Current advances and trends in electro-Fenton process using heterogeneous catalysts – A review

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Abstract

Over the last decades, advanced oxidation processes have often been used alone, or combined with other techniques, for remediation of ground and surface water pollutants. The application of heterogeneous catalysis to electrochemical advanced oxidation processes is especially useful due to its efficiency and environmental safety. Among those processes, electro-Fenton stands out as the one in which heterogeneous catalysis has been broadly applied. Thus, this review has introduced an up-to-date collation of the current knowledge of the heterogeneous electro-Fenton process, highlighting recent advances in the use of different catalysts such as iron minerals (pyrite, magnetite or goethite), prepared catalysts by the load of metals in inorganic and organic materials, nanoparticles, and the inclusion of catalysts on the cathode. The effects of physical-chemical parameters as well as the mechanisms involved are critically assessed. Finally, although the utilization of this process to remediation of wastewater overwhelmingly outnumber other utilities, several applications have been described in the context of regeneration of adsorbent or the remediation of soils as clear examples of the feasibility of the electro-Fenton process to solve different environmental problems.

Keywords: Fe^{2+}/Fe^{3+}; iron minerals; nanoparticles; modified cathode; electro-Fenton; photoelectro-Fenton.
1. Introduction

Water quality has been severely deteriorated over the last decades mainly due to population growth, urban development, increased industrialization, and unsustainable utilization of natural water resources. The diversity and quantity of pollutants reaching water streams has increased. Among the existing contaminants, emerging pollutants such as solvents, surfactants, pharmaceutical and personal care products, and pesticides are becoming an increasing concern. According to Geissen et al. (2015), more than 700 emerging pollutants, their metabolites, and transformation by-products have been identified in European aquatic environments.

Nowadays, biological treatments are the most widespread processes employed in wastewater treatment plants because of its cost-effectiveness (Ganzenko et al., 2014). However, these conventional plants were not originally designed to eliminate biorefractory pollutants and their metabolites, with their concomitant entrance into the aquatic environment via sewage effluents (Luo et al., 2014). This situation has increased public awareness of environmental issues and resulted in legislation to protect the environment and several actions to reduce the harmful effects of pollutants. In particular, within the European Union legislation, this issue has been addressed by the Directive 2013/39/UE and the Watch List present in the Decision 2015/495/UE, according to which 41 organic priority substances and 17 contaminants of emerging concern, respectively, should be monitored in surface water. Additionally, the Directive 2013/39/UE highlights the demand to develop new water treatment solutions for the elimination of those substances (Sousa et al., 2018). As a consequence, the development of these alternative water treatments has received considerable research attention (Richardson and Kimura, 2017). Among new water treatment technologies, advanced oxidation processes (AOPs)
have emerged as useful alternatives for treating wastewater containing non-biodegradable, or poorly biodegradable, toxic organic compounds.

AOPs are based on the generation of powerful oxidizing agents such as the hydroxyl radical (HO\(^\bullet\)) that can destroy many pollutants present in water streams. The generation of HO\(^\bullet\) is an essential step to ensure the efficiency of AOPs (Martínez-Huitle et al., 2015; Dewil et al., 2017). Different mechanisms have been proposed for the production of these radicals. The processes are classified based on the use of electric field, light irradiation, ultrasound, and also considering if the reaction occurs in a homogeneous or heterogeneous system. From among all these available processes, electrochemical advanced oxidation processes (EAOPs) are considered to be a very promising technology with significant advantages such as relatively low operational cost (Brillas et al., 2009; Chaplin, 2014) and high pollutants mineralization (Sirés et al., 2014; Ganzenko et al., 2014). There are different types of EAOPs, based on the manner in which they generate HO\(^\bullet\), which can be used alone or combined.

