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REVIEW ARTICLE

Minerals as catalysts of heterogeneous Electro-Fenton and derived processes for wastewater treatment: a review

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Abstract
Advanced oxidation processes (AOPs) such as Fenton's reagent, which generates highly reactive oxygen species, are efficient in removing biorefractory organic pollutants from wastewater. However, Fenton's reagent has drawbacks such as the generation of iron sludge, high consumption of H_2O_2, and the need for pH control. To address these issues, Electro-Fenton (EF) and heterogeneous Electro-Fenton (HEF) have been developed. HEF, which uses solid catalysts, has gained increasing attention, and this review focuses on the use of mineral catalysts in HEF and derived processes. The reviewed studies highlight the advantages of using mineral catalysts, such as efficiency, stability, affordability, and environmental friendliness. However, obstacles to overcome include the agglomeration of unsupported nanoparticles and the complex preparation techniques and poor stability of some catalyst-containing cathodes. The review also discusses the optimal pH range and dosage of the heterogeneous catalysts and compares the performance of iron sulfides versus iron oxides. Although natural minerals appear to be the best choice for effluents at pH>4, no scale-up reports have been found. The need for further development in this field and the importance of considering the environmental impact of trace toxic metals or catalytic nanoparticles in the treated water on the receiving ecosystem is emphasized. Finally, the article acknowledges the high energy consumption of HEF processes at the lab scale and calls for their performance development to achieve environmentally friendly and cost-effective results using real wastewaters on a pilot scale.

Keywords Electro-Fenton · Photoelectro-Fenton · Heterogeneous catalysis · Iron minerals · Real wastewaters

Introduction

Wastewater is presently one of the critical environmental harms to human society and the environment. Organic pollutants in wastewater cause serious damage to environmental and human health (e.g., Gwenzi and Chaukura 2018). Despite the enormous R&D efforts on this problem, regional law enforcement and some local improvements, water pollution keeps growing globally, as most environmental issues do. Consequently, the development of novel methods for the destruction of pollutants represents an urgent challenge for the scientific community since the currently operating treatments at full scale are not very effective in removing such a broad range of noxious wastes (Casado 2019).

Advanced oxidation processes (AOPs) are chemical processes characterized by the generation of highly reactive oxygen species, typically hydroxyl radicals (OH), which can destroy most organic compounds to mineralization into CO_2, H_2O and inorganic ions (Andreozzi et al. 1999; Casado et al. 2003). Examples of AOP are anodic oxidation (Brillas et al. 1998), photocatalysis (Peral et al. 1988; Hoffmann et al. 1995), ozonation (Canton et al. 2003; Von Gunten 2003), and the processes of Fenton (Pignatello et al. 2006), Photo-Fenton (Zepp et al. 1992), Electro-Fenton (Brillas et al. 1996), Photoelectro-Fenton (Casado et al. 2005; Ganiyu et al. 2018), and Peroxycoagulation (Brillas and Casado 2002).

Fenton's reagent is a mixture of H2O2 and Fe^{2+} that has been used for more than a century to oxidize organics (Fenton, 1894). Fenton's reagent produces OH radicals, a powerful oxidant (E^o=2.80 V), according to the following reaction in acidic media (Walling, 1975):

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$$Fe^{2+} + H_2O_2 + H^+ \rightarrow Fe^{3+} + H_2O + OH \quad (1)$$

Fenton's reaction is used to degrade mainly organic pollutants in biorefractory wastewater. Reaction (1) works best at pH 2.8-3.0 (Sun and Pignatello 1993) since at pH<2.5, the protonation of H_2O_2 renders it electrophilic and reduces its reactivity towards Fe^{2+} (Oturan and Aaron 2014), and at pH>3, iron precipitates as Fe(OH)3 (e.g. Nidheesh et al. 2013). The continuous consumption of protons by reaction (1) tends to neutralize the medium and produces iron sludge (which is produced anyway upon final neutralization of the treated water). The separation and treatment of such unwanted sludge, the incapacity to recover and then reuse the catalyst, the high consumption of H_2O_2, and the cost of acid and base to control the pH during the Fenton process are the main concerns of this AOP (Ganiyu et al. 2018; Casado 2019). The presence of biradical O_2 is crucial in the propagation of the Fenton radical chain and minimizes the consumption of H_2O_2 (Utset et al. 2000), an unstable and dangerous oxidant to transport and store in high concentration.

This last concern was one of the reasons for the development of the Electro-Fenton (EF) process, where usually H_2O_2 is generated at the cathode of an undivided electrochemical cell by the $2e^-$ reduction of O_2 (Fig. 1):

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \quad (2)$$

and then undergoes the homogeneous catalytic Fenton reaction (1). The OH radicals produced work together with those produced by anodic oxidation to degrade and mineralize the pollutants in water (see "Classical EF process").

On the other hand, the EF process still has serious drawbacks related to the working pH near 3 and ferric sludge production upon the neutralization of the treated effluent (Casado 2019).

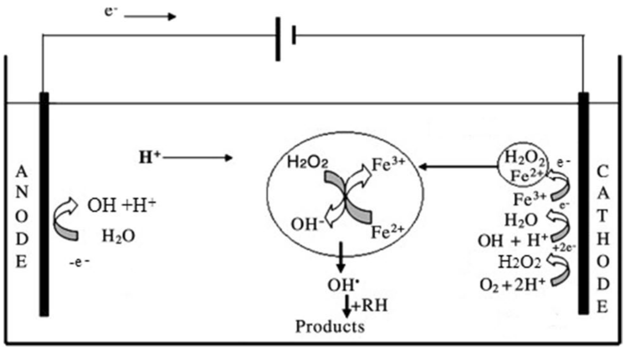

Fig. 1. General scheme of the main reactions involved in the homogeneous EF technology. The cell includes a carbon-based cathode and a stable anode, in the presence of oxygen and added Fe^{2+} as a catalyst (Casado 2019)

Heterogeneous Electro-Fenton (HEF) uses solid catalysts to avoid the main problems of the classic EF. There are recent reviews on the HEF process (e.g. Nidheesh et al. 2017; Poza-Nogueiras et al. 2018; Ganiyu et al. 2018; Meijide et al. 2021; Z. Wang et al. 2022; Gopinath et al. 2022). However, the number of publications on HEF in the last few years has increased exponentially: According to ScienceDirect, the number of articles on HEF jumped from 68 in 2012 to 772 in 2022. The total of articles is too large for a comprehensive review within a reasonable space for a journal article. Thus, we focus expressly on using minerals as catalysts in HEF, which has been developed only in the last 15 years and has not yet been reviewed in detail to the best of our knowledge. We chose this topic since those minerals are eco-friendly, cheap and widespread, in opposition to complex composite materials, which are often less stable and have associated costs and possible harms during their synthesis. In addition, trace minerals are often mixed with naturally occurring minerals, which could enhance their catalytic activity (but could also contaminate treated effluents). Anyway, we cover in here both natural and synthetic minerals. We mainly focus on the use of particle suspensions of them as the most simple and less expensive way of implementing heterogeneous catalysis, while avoiding mass-transfer limitations typical of immobilized catalysts. However, relevant studies using catalyst-loaded cathodes are discussed, too. We carefully revise the advances and trends in every mineral from a historical perspective and, thus, in chronological order. We also cover comparative studies of different minerals and works on real effluents in specific sections. However, developments of microbial fuel cells coupled with the EF process, usually referred to as bio-electro-Fenton (e.g., Monteil et al. 2019), are out of the scope of the present review.

EF-related technologies

Classical EF process

The classical EF process minimizes operating costs and harms by avoiding the continuous addition of H_2O_2 to the bulk solution (Lama et al. 2022). It works under standard conditions of pressure and temperature. Thus, it can be considered as a cold and wet incineration. The process decontaminates effluents containing toxic and biorefractory pollutants that cannot be treated by conventional processes. Since electricity can come from green sources and EF does not use harmful reagents, this method is considered environmentally friendly (Casado 2019).

The first patent of a practical EF system was filed in 1994 in Spain, and later in other states (Casado et al. 2001). Oxygen (or air) is diffused into a Pt-free carbon-PTFE gas diffusion electrode (GDE). O_2 is reduced to H_2O (Eq. 2) at the cathode/water interface without requiring dissolution in the aqueous media (Fig. 1). Thus, this system overcomes the natural limits that the low solubility of O_2 in water imposes to Eq. (2), so increasing the current densities by 2 orders of magnitude. Shortly afterwards, the first article appeared using such a system under Fenton conditions to mineralize organic substances in wastewater by means of the new "Electro-Fenton" process (Brillas et al. 1996).

In the homogeneous EF process, OH radicals are formed within the solution via the Fenton reaction (1). The pH environment is again crucial, and a pH value of 3 is vital for fast process kinetics while avoiding Fe^{3+} precipitation. OH radicals are also produced at the anode surface from water oxidation (Fig. 1) as an intermediate step of oxygen evolution:

$$2H_2O - 4e^- \rightarrow O_2 + 4H^+ \tag{3}$$

The released oxygen from Eq. 3 can feed the cathode to produce more H_2O_2 (Eq. 2).

OH radicals, coming from both anodic and cathodic sources, work together to deeply oxidize organic pollutants in wastewater, mainly via H atom abstraction (producing H_2O) or via OH addition to multiple bonds and intermediate organic radicals (hydroxylation). The products of successive oxidation steps are short-chain organic acids (e.g. oxalic acid), which are relatively stable to further oxidation by OH, especially in the presence of Fe^{3+} complexing ions (Brillas et al. 2000). Eventually, complete mineralization is reached under certain conditions (Casado et al. 2005; Oturan et al. 2008). In this way, the EF process allows the mineralization of most organic pollutants to CO_2, H_2O and inorganic species.

The mentioned pH increase during the Fenton reaction is offset in the EF process by the generation of protons from the anodic oxygen evolution (Eq. 3) and by the carboxylic acids resulting from the degradation of pollutants (Nidheesh et al. 2017).

Other cathodic reactions involved in the EF mechanism are detrimental OH radical quenching to water (Fig. 1) and favourable Fe^{2+} regeneration from Fe^{3+} resulting from the Fenton reaction (1):

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \tag{4}$$

In this way, the EF process avoids the accumulation of Fe^{3+} in the medium and reduces the production of ferric sludge compared to the classical Fenton treatment.

Since the above-mentioned seminal works, EF and derived processes have had a growing scientific impact (ca. 10,000 articles from ScienceDirect and over 3,000,000 results from a Google search), including more than 100 derivative patent applications. The historical growth of scientific articles on the EF process has been exponential. For example, 27 articles were published in 2002, 201 in 2012 and 1580 in 2022. However, EF has attained much less impact in treating authentic wastewater at an industrial scale, which is due in part to the patent protection and in part to technical or economic drawbacks of the process. Most research on EF has been reported at the lab scale, with less attention on scale-up engineering or economic issues, which should be coped with to achieve industrial implementation (Casado 2019).

