2007), and even carboxylated single-walled carbon nanotubes (Allen et al., 2009), under neutral pH with low H\(_2\)O\(_2\) concentrations (Cheng et al., 2006; Zhang et al., 2009).

Herein, the oxidation of phenol (Allen et al., 2009; Magario et al., 2012) is briefly described as an example of the reaction mechanism of the HRP/H\(_2\)O\(_2\) system. First, H\(_2\)O\(_2\) binds to the heme Fe(III) of HRP to form a precursor complex, which undergoes protein-assisted heterolytic cleavage and loses a water molecule. Hence, the precursor complex is transformed to Compound I, which is comprised of Fe(IV) and a porphyrin cation radical. Then phenol is oxidized by Compound I to generate phenoxy radical, while Compound I undergoes one-electron reduction to form Compound II, which is still comprised of Fe(IV) and a porphyrin cation radical. The formed Compound II can oxidize another phenol to phenoxy radical and regenerates HRP. Phenoxy radicals react to generate dimers, oligomers and polymers with low solubility, which should be further removed by precipitation or filtration. Therefore, the ROS in the HRP/H\(_2\)O\(_2\) system is Fe(IV).

It is noteworthy that HRP is expensive. Both the interaction between the generated free radicals and the active center of HRP and the entrapment of HRP by oligomeric or polymeric products inactivate HRP (Magario et al., 2012). However, the catalytic lifetime of HRP can be extended by recycling through the proper treatment process (Escalona et al., 2014), the use of additives (Magario et al., 2012) and enzyme immobilization (Cheng et al., 2006).

Cheng et al. (2006) found that immobilizing HRP on Al-PILC resulted in good phenol removal with H\(_2\)O\(_2\) over a broad pH range (pH 4.5–9.3), and a better storage stability compared to free HRP. The oxidation mechanism of the immobilized HRP/H\(_2\)O\(_2\) system was thought to be the same as that of the free HRP/H\(_2\)O\(_2\) system. The addition of a highly hydrophilic additive, polyethylene glycol (PEG), could significantly improve the oxidation efficiency. PEG can form a protective layer in the vicinity of the active centers of HRP to restrict the attack of the generated phenoxy radicals. It can also combine with the polymer products to prevent the entrapment of HRP. Nevertheless, the performance of the immobilized HRP decreased markedly after reuse. Hence, the reusability needed to be improved.

4. Conclusions and perspectives

Heterogeneous Fenton reactions stand out among various AOPs, due to the structural stability and reusability of the catalysts, wide application pH range, high oxidation efficiency and low operating costs. Heterogeneous reactions including interfacial H\(_2\)O\(_2\) decomposition, possible active metal dissolution and organics adsorption, and possible homogeneous Fenton chain reactions contribute to the complex reaction
mechanisms of heterogeneous Fenton systems. A more comprehensive knowledge of reaction mechanisms will promote the industrial application of such a promising technology.

(1) Some mechanisms of ROS generation, especially, the detailed interfacial electron-transfer processes, remain as basic scientific problems in heterogeneous Fenton chemistry. High-valent iron, whether existing in a surface-bound form or in a freely dissolved form, needs direct detection or even quantification. Whether the decomposed H₂O₂ should be pre-complexed to the catalysts surface, and whether the homolytic O–O bond cleavage of H₂O₂ involves the redox action of surface Fe(II)/Fe(III), also need direct experimental evidences. The existence and the reaction mechanism of oxygen vacancies in iron-based materials need intensive investigations. Moreover, the mechanisms of ROS utilization are still controversial as mentioned in Section 2.2.

(2) Combinations of various measurement techniques may provide better insights into the reaction mechanisms. Real-time quantification of ROS, isotope tracing techniques, and theoretical chemistry methods can provide more clues to the reaction process. Spectroscopic technologies, especially when connected with in-situ reactions, offer more information on a molecular scale like interfacial changes.

(3) Three primary issues, i.e., the degradation efficiency, the reactivity and stability of the catalyst, and the efficiency of H₂O₂ utilization, should be considered simultaneously in designing and applying heterogeneous Fenton systems. Since the pure iron (hydroxides) suffer from relatively low catalytic reactivity or serious iron leaching, a supported multimetallic iron-based material (e.g., FeCu/HMS (Wang et al., 2015a), CuFe-MC (Wang et al., 2015b), MgO@Fe₂O₃/KIT-6 (Zheng et al., 2015)) may possess the advantage of low H₂O₂ consumption, high catalytic reactivity and good structural stability, thus providing a promising heterogeneous Fenton catalyst.

(4) As for industrial applications, other treatment processes, such as filtration and biological treatment (Melero et al., 2015), CuFe-MC (Wang et al., 2015b), MgO@Fe₂O₃/KIT-6 (Zheng et al., 2015)) may possess the advantage of low H₂O₂ consumption, high catalytic reactivity and good structural stability, thus providing a promising heterogeneous Fenton catalyst. The treatment of coking wastewater by an advanced Fenton oxidation process using iron powder and hydrogen peroxide. Chemosphere 86, 409–414.

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