Electro-Fenton is one of the most powerful and environmentally friendly emerging technologies for the remediation of wastewater containing organic compounds such as aromatics (Nidheesh and Gandhimathi, 2012; Barhoumi et al., 2016). This technology has been developed and extensively applied by several research groups outstanding the Brillas and Oturan groups (Brillas et al., 2009; Oturan and Aaron, 2014). The mechanism of this process involves several steps: i) \textit{in-situ} H\(_2\)O\(_2\) electrogeneration via cathodic reduction of oxygen (Eq. (1)), which depends on the applied current intensity and dissolved oxygen (Liu et al., 2007; Ammar et al., 2015); ii) generation of HO\(^\bullet\) (Eq. (2)) via Fenton’s reaction between ferrous ion and electrogenerated H\(_2\)O\(_2\); iii) promoting the formation of HO\(^\bullet\) physisorbed (anode(HO\(^\bullet\))) on the electrode surface when materials as boron doped diamond (BDD) are used as anode, following the reactions shown in Eqs.
(3) and (4) (Hammami et al., 2008; Barhoumi et al., 2017); iv) regeneration of Fe\textsuperscript{3+}/Fe\textsuperscript{2+} by direct reduction on the cathode (Eq. (5)) (El-Ghenemy et al., 2014; Qiu et al., 2015).

\[
\begin{align*}
O_2 + 2H^+ + 2e^- &\rightarrow H_2O_2 & (1) \\
Fe^{2+} + H_2O_2 + H^+ &\rightarrow Fe^{3+} + OH^- + HO^* & (2) \\
BDD + H_2O &\rightarrow BDD(OH) + H^+ + e^- & (3) \\
BDD(OH) + organic compounds &\rightarrow BDD + oxidized products & (4) \\
Fe^{3+} + e^- &\rightarrow Fe^{2+} & (5)
\end{align*}
\]

Another interesting EAOP is the photoelectro-Fenton in which the electro-Fenton is combined with light irradiation (UV light (Ramírez et al., 2010; Babuponnusami and Muthukumar, 2013; Wu et al., 2013) or sunlight (Espinoza et al., 2016; Gozzi et al., 2017; Murillo-Sierra et al., 2018)). In this case, ferrous regeneration and the generation of HO\textsuperscript{*} also take place by the reactions described in Eqs. (6) and (7) and the photodecarboxylation of iron complexes generates carbon dioxide and ferrous iron (Eq. (8)) (Masomboon et al., 2010; Komtchou et al., 2017).

\[
\begin{align*}
Fe^{3+} + H_2O &\rightarrow Fe(OH)^{2+} + H^+ & (6) \\
Fe(OH)^{2+} + h\nu &\rightarrow Fe^{2+} + HO^* & (7) \\
Fe(OOCR)^{2+} + h\nu &\rightarrow Fe^{2+} + CO_2 + R^* & (8)
\end{align*}
\]

Another EAOP is the sonoelectro-Fenton process where an ultrasound technique is coupled to electro-Fenton favouring the regeneration of Fe\textsuperscript{2+} from the intermediate complex (Eq. (6)) by the reaction described in Eq. (9). In addition, ultrasound can improve the efficiency of the process through physical and chemical mechanisms. The physical mechanism causes a high degree of mixing and the cleaning of the electrode surfaces by dissolving the inhibiting layers. This mainly results in an increased mass transfer between electrode and solution (Li et al., 2010a; Chen and Huang, 2014). The chemical mechanism corresponds to violent collapses of micro bubbles, which generate oxidizing species by
the homolytic cleavage of molecules, and in the presence of oxygen radicals such as HO•, HO2• (Eqs. (10) and (11)) (Oturan et al., 2008; Babuponnusami and Muthukumar, 2012).

\[
\text{Fe(OH)}^{2+} \rightarrow \text{Fe}^{2+} + \text{HO}_2^\cdot \quad (9)
\]

\[
\text{H}_2\text{O} \rightarrow \text{HO}^\cdot + ^\cdot \text{H} \quad (10)
\]

\[
^\cdot \text{H} + \text{O}_2 \rightarrow \text{HO}_2^\cdot \quad (11)
\]

In addition, the electro-Fenton process could be used as a preliminary treatment step coupled with biological treatment methods. This bioelectro-Fenton process combines the high oxidation power of the electro-Fenton and the cost-effectiveness of biological methods (Olvera-Vargas et al., 2016; Ganzenko et al., 2017; Roshini et al., 2017).