Experiments are usually performed in an undivided cell (Fig. 1) equipped with a carbon-PTFE GDE cathode, although other carbon-based cathodes have also been used (Casado 2019). The cathode material is critical for the catalytic reduction of oxygen to H_2O_2 rather than to H_2O. Carbon materials such as graphite, graphite felt, and activated carbon fibre are inefficient for H_2O_2 production (A. Wang et al. 2005; Salari et al. 2009; L. Zhou et al. 2013) because they are limited by the mass transfer of dissolved oxygen in water (8 mg/L under standard conditions). For example, H_2O_2 generation rates of about 0.4 mg/h/cm^2 have been obtained for graphite felts (Da Pozzo et al. 2005; L. Zhou et al. 2013, 2013b). Graphene cathodes coated with reduced graphene oxide performed better than uncoated graphene for dye decolourisation using the heterogeneous EF process (Akerdi et al. 2017; see below).

The fastest H_2O_2 yields and highest current efficiencies have been reported for GDEs (Brillas and Casado 2002; Da Pozzo et al. 2005; Y. Wang et al. 2012). Brillas and Casado (2002) have reported current efficiencies of 80% after the first 30 min of electrolysis at 100mA/cm2, i.e. H_2O_2 productivity of 50 mg/h/cm^2. The same group reported the highest H_2O_2 accumulation of a GDE at pH 3 in an undivided cell: 73 mM after 3 h of electrolysis at 450 mA (Brillas et al. 2000).

The anodes are generally chemically inert electrodes made of metals and metal oxides, such as platinized Ti, PbO_2 or dimensionally stable anodes (DSA®). Boron-doped diamond (BDD) anodes have received increased attention lately due to their better performance (e.g. Nidhessh et al., 2019). However, BDD and precious metal anodes are expensive, and their full-scale application for the non-profit remediation of wastewater does not seem to be realistic (Casado 2019).

EF processes have reached increased attention because oxidation rates of organic pollutants are higher than those of anodic oxidation or Fenton reaction (Fig. 2; e.g. H. Zhang et al. 2012b), up to the point of showing a synergistic effect under particular conditions (e.g. Gao et al. 2015). This superior performance is due to the mentioned

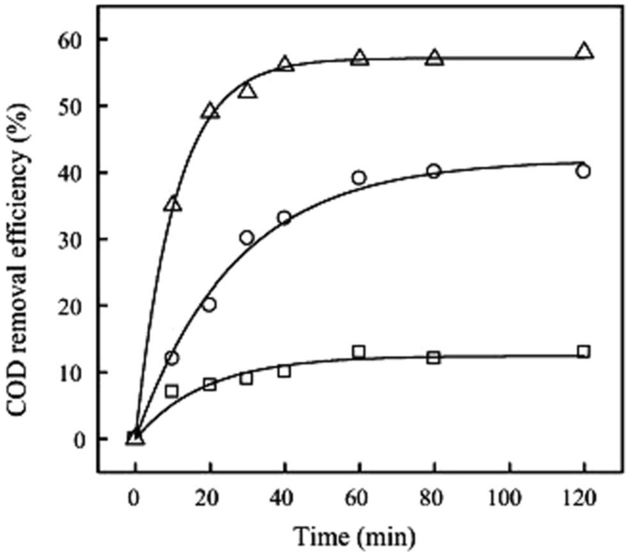

Fig. 2. Comparison of chemical oxygen demand (COD) removal by anodic oxidation, Fenton's reagent and EF process for landfill leachate. (□) electro-oxidation; (○) Fenton; (△) EF . Courtesy of H. Zhang et al. (2012a)

double pathway for OH generation, and to the cathodic regeneration of Fe^{2+} (Eq. 4; Brillas et al. 1996):

Thus, the EF method needs less Fe^{2+} than the Fenton process and can avoid Fe^{3+} accumulation in the solution and the precipitation of iron sludge during the process. However, the homogeneous catalyst produces some sludge upon the final neutralization step. A weakness of the original EF system is that, like the Fenton process, it requires pH 3 to reach its maximum efficiency. Therefore, it becomes too expensive if bulky quantities of reagents are needed to regulate pH before and after oxidation (Casado 2019).

Photoelectro-Fenton process (PEF)

The photo-Fenton method is a significant improvement of the Fenton reaction under illumination (e.g. Sun and Pignatello 1993). The corresponding improvement of EF is currently known as Photoelectro-Fenton process (PEF). The treated solution is exposed to UV/visible light, either during or after the EF treatment, favouring the photodegradation of Fe(III)–carboxylate complex:

$$R(COO)Fe^{2+} + h\nu \longrightarrow Fe^{2+} + R + CO_2 \tag{5}$$

and the regeneration of OH via photolysis of Fe^{3+} hydroxo-complexes:

$$Fe(OH)^{2+} + h\nu \longrightarrow Fe^{2+} + OH \tag{6}$$

Both reactions lead to the regeneration of Fe^{2+}, favouring the continuation of the Fenton reaction in the presence of H_2O_2 (Casado 2019).

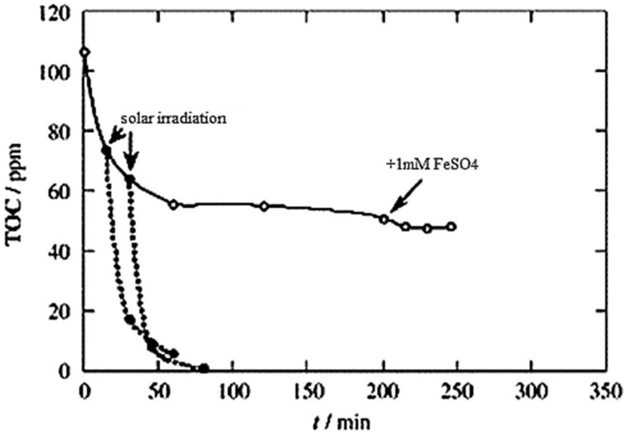

Fig. 3. Total organic carbon (TOC) vs. time for the Helielectro-Fenton mineralization of 10 L of a 1.3 mM benzoic acid solution. After minutes of EF treatment, samples were exposed to sunlight (Casado et al. 2006)

As a rule, researchers obtain higher and faster pollutant removals in PEF than in the EF process (Brillas et al. 1996, 2000; Ting et al. 2008; Dhaouadi and Adhoum 2009; Babuponnusami and Muthukumar 2012; de Luna et al. 2013; S. Liu et al. 2013). Nevertheless, scaling PEF to the industrial level remains a serious challenge due to the extra energy required and the high price of UV lamps. This was the reason for the development of the Helielectro-Fenton or solar PEF process, which uses free sunlight instead of UV lamps. The degradation of various pollutants by this process was first reported by Casado et al. (20052006). After EF treatment for less than 1 h, effluent samples were exposed to sunlight, and almost complete mineralization was achieved within minutes at no additional cost (Fig. 3) via Eq. (5).

Heterogeneous catalysis in EF systems using minerals

To avoid the cited problems of homogeneous EF treatment (*i.e.* pH regulation, loss of iron catalyst, post-treatments such as neutralization, sludge separation and disposal) many attempts have been carried out on the use of (mainly) iron-based heterogeneous catalyst. In HEF processes, sparingly soluble iron-containing species are dispersed in the aqueous media, alone or supported on various materials (carbon, resin, Nafion® membrane, etc.) or the cathode for in-situ generation of Fenton's reagent (Casado 2019). A slight leaching of Fe at acidic pH allows for keeping the catalyst surface clean. Thus, iron minerals usually maintain catalytic activity even after several reuses (Poza-Nogueiras et al. 2018). As we will discuss in the following sections, two alternative mechanisms may be at work: the homogeneous catalytic mechanism, described above for the

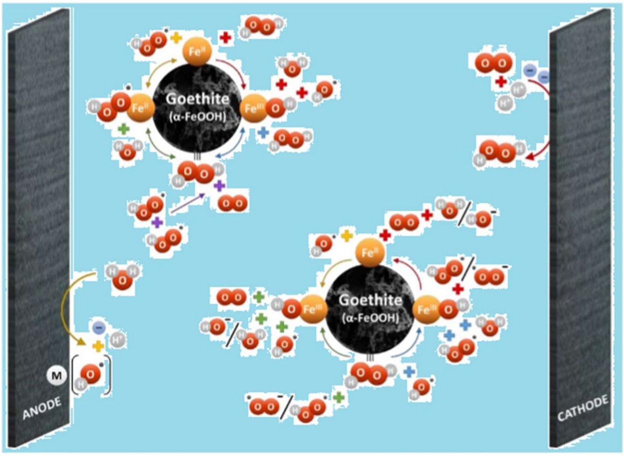

Fig. 4. Electro-Fenton reaction mechanistic scheme using goethite particles as heterogeneous catalyst. Adapted from Poza-Nogueiras et al. (2018)

classical EF process, through the leaching of Fe^{2+} from the mineral at acidic pH, and the purely heterogeneous pathway (Fig. 4), where surface-bound Fe(II) plays the primary catalytic role in the Fenton reaction. This heterogeneous process can operate over a wide pH range and thus neutralization of the final effluent can be avoided. All things considered, the use of HEF presents several advantages, such as avoiding the formation of iron sludge, allowing the easy recovery and reuse of the catalyst, and enabling the operation in continuous mode (Sánchez-Sánchez et al. 2007; Nidheesh et al. 2014; Poza-Nogueiras et al. 2018; Casado 2019). Besides, Heterogeneous PEF (HPEF) usually gives better mineralization and current efficiency than HEF, thanks to the enhancement effect provided by Eqs. (5) and (6) (Ganiyu et al. 2018).

However, there are also problems with HEF and HPEF systems. Most non-supported heterogeneous catalysts, such as Fe_2O_3 and Fe_3O_4, are usually used as nanoparticles, which tend to agglomerate, so reducing the effective surface and the efficiency of the process (X. Zeng et al. 2011; Akerdi et al. 2017; Hafaiedh et al. 2018; Nguyen et al. 2019). Excessive dissolution at pH 3 can also be an issue (Ganiyu et al. 2018).

In the case of supported catalysts, fall-off and multi-step/complex techniques for catalyst or functionalized cathode preparation, are some of the major problems encountered in the cited wastewater treatments (Ganiyu et al. 2018). The mechanical wearing and fall-off of the catalyst from the cathode increase with treatment time as the reactive species degrades the adhesive bond between the catalyst and the support. That is a difficult challenge, which underlines the suitability of employing particulate catalysts in suspension. However, in the case of cathode-functionalised carbon aerogels, the catalyst firmly embedded in the aerogel bulk becomes part of its three-dimensional network, and the aforementioned-problem can be alleviated to a large extent (H. Zhao et al. 2012; Y. Wang et al. 2016; Ganiyu et al. 2018). Besides, most synthetic catalysts and Fe-functionalized cathodes require either multi-step or complex preparation techniques, limiting most studies on HEF systems to lab scale. This is one of the reasons why we have chosen to examine simple minerals as the most promising, simple and effective catalysts for wastewater treatment. Each of these is discussed separately in the following subsections.