All the aforementioned EAOPs have in common that the processes typically take place in homogeneous systems which require an optimum pH of 3 and the presence of free Fe\(^{2+}\) that must be precipitated for disposal, generating undesirable iron sludge. EAOPs have been mostly investigated on small laboratory scale and their application at pilot or full-scale has yet to be done. Brillas et al. (2009) noted that this gap between laboratory research and practical applications can often be attributed to environmental, technological, and economic factors, which can be overcome using the following modifications:

- improvement of electrochemical cell/reactor designs;
- development of novel electrodes (high-performance anodes and cathodes with enhanced electrocatalytic properties);
- enhancement of mass transfer within the electrochemical cell;
- design of effective catalysts;
- improvement of operating conditions (current intensity or electric potential, catalyst dosage, pH, temperature);
- process modelling and prediction of pollutant behaviour.
To overcome the limitation of homogeneous EAOPs, recent studies have demonstrated that a heterogeneous catalyst is more efficient than its homogeneous counterpart at degrading organic pollutants in wastewater (Nidheesh et al., 2017). The heterogeneous process has additional benefits such as:

- could be operated in an extended pH range and therefore neutralization of the final effluent may be avoided;
- reduces the formation of iron hydroxide sludge and associated issues;
- catalyst is easy to handle, safe to store, can be efficiently recovered and has the possibility to be reused.

Since the catalytic process takes place on the catalyst surface, it must be accessible to the reactants and, in addition, the desired structures of the catalysts should present: i) high activity and selectivity to hydroxyl radical generation, ii) large surface area, iii) homogeneity, iv) porous structure, v) high stability, and vi) low cost. Generally, the catalytic active phase either can be already present in a natural material or artificially introduced or fixed on a pre-existing solid by a process, which intrinsically depends on the support surface (Campanati et al., 2003). Figure 1 shows a typical setup for heterogeneous electro-Fenton, including the scanning electron microscope (SEM) images of several usual heterogeneous catalyst.

In the last decade, research on the application of heterogeneous catalysis to the Fenton and photo-Fenton processes has been reported in several reviews (Wang et al., 2012; Nidheesh, 2015) and book chapters (Pariente et al., 2013; Carabineiro et al., 2014), using mainly iron oxides (Pereira et al., 2012; Rahim Pouran et al., 2014; Munoz et al., 2015), but also employing clays, silicates, zeolites (Herney-Ramirez et al., 2010; Navalon et al., 2011), and nanoparticles (Dhakshinamoorthy et al., 2012). However, to our knowledge, when it comes to the electro-Fenton process there is only a book chapter (Nidheesh et al.,
2017) that discusses the application of heterogeneous catalysis. Therefore, it is necessary to address this topic providing a comprehensive analysis of the diverse solid catalysts that have been applied to heterogeneous electro-Fenton.

In the following sections, different catalysts and methods for their preparation are discussed, highlighting both the mechanisms and the important topics related to the degradation of organic pollutants.