Goethite (*α*-FeOOH)

Goethite, the most abundant of mineral iron oxides, is thermodynamically stable and non-toxic. It crystallizes in the orthorhombic system and has appealing properties such as its high catalytic activity and iron-leaching self-regulation. A possible EF's heterogeneous catalytic mechanism at the goethite surface is presented in Fig. 4 (Poza-Nogueiras et al. 2018).

Goethite was the first catalyst employed in HEF systems. Sankara Narayanan et al. (2003) reported that adding goethite did not significantly improve EF efficiency. However, we found high aniline mineralization over a wide range of experimental conditions when Fe^{2+} was replaced by goethite (Sánchez-Sánchez et al. 2007). Under optimal conditions, the HEF process produces 95% mineralization in the presence of only 2 ppm of soluble iron, compared to 55 ppm in the homogeneous EF (Fig. 5). The low soluble iron concentration points to a high stability and reusability of goethite.

The use of mixed-phase goethite/lepidocrocite nanoparticles supported on an active-carbon cathode to remove

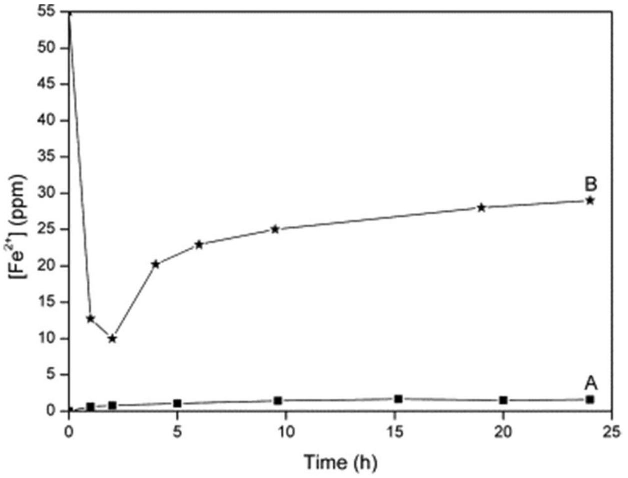

Fig. 5. $[Fe^{2+}]$ evolution for a solution of 100 ppm aniline, 0.5 M Na_2SO_4 and pH 3 at 25 °C and 50 mA/cm^2, using different catalysts: (A) 1 g/L goethite and (B) 1 mM $FeSO_4$ (Sánchez-Sánchez et al. 2007)

amaranth azo dye confirmes the catalysis of the HEF process by FeOOH (Zhang et al. 2012b). However, the leaching of Fe ions is considerably larger, suggesting lower reusability of that catalyst.

Meijide et al. (20182019) degraded 1-butylpyridinium chloride (500 mg/L) and the pesticide acetamiprid (60 mg/L) with a new heterogeneous catalyst containing goethite within a polyvinyl alcohol-alginate matrix. They obtained 94 and 90% TOC removal, respectively. The catalyst has good stability and is reusable. The resulting inorganic pollutants, Cl^- NO_3^- and NH_4^+ could be removed by simulated adsorption onto activated C (Meijide et al. 2018).

Although there is room for optimization, in these examples electrolysis times of up to 24 h were required to achieve substantial mineralization. Besides, the operating pH was 3, leaving the aforementioned pH problem unresolved. If goethite catalysis were predominantly mediated by iron leaching (homogeneous mechanism), the reaction would become slower at higher pHs due to the very low solubility of iron at pH > 4. For the same reason, the heterogeneous mechanism (Fig. 4) should generally predominate at pH around 7 for any Fe- or Cu-containing catalyst (Ganiyu et al. 2018).

Magnetite (Fe_3O_4)

Magnetite is an abundant iron mineral and one of the main iron ores. It crystallizes in the cubic system. Its high ability to degrade refractory pollutants compared to conventional iron-supported catalysts derives from the stable magnetite structure, which can readily accommodate both Fe^{2+} and Fe^{3+}. So, Fe^{2+} can be reversibly oxidized and reduced within the crystal lattice (Fig. 6). Therefore, magnetite exhibits high catalytic activity in oxidative processes such as the Fenton reaction (e.g. Muñoz et al. 2015). Magnetite possesses exceptional electromagnetic properties with confirmed reusability (Xu and Wang 2012; Liu et al. 2013; Nidheesh et al. 2014; Kalantary et al. 2018; Pinheiro et al. 2020; Gholizadeh et al. 2021; Huang et al. 2022). Moreover, its intense magnetism and low solubility facilitate its separation from the treated effluent for further reuse. For these reasons, it has been the most studied iron mineral as a HEF catalyst.

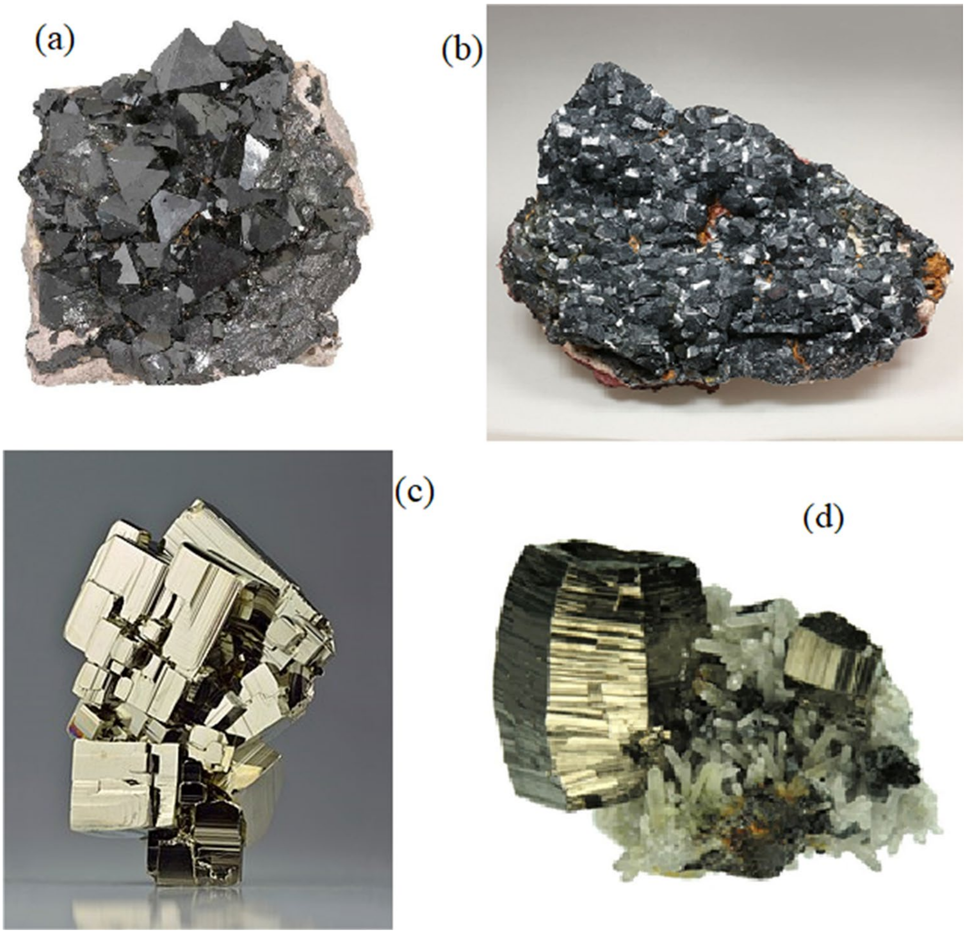

Fig. 6. Crystalline habits of selected iron minerals used as catalysts in the HEF process: **a** octahedral crystals of magnetite (Bolivia); **b** tabular crystals of hematite (Ste. Marie-aux-Mines, France); **c** cubic crystals of pyrite (Huanzala mine, Peru); **d** striated hexagonal prisms of pyrrhotite (Dalnegorsk, Russia).

Total degradation of 4,6-dinitro-o-cresol was reported using magnetite nanoparticles (MNPs) as the catalyst (X. Zeng et al. 2011). The homogeneous reaction dominates at acidic pH, whilst anodic oxidation prevails around pH 7. Z. He et al. (2014) employed MNPs for the degradation of C. I. Reactive Blue 19 (RB19) and concluded that MNPs facilitate the decomposition of H_2O_2 to generate OH. Increasing the dosage of MNPs enhances the rate of RB19 degradation. However, too high Fe_3O_4 dosages inhibit the reaction. The mineralization of RB19 proceeds rapidly only at pH 3. The removal efficiency of TOC reaches 87 % after 2 h at a current density of 3 mA/cm2 using 1 g/L of MNPs. Nidheesh et al. (2014) achieved 97% Rhodamine B (RhB) dye degradation after 3 h. Such efficiency is comparable with that of homogeneous EF catalysts. The optimal catalyst dosage for the EF process is much smaller than for the Fenton reaction. Similarly, Akerdi et al. (2017) boosted the bleaching of two dyes using Fe_3O_4 nanoparticles at a pH range of 3-11. Synthetic MNPs confirmed better catalytic capacity than iron salts at the same pH range, based on results in the decolourization of two azo dyes (Es'haghzade et al. 2017). The presence of NaCl salt favours dye removal, probably by intermediate ClO^-/HClO.

Kalantary et al. (2018) obtained a removal efficiency of 98% for amoxicillin using MNPs as catalyst and a modified graphite felt, which increases 5 times the production of H_2O_2 without forced aeration. The HPEF process using sunlight and MNPs outperforms EF and UV-PEF, reaching 100% of decay of Sunset Yellow dye and high TOC removal at 1.5 h of electrolysis (Pinheiro et al. 2020). There was no detection of Fe^{2+} ions after the process at pH 3, suggesting a predominant heterogeneous catalytic mechanism. That unusual behaviour could be due to the high light absorption of magnetite in the visible range (band gap 0.1 eV).

On the other hand, the agglomeration of magnetic Fe-containing catalyst particles like MNPs is a known drawback (Ganiyu et al. 2018). The nanoparticles are attached to each other and make it hard to agitate the electrolytic system. That's one of the reasons why magnetite particles have also been embedded in the cathode. S. Liu et al. (2013) studied the degradation of the antibiotic tetracycline using a Fe_3O_4–graphite cathode. They compared UV light, EF and PEF processes. The reported degradation efficiency is, as usual, in the order PEF > EF > UV light. The catalysed cathode could be reused. Gholizadeh et al. (2021) used magnetite nanoparticles-activated carbon (MNP-AC) cathode to degrade Phenazopyridine. Degradation reaches 98% and TOC decay is 87% at pH 3 and surface ratio of MNP-AC 1:1. The degradation decreases to 54% in the presence of ethanol as OH scavenger, which evidences the role of the OH radical in the process.

Y. Choe et al. (2021) have shown that Fe_3O_4-coated stainless steel (SS) meshes can be an effective cathode for the EF system in neutral conditions with minimal Fe^{2+} leaching, suggesting a heterogeneous catalytic mechanism. Total removal of methylene blue is achieved in 2.5 h, compared to 4.0 h for the EF process using SS alone (which is well known to be a poor cathode for EF).