**Figure 1.** Heterogeneous electro-Fenton setup and SEM images of several catalysts.
2. Iron minerals

To overcome the drawbacks of classical Fenton treatments, attempts have been made to use heterogeneous catalysts containing iron oxides instead of soluble iron salts. Their use may be especially advantageous for in situ remediation of contaminated groundwater where pH cannot be adjusted and the catalyst cannot be easily recovered for further use. In addition, this catalytic action may be exploited for in situ chemical oxidation treatment where endogenous iron oxides are present. Several iron minerals have been selected as catalysts in AOPs because of their ubiquity in nature, their widespread abundance in natural soils and sediments, frequently associated with clays and silica sands, and their low cost (Matta et al., 2008; Munoz et al., 2017). Some studies have suggested a relationship between the type of iron used and the oxidation rate. The most common iron minerals used in AOPs are pyrite, magnetite, ferrihydrite, hematite, goethite, wüstite, and lepidocrocite. However, ferrihydrite, hematite, and lepidocrocite have received less study as potential catalysts in EAOPs compared to the other iron oxides. Some of the most significant studies using pyrite, magnetite, and goethite as catalysts in heterogeneous electro-Fenton process are commented in the following sections and summarised in Table 1.
Table 1. Overview of the studies reported in the literature using in the area of heterogeneous electro-Fenton

<table>
<thead>
<tr>
<th>Pollutant / mg L(^{-1})</th>
<th>Catalyst / g L(^{-1})</th>
<th>Anode/Cathode</th>
<th>Electric field</th>
<th>Operational conditions</th>
<th>Maximum degradation</th>
<th>Maximum mineralization / MCE</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>IRON MINERALS</strong></td>
<td></td>
<td></td>
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<td></td>
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</tr>
<tr>
<td>Aniline / 100</td>
<td>Hematite / 1</td>
<td></td>
<td>0.25 A</td>
<td>0.2 M Na(_2)SO(_4), pH 3, AFR 0.5 L min(^{-1})</td>
<td>TOC: 33% (24 h)</td>
<td>TOC: 78.7% (24 h)</td>
<td>Expósito et al. (2007)</td>
</tr>
<tr>
<td></td>
<td>Wüstite / 1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Magnetite / 1</td>
<td>Pt/Carbo n-PTFE</td>
<td>0.25 A</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Goethite / 1</td>
<td></td>
<td></td>
<td>*UV lamp λ = 254 nm + Idem previous conditions</td>
<td></td>
<td>TOC: 90.2% (5 h)*</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Magnetite / 1</td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Rhodamine B / 10</td>
<td>Magnetite / 0.010</td>
<td>Graphite/Graphite</td>
<td>8 V</td>
<td>pH 3, aeration</td>
<td>97.3% (3 h)</td>
<td>-</td>
<td>Nidheesh et al. (2014)</td>
</tr>
<tr>
<td>Levofloxacin / 0.23 mM</td>
<td>Pyrite / 1</td>
<td>BDD/CF</td>
<td>0.3 A</td>
<td>0.05 M Na(_2)SO(_4), pH 3, AFR 1 L min(^{-1})</td>
<td>TOC: 95% (8 h) / MCE: 3% (8 h)</td>
<td>Barhoumi et al. (2015)</td>
<td></td>
</tr>
<tr>
<td>Tyrosol / 41</td>
<td>Pyrite / 1</td>
<td>BDD/CF</td>
<td>0.3 A</td>
<td>0.05 M Na(_2)SO(_4), pH 3, AFR 1 L min(^{-1})</td>
<td>100% (6 min)</td>
<td>TOC: &gt;90% (6 h) / MCE: 8% (6 h)</td>
<td>Ammar et al. (2015)</td>
</tr>
<tr>
<td>AHPS / 175</td>
<td>Pyrite / 2</td>
<td>BDD/CF</td>
<td>0.3 A</td>
<td>0.05 M Na(_2)SO(_4), pH=3, AFR 1 L min(^{-1})</td>
<td>-</td>
<td>TOC: &gt;96% (4 h) / MCE: 11% (4 h)</td>
<td>Labiadh et al. (2015)</td>
</tr>
<tr>
<td>Tetracycline / 0.2 mM</td>
<td>Pyrite / 2</td>
<td>BDD/CF</td>
<td>0.3 A</td>
<td>0.05 M Na(_2)SO(_4), pH 3, AFR 1 L min(^{-1})</td>
<td>100% (15 min)</td>
<td>TOC: &gt;95% (6 h) / MCE: 39% (8 h)</td>
<td>Barhoumi et al. (2017)</td>
</tr>
<tr>
<td>PSA / 100</td>
<td>Pyrite / 2</td>
<td>BDD/CF</td>
<td>0.2 A</td>
<td>0.05 M Na(_2)SO(_4), pH 3, AFR 1 L min(^{-1})</td>
<td>97.70% (2 h)</td>
<td>TOC: &gt;95% (6 h) / MCE: 1% (8 h)</td>
<td>Bouzayani et al. (2017)</td>
</tr>
<tr>
<td>Sulfamethazine / 0.2 mM</td>
<td>Pyrite / 2</td>
<td>BDD/CF</td>
<td>1 A</td>
<td>0.05 M Na(_2)SO(_4), natural pH 3, AFR 1 L min(^{-1})</td>
<td>≥100% (30 min)</td>
<td>TOC: &gt;97% (8 h) / MCE: 1.35% (4 h)</td>
<td>Barhoumi et al. (2016)</td>
</tr>
<tr>
<td>Vanillic acid / 0.1 mM</td>
<td>Pyrite / 1</td>
<td>Pt/CF</td>
<td>0.3 A</td>
<td>0.05 M Na(_2)SO(_4), pH 3, AFR 1 L min(^{-1})</td>
<td>100% (12 min)</td>
<td>TOC: &gt;89.2% (4 h) / MCE: 1.35% (4 h)</td>
<td>Ouiriemmi et al. (2017)</td>
</tr>
<tr>
<td>Aniline / 100</td>
<td>Goethite / 1</td>
<td>Pt/Carbo n-PTFE</td>
<td>50 mA cm(^{-2})</td>
<td>0.05 M Na(_2)SO(_4), pH 3, AFR 0.5 L min(^{-1})</td>
<td>-</td>
<td>TOC: 93% (24 h)</td>
<td>Sánchez-Sánchez et al. (2007)</td>
</tr>
<tr>
<td>1-butylpyridinium chloride / 500</td>
<td>Goethite/PVA alginate beads / 2</td>
<td>BDD/CF</td>
<td>0.3 A</td>
<td>0.01 M Na(_2)SO(_4), pH 3, AFR 1 L min(^{-1})</td>
<td>98% (2 h)</td>