Fe_3O_4 loaded on graphite felt cathode can be used in a pH range from 3.0 to 6.9, to catalyse the production of OH radicals that degrade levofloxacin (Huang et al. 2022). The TOC removal reaches 81% at 6 h, and neither Fe leaching nor sludge are detected at pH 6.9.

Hematite (*α*-Fe_2O_3)

Hematite crystallizes in the hexagonal system (Fig. 6). It has been considered a promising catalyst in HEF processes because it is a stable, cost-effective, non-toxic and environmentally friendly form of iron oxide (Cong et al. 2012; Özcan et al. 2017). However, hematite has rarely been used alone as a single catalyst.

Cong et al. (2012) synthesized uniformly dispersed α-Fe_2O_3/TiO_2 nanotubes for phenol degradation by the HPEF process. Such electrodes are more effective than the separated catalysts, and 100% phenol removal is obtained after 1 h. The low band gap of α-Fe2O3 (2.2 eV) enhances the absorbance of visible light of α-Fe_2O_3/TiO_2, displaying good photocatalytic activity and stability. Thus, heterogeneous photocatalysis can contribute to the HPEF process when using semiconductors illuminated by photons having energy above their band gap.

Özcan et al. (2017) used a Fe_2O_3-modified kaolin catalyst and a three-dimensional carbon felt cathode to decompose the antibiotic enoxacin. TOC removal ca. 90% was reported at pH values between 2 and 7, although the process is faster at a more acidic pH. The trace of leached Fe (ca. 6 10^{-3} mM) could be related to the absence of Fe^{2+} in hematite and suggests that heterogeneous reactions at surface Fe sites are the main pathway.

Ghanbari et al. (2021) degraded paracetamol (PCT) under ultrasound-assisted HEF catalysed by hematite nanoparticles (HNPs). The ultrasound helps to avoid the agglomeration of particles. Such a process results in a PCT removal of 99% within 1h under optimum conditions (pH 5, HNPs 0.15 g/L, 230 mA, $[PCT]_0$ 20 mg/L). Besides, the system detoxifies the PCT solution. Scavenging experiments indicate a negligible role of O_2. Nitrate ions have a strong inhibitory effect, which could be due to the OH-scavenging effect of nitrite resulting from the cathodic reduction of nitrate, a reduction that also directly competes with Eq. 2. The HNPs show higher activity than homogeneous transition metals, but the reusability test of HNPs reveals a 14% drop at the end of the fourth cycle.

Guo et al. (2021) designed a HEF system with a Fe_2O_3 nanoparticle-filled carbon nanotube flow-through cathode for the degradation of traces of tetracycline (up to 0.04mM).

The confined Fe_2O_3 catalyst rate is 1.65 times that of unconfined Fe_2O_3. The kinetics of the flow-through configuration is 5.1 times faster than that of a batch reactor. Continuous treatment of 0.002 mM tetracycline was performed in the single-pass mode for three days, obtaining a tetracycline removal >85%. The presence of silicate increases the H_2O_2 yield by preventing the dissociation of the O-O bond and increases TOC removal, but only up to 39.8% after 3 h at pH 7. This modest result can also be attributed to the absence of Fe^{2+}.

Hematite-containing composites such as $Fe@Fe_2O_3$ and $Fe_3O_4@Fe_2O_3$ appear to be efficient catalysts as they can provide Fe^{2+} to the system. For instance, Z. Ai et al. (2007) proposed a GDE of $Fe@Fe_2O_3$ nanowires on carbon nanotubes with PTFE, able to degrade 91% of RhB dye in 2 h at neutral pH. Nanostructured $Fe@Fe_2O_3$ was also loaded on active carbon fibre as GDE (J. Li et al. 2009). Regarding the degradation of RhB, this system shows a higher yield (74.1%) than similar systems with Fe^0 (47.6%) and Fe^{2+} (25.5%) after 2 h at neutral pH. $Fe_3O_4@Fe_2O_3$ grown on activated carbon aerogel has been used as a bifunctional cathode to mineralize the insecticide imidacloprid with high efficiency (up to 90%) in the pH range 3-9 (H. Zhao et al. 2012). Using a similar cathode, Y. Wang et al. (2013) proposed an electrosorption-enhanced EF method. The system also works at neutral pH and mineralizes 93% of imidacloprid in 2.5 h.

Further works using hematite as a HEF catalyst are comparative studies of various minerals, and are discussed in a specific section below.

Pyrite (FeS_2)

Pyrite is one of the most common and low-cost iron minerals found on earth. It crystallizes in the cubic system (Fig. 6). Pyrite is present in many hydrothermal deposits, accompanies numerous ore deposits, and is a nontoxic semiconductor (Mozia et al. 2013). Its surface is reported to be hydrophilic or hydrophobic depending on the media pH (Khabbaz and Entezari 2017), which is another attractive property from a catalytic point of view.

Pyrite is a useful heterogeneous catalyst in EF, showing $Fe^{2+}$and pH self-regulation, due to reactions such as its oxidation by dissolved oxygen and H_2O_2 in aqueous media (Bonnissel-Gissinger et al. 1998; Nidheesh et al. 2017):

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

$$2FeS_2 + 15H_2O_2 \rightarrow 2Fe^{3+} + 14H_2O + 4SO_4{}^{2-} + 2H^+ \quad (8)$$

$$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4{}^{2-} + 16H^+ \quad (9)$$

Therefore, it is generally accepted that the catalytic mechanism mainly proceeds homogeneously. Fe^{3+} also readily oxidizes pyrite (Eq. 9; Chandra and Gerson 2010), which thus plays a central role in Fe^{2+} regeneration in Fenton and EF processes.

Quasi-complete mineralization of the synthetic dye AHPS in 8h using pyrite (2 g/L) has been reported (Labiadh et al. 2015). Suspensions containing >5 mg/L reach pH close to 3 spontaneously within the first 10 minutes of the reaction without further significant change during the experiment. Fast degradation of AHPS was attributed to quick regeneration of Fe^{2+} via Eqs. 7-9. The HEF process is more cost-effective than classical EF.

Other studies confirm the effectiveness of pyrite as a catalyst. Ouiriemmi et al. (2017) reported an 89% mineralisation of 0.1 mM vanillic acid in 4 h with a pyrite dosage of 1 g/L. Similar results were obtained for an initial pH between 3 and 7. Bouzayani et al. (2017) reported a 95% TOC removal for the dye anthrapyridone polyvinylamine sulphonate at a pyrite dosage of 2 g/L.

The optimal amount of added pyrite powder was reported to be 1–2 g/L (Nidheesh et al. 2019) since an excess of Fe^{2+} ions released from Eq. 7 consumes OH according to Eq. 10, thus decreasing efficiency.

$$Fe^{2+} + OH \rightarrow Fe^{3+} + OH^- \quad (10)$$

However, 85% TOC is removed in 3 h using 8 g/L of pyrite in the HEF treatment of diclofenac at initial pH 7 (Yu et al. 2020). The process also works at initial pH 3 and 9, removing the effluent toxicity. The authors highlighted that the molecular O_2 activation by pyrite-bound Fe(II) generates $O_2{}^-$, which accelerates the Fe^{2+}/Fe^{3+} cycle. Good TOC removals are also obtained with only 40 mg/L of other catalysts (Table 1).

As a general rule, this process is found to be more efficient than EF due to the mentioned self-regulation system (Labiadh et al. 2015; Nidheesh et al. 2017). However, the catalyst is degraded during the process via Eqs. 7-9, leaching excess iron and sulfate into the wastewater. Other intermediates of these reactions, such as elemental S, H_2S and polysulfides, can play an active role in AOPs (Feng et al. 2019) but can also contribute to unwanted sludge and limit pyrite reuse.

Nonetheless, cathodic polarization seems to protect pyrite from oxidation to some extent. Pyrite-modified carbon felt (FeS_2/CF) cathode was reported to provide Fe(II) sites and oxysulfide continuously through the HEF process, which further induce the formation of $SO_4{}^{\bullet-}$ and OH, without iron leaching (L. Chu et al. 2020). The concentration of OH is about twice that in the system with CF only. The FeS_2/CF cathode shows >80% efficiency for anthracene degradation in a pH range of 3–9 and could be used six times. Similar

Table 1. Main results of studies comparing several mineral catalysts on HEF process

Catalyst/Dosage	Pollutant	pH	Time (h)	TOC removal (%)	Energy Cost (kWh/kg TOC)	Reference
Hematite 1g/L	Aniline 0.1 g/L	3	24	33		Expósito et al. 2007
Wüstite 1 g/L	Aniline 0.1 g/L	3	24	79		Expósito et al. 2007
Magnetite 1 g/L	Aniline 0.1 g/L	3	24	79.5		Expósito et al. 2007
Goethite 1 g/L	Aniline 0.1 g/L	3	24	92		Expósito et al. 2007
Pyrite 1g/L	Catechol 0.45 mM	Initial 5-6	1 7	36 86		Ltaïef et al. (2017)
Chalcopyrite 1 g/L	Catechol 0.45 mM	Initial 5-6	1 7	27 81		Ltaïef et al. (2017)
Pyrite 1g/L	Caffeic acid 0.1 g/L	3	2	65		Ltaïef et al. (2018)
Chalcopyrite 0.5 g/L	Caffeic acid 0.1 g/L	3	2	75		Ltaïef et al. (2018)
Magnetite 40 mg/L	Acid Red 18 40 mg/L	3	3	83		Hafaiedh et al. 2018
Hematite 80 mg/L	Acid Red 18 40 mg/L	3	3	83		Hafaiedh et al. 2018
Chalcopyrite 1g/L	Cefazolin 0.2mM	3	8	≥ 95	220-2580	Heidari et al. (2021)
Ilmenite, pyrite, chromite 1 g/L	Cefazolin 0.2mM	3	8	> 90	220-2580	Heidari et al. (2021)

results using this system for carbamazepine degradation have been obtained recently (T. Cui et al. 2021). A neutralization step at an extra cost is required before releasing or using the resulting effluents.

While the present work was in progress, a specific review on pyrite-mediated AOPs was published (B. Song et al. 2022).

Chalcopyrite ($CuFeS_2$)

Chalcopyrite is the principal copper ore in the world. It crystallizes in the tetragonal system. Its oxidation releases Cu^{2+} and Fe^{2+} ions in aqueous media following reactions analogous to Eqs. 7-9 for pyrite (Y. Li et al. 2013), e.g.:

$$CuFeS_2 + 16Fe^{3+} + 8H_2O \rightarrow Cu^{2+} + 17Fe^{2+} + 2SO_4{}^{2-} + 16H^+ \tag{11}$$

In this way, it reproduces the self-regulation of these ions at a pH near 3, as described for pyrite. Again, there is a slight degradation of chalcopyrite during the oxidation process. Chalcopyrite has been usually claimed to provide even better results than pyrite due to the supplementary contribution of the couple Cu^{2+}/Cu^+, which acts as a Fenton-like catalyst in addition to Fe^{3+}/Fe^{2+} (Pimentel et al. 2008; Nidheesh et al. 2019; Heidari et al. 2021). However, Ltaïef et al. (2017) obtained slightly worst results for TOC removal of catechol after 7 h of HEF treatment at 5 mA/cm2 using chalcopyrite instead of pyrite (Table 1). Y. Yao et al. (2021) found a similar trend in COD removal using Reactive Red X-3B as a model pollutant. The efficiency of both minerals improves in the presence of Cl^- (albeit Fe-C composite was the best catalyst studied). In general, the results with the two sulfides are comparable (Table 1), and the sometimes claimed advantage of chalcopyrite would be offset by the toxicity of Cu ions. The leached Cu ions can be removed from the effluent by precipitation at neutral pH. However, there is an additional cost associated with that final neutralization step and the disposal of the resulting precipitate.

Barhoumi et al. (2017) studied the degradation of tetracycline using chalcopyrite. The process is slightly more efficient than conventional EF, achieving 98% mineralization after 8 h using 1 g/L catalyst and is able to detoxify the solutions. Similarly, Labiadh et al. (2019) reported up to 96% TOC removal for Acid Orange 7 solutions. Interestingly, total mineralization is reached within 3 h for chalcopyrite in the PEF process, while only 88% of TOC is removed in the absence of illumination. This result can be explained similarly to the superior performance of classical PEF processes versus EF (Casado 2019). See also the comparative Section below.

Pyrrhotite (Fe_7S_8) and greigite (Fe_3S_4)

These less common iron minerals crystalize in the monoclinic and the cubic system, respectively (Fig. 6). Both sulfides, working together, are more efficient as a cathode-bonded heterogeneous catalyst than conventional Fe_2O_3, Fe_3O_4 or FeS_2 for phenol mineralization via enhanced OH production (Y. Choe et al. 2018). Fe_3S_4/Fe_7S_8 have more S-modified, surface-exposed Fe^{2+} sites to cleave H_2O_2 than FeS_2. However, phenol degradation performance decreases throughout recycle runs, which suggests degradation of the catalyst, in line with other sulfide minerals. Natural pyrrhotite has also been used as a cathodic catalyst in microbial fuel cells to treat landfill leachate (Y. Li et al. 2010).

Laterite and other minerals

Laterite is not a single mineral but a common mineral mixture (soil/rock) rich in iron oxides (e.g., goethite, ferrihydrite) and containing significant amounts of Al_2O_3 and TiO_2. Ganiyu et al. (2020) investigated the degradation of food colourant E123 by the HEF process catalysed by calcined laterite. Complete COD removal of 0.5 mM E 123 is achieved in less than 4 h using a Pt anode and a carbon felt cathode under optimal conditions (8.5 g/L laterite, pH 3 and 250 mA). Both homogeneous and heterogeneous catalytic pathways were reported to be at work depending on pH. Another study using laterite is discussed in the section on real wastewater.

Some other minerals have been studied as heterogeneous catalysts of the Fenton process but not in HEF systems. Examples are ferrihydrite ($Fe_{10}O_{14}(OH)_2$; Matta et al. 2007; Barreiro et al. 2007; Chen et al. 2021), chalcocite (Cu_2S; H. He et al. 2021), and bornite (Cu_5FeS_4; Z. Wang et al. 2021). These minerals are expected to perform similarly or even better as catalysts in the HEF process.

Comparative studies of diverse minerals

Expósito et al. (2007) compared goethite, magnetite, hematite, and wüstite (FeO) in HEF and HPEF treatments of aniline wastewater. Although wüstite and magnetite present the fastest mineralization, goethite has the highest TOC removal yield (>90%). The final Fe concentration is lower for goethite than other minerals (see Fig. 5), which explains why the process is slower if one assumes that the principal catalytic mechanism is homogeneous. On the other hand, the HPEF process did not improve the TOC removal efficiency of goethite, possibly because the goethite slurry was opaque to the UV light (see, however, Lizama-Bahena et al. 2015 and Mameri et al. 2016).

M. Sun et al. (2015) reported an air-cathode fuel cell strategy to utilize Fe^{2+} in the acid mine drainage to prepare HEF catalysts. Nano-structured iron oxide/graphite felt (GF) composites, including FeOOH/GF, Fe_2O_3/GF and Fe_3O_4/GF, were made up, and their catalytic activities were evaluated at pH 7 with RhB as a model pollutant. RhB removal efficiencies using the cited cathodes are significantly improved to 63%, 95% and 96%, respectively, proving the benefit of having Fe(II) in the catalyst lattice. The mineralization of RhB was not studied. The decomposition of H_2O_2 follows a surface-catalysed mechanism without iron leaching.

HEF mineralization of Acid Red 18 using either magnetite or hematite nanoparticles produces a maximum of 83% TOC removal after 3h of electrolysis with 40 mg/L Fe_3O_4 at pH 3, even if the activity of both oxides is similar (Hafaiedh et al. 2018). This study shows that low dosages of the nano-catalyst can be enough to obtain good results. From the significant iron concentration found in the bulk solution (1.4 mM) and the slight effect of the catalyst concentration on yield, it was inferred that the formation of OH occurs mainly through homogeneous EF. In the presence of an OH scavenger, decolourization remains total after 15 min, showing the involvement of anodic oxidation of the dye, but oxidation via OH is responsible for at least 50% of mineralization.

Ltaïef et al. (2018) performed a comparative study of pyrite, chalcopyrite, Fe_2O_3 and Fe_3O_4 for abating caffeic acid at acidic pH. Even if all catalysts allow near 90% contaminant removal, the lowest Fe^{2+} concentrations and mineralizations are achieved with Fe_2O_3 and Fe_3O_4. The best results (75% TOC removal in 2 h) were obtained using chalcopyrite and pressurized oxygen.

Heidari et al. (2021) compared ilmenite ($FeTiO_3$), pyrite, chromite ($FeCr_2O_4$) and chalcopyrite in the degradation of the antibiotic cefazolin (0.2 mM). Higher mineralization is obtained when chalcopyrite is used in the HEF process (Fig. 7), although TOC removal of all catalysts is very close (>90% after 6h at 500 mA with a dose of 1g/L). The authors concluded that all these minerals could be appropriate and cost-effective catalysts for HEF due to their high activity, availability, eco-friendly nature and low energy consumption, despite energy costs as high as 2580 kWh/kg TOC were reported. Such a cost is two orders of magnitude higher than the best energy needs of EF technologies (Casado 2019). The usual way to reduce the energy cost is using current densities on the order of 10 mA/cm^2 (e.g. P. Dong et al. 2021) and only up to obtaining an effluent that can be treated by a biological reactor. By the way, we proved that the energy requirement of

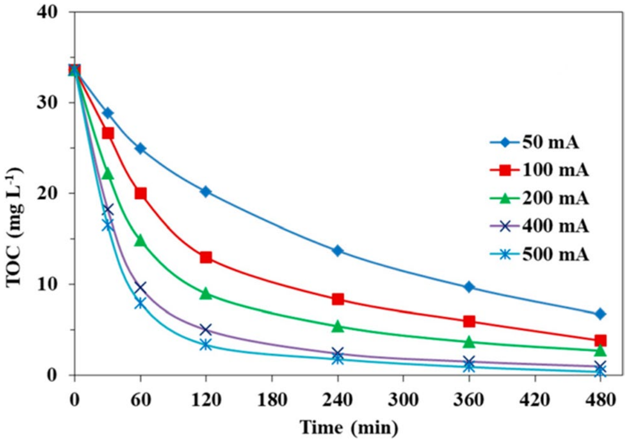

Fig 7. Effect of the applied current on the mineralization of a 0.2 mM cefazolin solution by the HEF system using chalcopyrite as catalyst. Adapted from Heidari et al. (2021)

EF-related processes can even be cut back to zero by using a short-circuited Fe/O_2 (or air) cell (Brillas et al. 1999).

Hematite, magnetite, siderite, limonite and pyrite were compared in the HEF degradation of Gemcitabine by means of a GDE based on three-dimensional graphene (Hajiahmadi et al. 2021). The catalytic activity of magnetite, siderite and pyrite at pH 7 is higher than that of limonite and hematite at pH 3, which can be due to the absence of Fe(II) in the latter two minerals. Pyrite was considered the best one. The degradation yield and TOC removal reach 98% and 78%, respectively, after 5 h of electrolysis. Hajiahmadi et al. (2022) tested the same minerals to degrade 3 mg/L of Paclitaxel. Again, pyrite is the best catalyst, and magnetite and siderite show good activity at pH 3, probably via Fe^{2+} leaching. The degradation yield and TOC removal reach 99% and 78%, respectively, after 6 h using 4.5 g/L of pyrite. However, in both studies these minerals were not compared in terms of TOC removal.

Muzenda et al. (2022) have used ilmenite nanoparticles immobilized on graphite felt cathodes as catalysts for the HEF degradation of tetracycline. The system works over a wide pH range. Tetracycline is degraded in 2 h up to 61 and 40% TOC removal in synthetic and authentic wastewater matrices, respectively. Comparative studies of four iron oxides show TOC removals around 60%, with decreasing rates in the order magnetite > ilmenite > hematite > goethite. A slight Ti co-catalysis effect was observed by comparison of Ilmenite and hematite. Ilmenite was reused for six cycles without any noticeable loss of activity.

Some selected results of the comparative studies are summarized in Table 1. These studies rarely report the energy cost of the treatment. Noticeably, all of them worked at pH 3 though the HEF process is usually able to work also at circumneutral pH. In the cases of pyrite and chalcopyrite, this circumstance can be ascribed to the mentioned self-regulation of pH. The similar results reported for most minerals in acidic media under similar conditions suggest that the predominant pathway is homogeneous EF via Fe^{2+} leaching. In this context, the poor TOC removal of hematite can be ascribed to the absence of Fe(II) in this mineral. The better (albeit sluggish) results of goethite are noticeable and suggest that both the heterogeneous (Fig. 4) and the homogeneous pathway at low Fe^{2+} concentration (Fig. 5) would be at work simultaneously. Finally, some of the comparative studies reviewed suggest a better performance of iron sulfides versus iron oxides, possibly due to the self-regulating mechanism illustrated by Eqs. 7-10.

Practices on real wastewater treatment

Real wastewaters have complex compositions and properties. Thus, their electrochemical treatment may behave differently from synthetic wastewater in terms of efficiency and removal mechanisms. Treatment of authentic samples can involve unexpected issues such as the fouling of catalysts and cathodes (Casado 2019) and the OH scavenging effect of inorganic ions and natural organic matter, such as humic and fulvic acids. The role of these species in OH removal has already been discussed (e.g. Ganiyu et al. 2018; Meijide et al. 2021).

A real washing machine effluent was treated by HEF and HPEF processes combined with peroxymonosulfate (PMS) using MNPs as a catalyst (Ghanbari and Martínez-Huitle 2019). HPEF/PMS process removes 97 % of TOC after 3 h under pH = 5, 30 mA/cm2, MNPs = 100 mg/L, and 2 mM PMS. MNPs activity does not change after three times usage.