<td>TOC: 94% (8 h) / COD: 95% (8 h)</td>
<td>Meijide et al. (2017)</td>
</tr>
<tr>
<td>Acetamiprid / 60</td>
<td>Goethite/PVA alginate beads / 2</td>
<td>BDD/GF</td>
<td>0.1 A</td>
<td>0.01 M Na(_2)SO(_4), pH 3, AFR 1 L min(^{-1})</td>
<td>100% (75 min)</td>
<td>TOC: 90% (8 h) / MCE: 39% (8 h)</td>
<td>Meijide et al. (2018)</td>
</tr>
<tr>
<td>Pollutant / mg L$^{-1}$</td>
<td>Catalyst / g L$^{-1}$</td>
<td>Anode/ Cathode</td>
<td>Electric field</td>
<td>Operational conditions</td>
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<td>Maximum mineralization / MCE</td>
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</tr>
<tr>
<td>Amaranth / 80</td>
<td>Goethite-lepidocrocite/AC / 150</td>
<td>Pt/GF</td>
<td>-0.64 V</td>
<td>0.2 M Na$_2$SO$_4$, pH 4, aerated</td>
<td>100% (4 h)</td>
<td>TOC: 50% (6 h)</td>
<td>Zhang et al. (2012)</td>
</tr>
<tr>
<td>Lissamine green B / 8.5</td>
<td>Iron alginate beads / 58</td>
<td>Graphite/ Graphite</td>
<td>14.19 V</td>
<td>0.01 M Na$_2$SO$_4$, pH 2, AFR 1 L min$^{-1}$</td>
<td>98% $(\tau = 30$ min)</td>
<td>TOC: 93% $(\tau = 30$ min)</td>
<td>Rosales et al. (2012a)</td>
</tr>
<tr>
<td>Azure B / 4.83</td>
<td>Iron alginate beads / 58</td>
<td>Graphite/ Graphite</td>
<td>0.53 mA cm$^{-2}$</td>
<td>0.1 M Na$_2$SO$_4$, pH 3.0, AFR 0.25 mL min$^{-1}$</td>
<td>100% (1 h)</td>
<td>TOC: 89% (1 h)</td>
<td>Rosales et al. (2012a)</td>
</tr>
<tr>
<td>Indole / 20</td>
<td>Iron alginate beads / 0.2</td>
<td>Pt/CF</td>
<td>0.5 mA cm$^{-2}$</td>
<td>0.05 M Na$_2$SO$_4$, pH 3, AFR 0.75 L min$^{-1}$</td>
<td>98% $(\tau = 30$ min)</td>
<td>TOC: 88% (6 h)</td>
<td>Rosales et al. (2012a)</td>
</tr>
<tr>
<td>Imidacloprid / 100</td>
<td>Iron alginate beads / 28.5</td>
<td>BDD/ Graphite</td>
<td>5 V</td>
<td>0.01 M Na$_2$SO$_4$, pH 2, AFR 1 L min$^{-1}$</td>
<td>100% (2 h)</td>
<td>-</td>
<td>Iglesias et al. (2014)</td>
</tr>
<tr>
<td>5 imidazolium-based ionic liquids / 500</td>
<td>Iron alginate beads / 21.4</td>
<td>BDD/CF</td>
<td>0.3 A</td>
<td>0.05 M Na$_2$SO$_4$, pH 3, AFR 0.5 L min$^{-1}$</td>
<td>&gt;95% (1.5 h)</td>
<td>TOC: &gt; 80% (8 h)</td>
<td>Bocos et al. (2016a)</td>
</tr>
<tr>
<td>1,3-Bis(2,4,6-trimethylphenyl) imidazolinium chloride / 68</td>
<td>Iron alginate beads / 33.3</td>
<td>BDD/CF</td>
<td>0.17 A</td>
<td>0.01 M Na$_2$SO$_4$, pH 3, AFR 0.5 L min$^{-1}$</td>
<td>-</td>
<td>TOC: 76.98% (2 h)</td>
<td>Poza-Nogueiras et al. (2018)</td>
</tr>
<tr>
<td>Reactive black 5 / 100</td>
<td>Iron polycrylamide hydrogel / 3.3</td>
<td>Graphite/ Graphite</td>
<td>5 V</td>
<td>0.01 M Na$_2$SO$_4$, pH 2, AFR 2 L min$^{-1}$</td>
<td>=95% (2 h)</td>
<td>-</td>
<td>Bocos et al. (2014)</td>
</tr>
<tr>
<td>Reactive red 120 / 10</td>
<td>Fe-ZSM-5 / 0.5</td>
<td>Graphite/ Graphite</td>
<td>0.1 A</td>
<td>0.05 M Na$_2$SO$_4$, pH 3, aeration</td>
<td>=98% (30 min)</td>
<td>-</td>
<td>Rostamizadeh et al. (2018)</td>
</tr>
<tr>
<td>Neutral coking wastewater / 225 mg L$^{-1}$ COD</td>
<td>Iron zeolite Y / 250</td>
<td>Graphite/ 2-EAQ-GF</td>
<td>10 A m$^{-2}$</td>
<td>pH 7.2, AFR 0.5 L min$^{-1}$</td>
<td>=100% (1 h)</td>
<td>COD: 49.7% (1 h)</td>
<td>Li et al. (2011)</td>
</tr>
<tr>
<td>Neutral coking wastewater / 225 mg L$^{-1}$ COD</td>
<td>Iron zeolite Y / 250</td>
<td>Graphite/ 2-EAQ-GF</td>
<td>10 A m$^{-2}$</td>
<td>pH 7.2, AFR 0.5 L min$^{-1}$</td>
<td>=100% (1 h)</td>
<td>COD: 49.7% (1 h)</td>
<td>Li et al. (2011)</td>
</tr>
</tbody>
</table>