Fe_3O_4–Mn_3O_4 nanoparticles were used as a catalyst for purifying biologically pre-treated wastewater from instant coffee production (Nguyen et al. 2019). These particles also contain γ-Fe_2O_3 (maghemite), and are effective metal sources for Fenton reactions. After 1 h of treatment, the highest removal efficiencies of COD, colour, and TOC are 88%, 98%, and 93%, respectively, at 20 mA/cm^2 , pH 3.8, and 0.5 g/L catalyst.

Geraldino et al. (2020) evaluated the efficiency of HEF using a GDE modified with reduced graphene oxide (rGO) and MNPs for the electrogeneration of H_2O_2 and degradation of textile wastewater. The modification of the cathode with 5 % of rGO increases by 83 % the H_2O_2 generation. The catalyst attains 70% TOC removal and excellent stability during ten reuse cycles.

Low-cost carbon fibre paper cathode modified by MnO_2-Fe_3O_4 nanoparticles was employed in treating shale gas fracturing wastewater, leading to 65% TOC and 75% COD elimination after 4 h (P. Dong et al. 2021). The residual COD value of the treated wastewater is 80 mg/L, with a low energy consumption of 6.9 kWh/kg COD.

Nidheesh et al. (2022) treated mixed industrial wastewater by combining HEF and electrocoagulation (EC). Alkali-modified laterite soil was used as the catalyst. A 55% COD removal was reported after 1 h of the HEF treatment at pH 3. Further treatment was carried out with the EC process for 1 h, achieving a total of 85% COD removal. Although the efficiency is the same, HEF + EC is a better strategy than EC + HEF, as it avoids neutralization after the HEF process, improves biodegradability and generates less sludge at a lower cost. The specific energy consumption at 1V is 1.23 kWh/kg COD, which is a comparatively low value (see Table 1).

Muzenda et al. (2022) studied authentic wastewater containing tetracycline in a comparative study of diverse mineral catalysts (see Comparative studies). They emphasized that the effectiveness of these advanced technologies should be assessed in continuous-flow systems for real-world effluents in the presence of organic matter and other contaminants.

Pilot Scale works

Unfortunately, no HEF studies in pilot-scale reactors using minerals as particulate catalysts or incorporated into functionalized cathodes have been found in the literature so far (October 2022). Thus, there is a lack of this kind of study, which is needed for the industrial implementation of mineral-HEF processes to solve real-world pollution. Nonetheless, we comment on two related cases as examples of this kind of engineering study.

The drug diclofenac was removed from drinking water by a novel EF *filter* in a pilot reactor able to treat 200 L (Plakas et al. 2016). Carbon felt was the material for three pairs of electrodes, with cathodes loaded with synthetic γ-Fe2O3/Fe3O4 nanoparticles. Diclofenac and TOC removals at pH 7 are 85% and 36%, respectively.

Poza-Nogueiras et al. (2021) performed assays at a lab scale in a stirred-tank reactor and at a bench scale in a flow-through setup, including a jet aerator. A fluidized-bed reactor was implemented to retain the solid catalyst: iron-containing alginate beads. H2O2 generation and clofibric acid (CA, 10 ppm) removal were assessed. Homogeneous catalysis is complimentary due to some iron liberated from the alginate beads. The scaled treatment at 0.12 A is the best: 18 times more volume was treated (2.7 L), H2O2 production is 28 times higher, and the energy cost is more than halved (360 kWh/kg CA), highlighting the importance of reactor design and scale. However, 8 h are needed to remove CA, and the operational pH is 3, which does not solve the mentioned pH problem.

As noted in other works (e.g., Ganiyu et al. 2018**),** investigating the use of the HEF/HPEF system at a pilot scale and a thorough analysis of the economic and environmental impact of the HEF process on the ecosystem, as well as the treatment of real wastewater, are mandatory issues that need further work to bring these promising processes from the laboratory to real-world application.

Conclusions and Perspectives

The use of mineral catalysts in HEF processes has clear advantages over other catalysts. Most reviewed minerals are efficient and stable while being readily affordable and green materials. Their preparation and application are easier, particularly when they are used as particulate slurry. The performance of many of these catalysts opens up encouraging prospects for rapid and cost-effective wastewater treatment. However, the agglomeration of unsupported nanoparticles, especially magnetic ones, and the complex preparation techniques and poor stability of some of the catalyst-containing cathodes (with a corresponding increase in cost) are obstacles to overcome.

Good performances have been confirmed from pH 3 to basic pH. As a rule, the dominant catalytic pathway appears to be homogeneous from Fe^{2+} leaching at acidic pH or heterogeneous at circumneutral pH. The potential problem of excessive leaching of the heterogeneous catalyst at pH 3 is avoided by working at pH>4. The presence of Fe(II) in the crystal lattice is critical for good efficiency. Some of the comparative studies suggest a better performance of iron sulfides versus iron oxides, possibly due to the self-regulation mechanism of Eqs. 7-10. However, this advantage could be offset by the lower stability of sulfide minerals and the need for a neutralization step after the HEF process that would precipitate some residual sludge. Even so, many studies have shown the reusability of most minerals for a few consecutive runs.

The optimum dosage of heterogeneous catalysts seems to be of around 1 g/L. Nonetheless, good results have also been obtained for doses as low as 40 mg/L (of nanoparticles) and as high as 8.5 g/L (of laterite). Thus, for effluents at pH>4, using natural minerals as heterogeneous catalysts appears to be the best choice. However, no scale-up reports on them have been found. So, this field has a need for development. There are also much fewer works in the HPEF process despite its often better results than the HEF process.

The works reviewed do not address the environmental impact of trace toxic metals or catalytic nanoparticles in the treated water on the life of the receiving ecosystem. A maximum surface area of nanoparticles is preferable for high catalytic activity, but larger particle sizes have been found to have good efficiency with less agglomeration issues, and would be preferable considering cost, separability, reusability and toxicity, thus reducing the environmental impact of the spent catalyst.

Most reviewed studies try to obtain the full mineralization of the pollutant, but only a few measure the evolution of toxicity, which would be a more appropriate parameter. The expensive AOPs are more suitable to be combined with biological treatments once the biodegradability thresholds are reached (Oller et al. 2011; Meijide et al. 2021).

Despite their good mineralization results at the laboratory scale, and the virtual solution of pH and sludge problems of classical EF processes, the main weaknesses of the reviewed catalytic processes remain their high energy consumption and, thus, their high operating costs. Affordable costs have been reported only exceptionally in two real wastewater studies. So, the main challenges to face are their performance development to achieve environmental-friendly and cost-effective results on a pilot scale.

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Declarations

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Human and animal rights This research does not involve Human Participants and/or Animals.

Consent to Participate Not applicable.

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References

Ai Z, Mei T, Liu J, Li J, Jia F, Zhang L, Qiu J (2007) Fe@ Fe_2O_3 core-shell nanowires as an iron reagent. 3. Their combination with CNTs as an effective oxygen-fed gas diffusion electrode in a neutral electro-Fenton system. J Phys Chem C 111(40):14799–14803

Akerdi AG, Es'haghzade Z, Bahrami SH, Arami M (2017) Comparative study of GO and reduced GO coated graphite electrodes for decolorization of acidic and basic dyes from aqueous solutions through heterogeneous electro-Fenton process. J Environ Chem Eng 5(3):2313–2324

Andreozzi R, Caprio V, Insola A, Marotta R (1999) Advanced oxidation processes (AOP) for water purification and recovery. Catal Today 53(1):51–59

Babuponnusami A, Muthukumar K (2012) Advanced oxidation of phenol: a comparison between Fenton, electro-Fenton, sono-electro-Fenton and photo-electro-Fenton processes. Chem Eng J 183:1–9

Barhoumi N, Olvera-Vargas H, Oturan N, Huguenot D, Gadri A, Ammar S et al (2017) Kinetics of oxidative degradation/mineralization pathways of the antibiotic tetracycline by the novel heterogeneous electro-Fenton process with solid catalyst chalcopyrite. Appl Catal B Environ 209:637–647

Barreiro JC, Capelato MD, Martin-Neto L, Hansen HCB (2007) Oxidative decomposition of atrazine by a Fenton-like reaction in a H2O2/ferrihydrite system. Water Res 41(1):55–62

Bonnissel-Gissinger P, Alnot M, Ehrhardt JJ, Behra P (1998) Surface oxidation of pyrite as a function of pH. Environ Sci Technol *32*(19):2839–2845

Bouzayani B, Meijide J, Pazos M, Elaoud SC, Sanroman MA (2017) Removal of polyvinylamine sulfonate anthrapyridone dye by application of heterogeneous electro-Fenton process. Environ Sci Pollut Res 24(22):18309–18319

Brillas E, Calpe JC, Casado J (2000) Mineralization of 2,4-D by advanced electrochemical oxidation processes. Water Res 34(8):2253–2262

Brillas E, Casado J (2002) Aniline degradation by Electro-Fenton® and peroxi-coagulation processes using a flow reactor for wastewater treatment. Chemosphere 47(3):241–248

Brillas E, Mur E, Casado J (1996) Iron (II) Catalysis of the Mineralization of Aniline Using a Carbon-PTFE O_2-Fed Cathode. J Electrochem Soc 143(3):L49

Brillas E, Mur E, Sauleda R, Sanchez L, Peral J, Domènech X, Casado J (1998) Aniline mineralization by AOP's: anodic oxidation, photocatalysis, electro-Fenton and photoelectro-Fenton processes. Appl Catal B Environ 16(1):31–42

Brillas E, Sauleda R, Casado J (1999) Use of an acidic Fe/O_2 cell for wastewater treatment: degradation of aniline. J Electrochem Soc 146(12):4539

Canton C, Esplugas S, Casado J (2003) Mineralization of phenol in aqueous solution by ozonation using iron or copper salts and light. Appl Catal B Environ 43(2):139–149

Casado J (2019) Towards industrial implementation of Electro-Fenton and derived technologies for wastewater treatment: A review. J Environ Chem Eng 7(1):102823

Casado J, Coso EB, Bonany RMB, Vandermeiren M (2001) Electrolytic purification of contaminated waters by using oxygen diffusion cathodes. U.S. Patent No. 6,224,744. Washington, DC: U.S. Patent and Trademark Office

Casado J, Fornaguera J, Galán MI (2005) Mineralization of aromatics in water by sunlight-assisted electro-Fenton technology in a pilot reactor. Environ Sci Technol 39(6):1843–1847

Casado J, Fornaguera J, Galán MI (2006) Pilot scale mineralization of organic acids by electro-Fenton process plus sunlight exposure. Water Res 40(13):2511–2516

Casado J, Tratnyek PG, Scherer MM, Johnson TJ, Matheson LJ, … & Tarr MA(Ed.) (2003) Chemical degradation methods for wastes and pollutants: environmental and industrial applications. CRC press

Chandra AP, Gerson AR (2010) The mechanisms of pyrite oxidation and leaching: A fundamental perspective. Surf Sci Rep 65(9):293–315

Chen Y, Miller CJ, Waite TD (2021) Heterogeneous Fenton chemistry revisited: Mechanistic insights from ferrihydrite-mediated oxidation of formate and oxalate. Environ Sci Technol 55(21):14414–14425