**IRON SUPPORTING MATERIALS: ORGANIC POLYMERS**

**IRON SUPPORTING MATERIALS: INORGANIC MATERIALS**
<table>
<thead>
<tr>
<th>Pollutant / mg L⁻¹</th>
<th>Catalyst / g L⁻¹</th>
<th>Anode/ Cathode</th>
<th>Electric field</th>
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<th>Maximum degradation</th>
<th>Maximum mineralization / MCE</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Imidacloprid / 100</td>
<td>Iron zeolite Y-alginate / 28.7</td>
<td>BDD/ Graphite</td>
<td>5 V</td>
<td>0.01 M Na₂SO₄, pH 6, AFR 1 L min⁻¹</td>
<td>&gt;93% (3 h)</td>
<td>-</td>
<td>Iglesias et al. (2015a)</td>
</tr>
<tr>
<td>Chlorpyrifos / 1.3</td>
<td>Iron zeolite Y / 0.96</td>
<td>BDD/ Graphite</td>
<td>5 V</td>
<td>0.01 M Na₂SO₄, pH 2, AFR 1 L min⁻¹</td>
<td>&gt;96% (5 min)</td>
<td>-</td>
<td>Iglesias et al. (2015a)</td>
</tr>
<tr>
<td>Reactive black 5 / 100</td>
<td>Fe-zeolite / -</td>
<td>Graphite/ Graphite</td>
<td>0.6 V (MFC)</td>
<td>0.01 M Na₂SO₄, pH 2, AFR 1 L min⁻¹</td>
<td>&gt;100% (1.5 h)</td>
<td>-</td>
<td>Fernández de Dios et al. (2014)</td>
</tr>
<tr>
<td>Phenanthrene / 18</td>
<td>Iron loaded sepiolite / 20</td>
<td>BDD/ Graphite</td>
<td>5 V</td>
<td>0.01 M Na₂SO₄, pH 2, AFR 1 L min⁻¹</td>
<td>78% (30 h)</td>
<td>-</td>
<td>Iglesias et al. (2013a)</td>
</tr>
<tr>
<td>Reactive black 5 / 100</td>
<td>Iron-bentonite / 5</td>
<td>Graphite/ Graphite</td>
<td>125 mA cm⁻²</td>
<td>Natural pH 6.24, aeration</td>
<td>92.48% (3 h)</td>
<td>COD: 67.48% (3 h)</td>
<td>Qiao et al. (2015)</td>
</tr>
<tr>
<td>Phenol / 100</td>
<td>Iron-bentonite / 1.25</td>
<td>Graphite/ Graphite</td>
<td>14.29 mA cm⁻²</td>
<td>0.05 M Na₂SO₄, pH 6.4, aeration</td>
<td>98.89% (1 h)</td>
<td>COD: 71.57% (1 h)</td>
<td>Qiao et al. (2016)</td>
</tr>
<tr>
<td>Methyl orange / 100</td>
<td>Iron clay kaolin / 6.6</td>
<td>Graphite/ Graphite</td>
<td>2.1 A</td>
<td>0.05 M Na₂SO₄, pH 4.34, AFR 1 L min⁻¹</td>
<td>99.24% (1 h)</td>
<td>COD: 92.48% (1 h)</td>
<td>He et al. (2014a)</td>
</tr>
<tr>
<td>Acid orange II / 100</td>
<td>Iron clay kaolin / 1.7</td>
<td>BDD/CF</td>
<td>0.3 A</td>
<td>0.05 M Na₂SO₄, pH 5.1, aeration</td>
<td>&gt;100% (15 min)</td>
<td>TOC: 98% (7 h) / MCE: 3% (7 h)</td>
<td>Özcan et al. (2017)</td>
</tr>
<tr>
<td>Methylene blue / 100</td>
<td>Iron clay kaolin / 30</td>
<td>Graphite/ Graphite</td>
<td>69.23 mA cm⁻²</td>
<td>1.0 g L⁻¹ NaCl, pH 3</td>
<td>&gt;100% (40 min)</td>
<td>COD: 96.47% (40 min)</td>
<td>Ma et al. (2009)</td>
</tr>
</tbody>
</table>