Choe YJ, Byun JY, Kim SH, Kim J (2018) Fe3S4/Fe7S8-promoted degradation of phenol via heterogeneous, catalytic H2O2 scission mediated by S-modified surface Fe^{2+} species. Appl Catal B Environ 233:272–280

Choe YJ, Kim J, Byun JY, Kim SH (2021) An electro-Fenton system with magnetite coated stainless steel mesh as cathode. Catal Today 359:16–22

Chu L, Sun Z, Cang L, Fang G, Wang X, Zhou D, & Gao J (2020) A novel sulfite coupling electro-fenton reactions with ferrous sulfide cathode for anthracene degradation. Chem Eng J 400:125945

Cong Y, Li Z, Zhang Y, Wang Q, & Xu Q (2012) Synthesis of α-Fe2O3/TiO2 nanotube arrays for photoelectro-Fenton degradation of phenol. Chem Eng J 191:356–363

Cui T, Xiao Z, Wang Z, Liu C, Song Z, Wang Y et al (2021) FeS2/carbon felt as an efficient electro-Fenton cathode for carbamazepine degradation and detoxification: In-depth discussion of reaction contribution and empirical kinetic model. Environ Pollut 282:117023

Da Pozzo A, Di Palma L, Merli C, Petrucci E (2005) An experimental comparison of a graphite electrode and a gas diffusion electrode for the cathodic production of hydrogen peroxide. J Appl Electrochem 35(4):413–419

de Luna MDG, Colades JI, Su CC, Lu MC (2013) Comparison of dimethylsulfoxide degradation by different Fenton processes. Chem Eng J 232:418–424

Dhaouadi A, Adhoum N (2009) Degradation of paraquat herbicide by electrochemical advanced oxidation methods. J Electroanal Chem 637(1-2):33–42

Dong P, Chen X, Guo M, Wu Z, Wang H, Lin F et al (2021) Heterogeneous electro-Fenton catalysis with self-supporting CFP@MnO2-Fe3O4/C cathode for shale gas fracturing flowback wastewater. J Hazard Mater 412:125208

Es'haghzade Z, Pajootan E, Bahrami H, Arami M (2017) Facile synthesis of Fe3O4 nanoparticles via aqueous based electro chemical route for heterogeneous electro-Fenton removal of azo dyes. J Taiwan Inst Chem Eng 71:91–105

Expósito E, Sánchez-Sánchez CM, Montiel V (2007) Mineral iron oxides as iron source in electro-Fenton and photoelectro-Fenton mineralization processes. J Electrochem Soc 154(8):E116

Feng J, Tian H, Huang Y, Ding Z, Yin Z (2019) Pyrite oxidation mechanism in aqueous medium. J Chin Chem Soc 66(4):345–354

Fenton HJH (1894) LXXIII.—Oxidation of tartaric acid in presence of iron. J Chem Soc Trans 65:899-910

Ganiyu SO, Zhou M, Martínez-Huitle CA (2018) Heterogeneous electro-Fenton and photoelectro-Fenton processes: a critical review of fundamental principles and application for water/wastewater treatment. Appl Catal B Environ 235:103–129

Ganiyu SO, de Araujo Costa EC, Martinez-Huitle CA, dos Santos EV (2020) Electro-Fenton catalyzed by Fe-rich lateritic soil for the treatment of food colorant Bordeaux Red (E123): Catalyst characterization, optimization of operating conditions and mechanism of oxidation. Sep Purif Technol 242:116776

Gao G, Zhang Q, Hao Z, Vecitis CD (2015) Carbon nanotube membrane stack for flow-through sequential regenerative electro-Fenton. Environ Sci Technol 49(4):2375–2383

Geraldino HC, Freitas TK, Manholer DD, França F, Oliveira JH, Volnistem EA et al (2020) Electrochemical generation of H2O2 using gas diffusion electrode improved with rGO intensified with the Fe3O4/GO catalyst for degradation of textile wastewater. J Water Process Eng 36:101377

Ghanbari F, Martínez-Huitle CA (2019) Electrochemical advanced oxidation processes coupled with peroxymonosulfate for the treatment of real washing machine effluent: a comparative study. J Electroanal Chem 847:113182

Ghanbari F, Hassani A, Wacławek S, Wang Z, Matyszczak G, Lin KYA, Dolatabadi M (2021) Insights into paracetamol degradation in aqueous solutions by ultrasound-assisted heterogeneous electro-Fenton process: Key operating parameters, mineralization and toxicity assessment. Sep Purif Technol 266:118533

Gholizadeh AM, Zarei M, Ebratkhahan M, Hasanzadeh A (2021) Phenazopyridine degradation by electro-Fenton process with magnetite nanoparticles-activated carbon cathode, artificial neural networks modeling. J Environ Chem Eng 9(1):104999

Gopinath A, Pisharody L, Popat A, Nidheesh PV (2022) Supported catalysts for heterogeneous electro-Fenton processes: Recent trends and future directions. Curr Opinion Solid State Mater Sci 26(2):100981

Guo D, Liu Y, Ji H, Wang CC, Chen B, Shen C et al (2021) Silicate-enhanced heterogeneous flow-through electro-Fenton system using iron oxides under nanoconfinement. Environ Sci Technol 55(6):4045–4053

Gwenzi W, Chaukura N (2018) Organic contaminants in African aquatic systems: current knowledge, health risks, and future research directions. Sci Total Environ 619:1493–1514

Hafaiedh NB, Fourcade F, Bellakhal N, Amrane A (2018) Iron oxide nanoparticles as heterogeneous electro-Fenton catalysts for the removal of AR18 azo dye. Environ Technol

Hajiahmadi M, Zarei M, Khataee A (2021) Introducing an effective iron-based catalyst for heterogeneous electro-Fenton removal of Gemcitabine using three-dimensional graphene as cathode. J Ind Eng Chem 96:254–268

Hajiahmadi M, Zarei M, Khataee A (2022) An effective natural mineral-catalyzed heterogeneous electro-Fenton method for degradation of an antineoplastic drug: Modeling by a neural network. Chemosphere 291:132810

He H, Sun M, Wu D, Di G, Fei X (2021) Cu (III) generation and air sparging extend catalytic effectiveness of Cu2S/H2O2 from neutral to acidic condition: performance and mechanism in comparison with CuS/H2O2. J Clean Prod 278:123572

He Z, Gao C, Qian M, Shi Y, Chen J, Song S (2014) Electro-Fenton process catalyzed by Fe3O4 magnetic nanoparticles for degradation of CI Reactive Blue 19 in aqueous solution: operating conditions, influence, and mechanism. Ind Eng Chem Res 53(9):3435–3447

Heidari Z, Pelalak R, Alizadeh R, Oturan N, Shirazian S, Oturan MA (2021) Application of mineral iron-based natural catalysts in electro-Fenton process: a comparative study. Catalysts 11(1):57

Hoffmann MR, Martin ST, Choi W, Bahnemann DW (1995) Environmental applications of semiconductor photocatalysis. Chem Rev 95(1):69–96

Huang ZH, Liu JM, Ji ZY, Yuan P, Guo XF, Li SM et al (2022) Effective and continuous degradation of levofloxacin via the graphite felt electrode loaded with Fe3O4. Sep Purif Technol 281:119902

Kalantary RR, Farzadkia M, Kermani M, Rahmatinia M (2018) Heterogeneous electro-Fenton process by Nano-Fe3O4 for catalytic degradation of amoxicillin: process optimization using response surface methodology. J Environ Chem Eng 6(4):4644–4652

Khabbaz M, Entezari MH (2017) Degradation of Diclofenac by sonosynthesis of pyrite nanoparticles. J Environ Manag 187:416–423

Labiadh L, Oturan MA, Panizza M, Hamadi NB, Ammar S (2015) Complete removal of AHPS synthetic dye from water using new electro-fenton oxidation catalyzed by natural pyrite as heterogeneous catalyst. J Hazard Mater 297:34–41

Labiadh L, Ammar S, Kamali AR (2019) Oxidation/mineralization of AO7 by electro-Fenton process using chalcopyrite as the heterogeneous source of iron and copper catalysts with enhanced degradation activity and reusability. J Electroanal Chem 853:113532

Lama G, Meijide J, Sanromán A, Pazos M (2022) Heterogeneous Advanced Oxidation Processes: Current Approaches for Wastewater Treatment. Catalysts 12(3):344

Li J, Ai Z, Zhang L (2009) Design of a neutral electro-Fenton system with Fe@ Fe2O3/ACF composite cathode for wastewater treatment. J Hazard Mater 164(1):18–25

Li Y, Lu A, Ding H, Wang X, Wang C, Zeng C, Yan Y (2010) Microbial fuel cells using natural pyrrhotite as the cathodic heterogeneous Fenton catalyst towards the degradation of biorefractory organics in landfill leachate. Electrochem Commun 12(7):944–947

Li Y, Kawashima N, Li J, Chandra AP, Gerson AR (2013) A review of the structure, and fundamental mechanisms and kinetics of the leaching of chalcopyrite. Adv Colloid Interf Sci 197:1–32

Liu S, Zhao XR, Sun HY, Li RP, Fang YF, Huang YP (2013) The degradation of tetracycline in a photo-electro-Fenton system. Chem Eng J 231:441–448

Lizama-Bahena C, Álvarez-Gallegos A, Hernandez JA, Silva-Martinez S (2015) Elimination of bio-refractory chlorinated herbicides like atrazine, alachlor, and chlorbromuron from aqueous effluents by Fenton, electro-Fenton, and peroxi-coagulation methods. Desalin Water Treat 55(13):3683–3693

Ltaïef AH, D'Angelo A, Ammar S, Gadri A, Galia A, Scialdone O (2017) Electrochemical treatment of aqueous solutions of catechol by various electrochemical advanced oxidation processes: Effect of the process and of operating parameters. J Electroanal Chem 796:1–8

Ltaïef AH, Sabatino S, Proietto F, Ammar S, Gadri A, Galia A, Scialdone O (2018) Electrochemical treatment of aqueous solutions of organic pollutants by electro-Fenton with natural heterogeneous catalysts under pressure using Ti/IrO2-Ta2O5 or BDD anodes. Chemosphere 202:111–118

Mameri Y, Debbache N, El Mehdi Benacherine M, Seraghni N, Sehili T (2016) Heterogeneous photodegradation of paracetamol using Goethite/H2O2 and Goethite/oxalic acid systems under artificial and natural light. J Photochem Photobiol A Chem 315:129–137

Matta R, Hanna K, Chiron S (2007) Fenton-like oxidation of 2, 4, 6-trinitrotoluene using different iron minerals. Sci Total Environ 385(1-3):242–251

Meijide J, Rodríguez S, Sanromán MA, Pazos M (2018) Comprehensive solution for acetamiprid degradation: Combined electro-Fenton and adsorption process. J Electroanal Chem 808:446–454

Meijide J, Pazos M, Sanromán MÁ (2019) Heterogeneous electro-Fenton catalyst for 1-butylpyridinium chloride degradation. Environ Sci Pollut Res 26(4):3145–3156

Meijide J, Dunlop PS, Pazos M, Sanromán MA (2021) Heterogeneous electro-fenton as "Green" technology for pharmaceutical removal: A review. Catalysts 11(1):85

Monteil H, Pechaud Y, Oturan N, Oturan MA (2019) A review on efficiency and cost effectiveness of electro-and bio-electro-Fenton processes: Application to the treatment of pharmaceutical pollutants in water. Chem Eng J 376:119577

Mozia S, Darowna D, Przepiórski J, Morawski AW (2013) Evaluation of performance of hybrid photolysis-DCMD and photocatalysis-DCMD systems utilizing UV-C radiation for removal of diclofenac sodium salt from water. Pol J Chem Technol 15(1):51–60

Muñoz M, De Pedro ZM, Casas JA, Rodriguez JJ (2015) Preparation of magnetite-based catalysts and their application in heterogeneous Fenton oxidation–a review. Appl Catal B Environ 176:249–265

Muzenda C, Nkwachukwu OV, Arotiba OA (2022) Synthetic Ilmenite ($FeTiO_3$) Nanoparticles as a Heterogeneous Electro-Fenton Catalyst for the Degradation of Tetracycline in Wastewater

Nguyen DDD, Nguyen CNT, Huynh KA, Nguyen TP (2019) Optimization of electro-Fenton process for the removal of non-biodegradable organic compounds in instant coffee production wastewater using composite Fe3O4–Mn3O4 nanoparticle catalyst. Res Chem Intermed 45(11):5341–5356

Nidheesh PV, Gandhimathi R, Ramesh ST (2013) Degradation of dyes from aqueous solution by Fenton processes: a review. Environ Sci Pollut Res 20(4):2099–2132

Nidheesh PV, Gandhimathi R, Velmathi S, Sanjini NS (2014) Magnetite as a heterogeneous electro Fenton catalyst for the removal of Rhodamine B from aqueous solution. RSC Adv 4(11):5698–5708

Nidheesh PV, Olvera-Vargas H, Oturan N, Oturan MA (2017) Heterogeneous Electro-Fenton Process: Principles and Applications. In: Zhou M, Oturan M, Sirés I (eds) Electro-Fenton Process. The Handbook of Environmental Chemistry, vol 61. Springer, Singapore. https://doi.org/10.1007/698_2017_72

Nidheesh PV, Divyapriya G, Oturan N, Trellu C, Oturan MA (2019) Environmental applications of boron-doped diamond electrodes: 1. Applications in water and wastewater treatment. Chem Electro Chem 6(8):2124–2142

Nidheesh PV, Behera B, Babu DS, Scaria J, Kumar MS (2022) Mixed industrial wastewater treatment by the combination of heterogeneous electro-Fenton and electrocoagulation processes. Chemosphere 290:133348

Oller I, Malato S, Sánchez-Pérez J (2011) Combination of advanced oxidation processes and biological treatments for wastewater decontamination—a review. Sci Total Environ 409(20):4141–4166

Oturan MA, Pimentel M, Oturan N, Sirés I (2008) Reaction sequence for the mineralization of the short-chain carboxylic acids usually formed upon cleavage of aromatics during electrochemical Fenton treatment. Electrochim Acta 54(2):173–182

Oturan MA, Aaron JJ (2014) Advanced oxidation processes in water/wastewater treatment: principles and applications. A review. Crit Rev Environ Sci Technol 44(23):2577–2641

Ouiriemmi I, Karrab A, Oturan N, Pazos M, Rozales E, Gadri A et al (2017) Heterogeneous electro-Fenton using natural pyrite as solid catalyst for oxidative degradation of vanillic acid. J Electroanal Chem 797:69–77

Özcan A, Özcan AA, Demirci Y, Şener E (2017) Preparation of Fe2O3 modified kaolin and application in heterogeneous electro-catalytic oxidation of enoxacin. Appl Catal B Environ 200:361–371

Peral J, Casado J, Doménech J (1988) Light-induced oxidation of phenol over ZnO powder. J Photochem Photobiol A Chem 44(2):209–217

Pignatello JJ, Oliveros E, MacKay A (2006) Advanced oxidation processes for organic contaminant destruction based on the Fenton reaction and related chemistry. Crit Rev Environ Sci Technol 36(1):1–84

Pimentel M, Oturan N, Dezotti M, Oturan MA (2008) Phenol degradation by advanced electrochemical oxidation process electro-Fenton using a carbon felt cathode. Appl Catal B Environ 83(1-2):140–149

Pinheiro AC, Bernardino TS, Junior FE, Lanza MR, Barros WR (2020) Enhanced electrodegradation of the Sunset Yellow dye in acid media by heterogeneous Photoelectro-Fenton process using Fe3O4 nanoparticles as a catalyst. J Environ Chem Eng 8(1):103621

Plakas KV, Sklari SD, Yiankakis DA, Sideropoulos GT, Zaspalis VT, Karabelas AJ (2016) Removal of organic micropollutants from drinking water by a novel electro-Fenton filter: pilot-scale studies. Water Res 91:183–194

Poza-Nogueiras V, Rosales E, Pazos M, Sanroman MA (2018) Current advances and trends in electro-Fenton process using heterogeneous catalysts–a review. Chemosphere 201:399–416

Poza-Nogueiras V, Moratalla Á, Pazos M, Sanromán Á, Sáez C, Rodrigo MA (2021) Towards a more realistic heterogeneous electro-Fenton. J Electroanal Chem 895*:*115475

Salari D, Niaei A, Khataee A, Zarei M (2009) Electrochemical treatment of dye solution containing CI Basic Yellow 2 by the peroxi-coagulation method and modeling of experimental results by artificial neural networks. J Electroanal Chem 629(1-2):117–125

Sánchez-Sánchez CM, Expósito E, Casado J, Montiel V (2007) Goethite as a more effective iron dosage source for mineralization of organic pollutants by electro-Fenton process. Electrochem Commun 9(1):19–24

Sankara Narayanan TSN, Magesh G, Rajendran N (2003) Degradation of O-chlorophenol from aqueous solution by electro-Fenton process. Fresenius Environ Bull 12(7):776–780

Song B, Zeng Z, Almatrafi E, Shen M, Xiong W, Zhou C et al (2022) Pyrite-mediated advanced oxidation processes: Applications, mechanisms, and enhancing strategies. Water Res 118048

Sun M, Ru XR, Zhai LF (2015) In-situ fabrication of supported iron oxides from synthetic acid mine drainage: high catalytic activities and good stabilities towards electro-Fenton reaction. Appl Catal B Environ 165:103–110

Sun Y, Pignatello JJ (1993) Photochemical reactions involved in the total mineralization of 2, 4-D by iron (3+)/hydrogen peroxide/UV. Environ Sci Technol 27(2):304–310

Ting WP, Lu MC, Huang YH (2008) The reactor design and comparison of Fenton, electro-Fenton and photoelectro-Fenton processes for mineralization of benzene sulfonic acid (BSA). J Hazard Mater 156(1-3):421–427

Utset B, Garcia J, Casado J, Domènech X, Peral J (2000) Replacement of H_2O_2 by O_2 in Fenton and photo-Fenton reactions. Chemosphere 41(8):1187–1192

Von Gunten U (2003) Ozonation of drinking water: Part I. Oxidation kinetics and product formation. Water Res 37(7):1443–1467

Walling C (1975) Fenton's reagent revisited. Acc Chem Res 8(4):125-131

Wang A, Qu J, Ru J, Liu H, Ge J (2005) Mineralization of an azo dye Acid Red 14 by electro-Fenton's reagent using an activated carbon fiber cathode. Dyes Pigments 65(3):227–233

Wang Y, Li X, Zhen L, Zhang H, Zhang Y, Wang C (2012) Electro-Fenton treatment of concentrates generated in nanofiltration of biologically pretreated landfill leachate. J Hazard Mater 229:115–121

Wang Y, Zhao H, Chai S, Wang Y, Zhao G, Li D (2013) Electrosorption enhanced electro-Fenton process for efficient mineralization of imidacloprid based on mixed-valence iron oxide composite cathode at neutral pH. Chem Eng J 223:524–535

Wang Y, Zhao H, Zhao G (2016) Highly Ordered Mesoporous Fe3O4@ Carbon Embedded Composite: High Catalytic Activity, Wide pH Range and Stability for Heterogeneous Electro-Fenton. Electroanalysis 28(1):169–176

Wang Z, Wang Y, Guo H, Yu N, Ren Q, Jiang Q et al (2021) Synthesis of one-for-all type Cu5FeS4 nanocrystals with improved near infrared photothermal and Fenton effects for simultaneous imaging and therapy of tumor. J Colloid Interface Sci 592:116–126

Wang Z, Liu M, Xiao F, Postole G, Zhao H, Zhao G (2022) Recent advances and trends of heterogeneous electro-Fenton process for wastewater treatment-review. Chin Chem Lett 33(2):653–662

Xu L, Wang J (2012) Fenton-like degradation of 2, 4-dichlorophenol using Fe3O4 magnetic nanoparticles. Appl Catal B Environ 123:117–126

Yao Y, Chen Q, Huang Z, Zhou J (2021) Catalytic activity comparison of typical iron-bearing particle electrodes in heterogeneous electro-Fenton oxidation processes. Environ Technol Innov 21:101321

Yu F, Wang Y, Ma H, Zhou M (2020) Hydrothermal synthesis of FeS2 as a highly efficient heterogeneous electro-Fenton catalyst to degrade diclofenac via molecular oxygen effects for Fe (II)/Fe (III) cycle. Sep Purif Technol 248:117022

Zeng X, Hanna K, Lemley AT (2011) Cathodic Fenton degradation of 4, 6-dinitro-o-cresol with nano-magnetite. J Mol Catal A Chem 339(1-2):1–7

Zepp RG, Faust BC, Hoigne J (1992) Hydroxyl radical formation in aqueous reactions (pH 3-8) of iron (II) with hydrogen peroxide: the photo-Fenton reaction. Environ Sci Technol 26(2):313–319

Zhang G, Wang S, Yang F (2012b) Efficient adsorption and combined heterogeneous/homogeneous Fenton oxidation of amaranth using supported nano-FeOOH as cathodic catalysts. J Phys Chem C 116(5):3623–3634

Zhang H, Ran X, Wu X (2012a) Electro-Fenton treatment of mature landfill leachate in a continuous flow reactor. J Hazard Mater 241:259–266

Zhao H, Wang Y, Wang Y, Cao T, Zhao G (2012) Electro-Fenton oxidation of pesticides with a novel Fe3O4@ Fe2O3/activated carbon aerogel cathode: High activity, wide pH range and catalytic mechanism. Appl Catal B Environ 125:120–127

Zhou L, Zhou M, Zhang C, Jiang Y, Bi Z, Yang J (2013) Electro-Fenton degradation of p-nitrophenol using the anodized graphite felts. Chem Eng J 233:185–192

Zhou L, Hu Z, Zhang C, Bi Z, Jin T, Zhou M (2013b) Electrogeneration of hydrogen peroxide for electro-Fenton system by oxygen reduction using chemically modified graphite felt cathode. Sep Purif Technol 111:131–136