**IRON SUPPORTING MATERIALS: ION-EXCHANGE RESINS AND MEMBRANES**

<table>
<thead>
<tr>
<th>Pollutant / mg L⁻¹</th>
<th>Catalyst / g L⁻¹</th>
<th>Anode/ Cathode</th>
<th>Electric field</th>
<th>Operational conditions</th>
<th>Maximum degradation</th>
<th>Maximum mineralization / MCE</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Orange II / 20</td>
<td>Amberlite / 0.67</td>
<td>Carbon cloth-TiO₂/ Carbon cloth</td>
<td>0.1 A</td>
<td>*UV mercury lamp 75 mW cm⁻², λ = 365 nm, Na₂SO₄ buffer, pH 3, aeration</td>
<td>-</td>
<td>TOC: 60% (1 h)*</td>
<td>Ramirez et al. (2010)</td>
</tr>
<tr>
<td>Purolite / 0.67</td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Nafion / 0.27</td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Pollutant / mg L(^{-1})</td>
<td>Catalyst / g L(^{-1})</td>
<td>Anode/ Cathode</td>
<td>Electric field</td>
<td>Operational conditions</td>
<td>Maximum degradation</td>
<td>Maximum mineralization / MCE</td>
<td>Reference</td>
</tr>
<tr>
<td>---------------------------</td>
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<td>----------------</td>
<td>------------------------</td>
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</tr>
<tr>
<td>Reactive black 5 / 100</td>
<td>Rooibos green nZVI / 0.34</td>
<td>Graphite/ Graphite</td>
<td>5 V</td>
<td>0.01 M Na(_2)SO(_4), pH 2, AFR 1 L min(^{-1})</td>
<td>70% (1 h)</td>
<td>-</td>
<td>Rosales et al. (2017)</td>
</tr>
<tr>
<td>Acid red 14 / 50</td>
<td>Magnetite nanoparticles / 0.6</td>
<td>Graphite/ Graphite</td>
<td>0.18 A</td>
<td>4 g L(^{-1}) NaCl, pH 3, aeration</td>
<td>-</td>
<td>99.39% (2 h)</td>
<td>Es'haghzade et al. (2017)</td>
</tr>
<tr>
<td>Acid blue 92 / 50</td>
<td>Magnetite nanoparticles / 1</td>
<td>Graphite-CNTs</td>
<td></td>
<td></td>
<td></td>
<td>-</td>
<td>Babuponnusami and Muthukumar (2013)</td>
</tr>
<tr>
<td>Phenol / 1000</td>
<td>nZVI/PVA-alginate beads / 0.5</td>
<td>Stainless steel/Stainless steel</td>
<td>12 mA cm(^2)</td>
<td>*UV lamp 8W, pH 3, 400 mg H(_2)O(_2) L(^{-1})</td>
<td>97.46% (1 h)*</td>
<td>COD: 96.4% (1 h)*</td>
<td>Babuponnusami and Muthukumar (2013)</td>
</tr>
<tr>
<td>Atrazine / 46 mM</td>
<td>Fe-allophane / -</td>
<td>Pt/Fe-allophane-GC</td>
<td>-1.04 V</td>
<td>0.5 M Na(_2)SO(_4), pH 3, aeration</td>
<td>96% (8 h)</td>
<td>-</td>
<td>Garrido-Ramírez et al. (2013)</td>
</tr>
<tr>
<td>Phenol / 0.5 mM</td>
<td>Fe-Cu-allophane / -</td>
<td>Pt/Fe-Cu-allophane-GC</td>
<td>-0.6 V</td>
<td>0.05 M Na(_2)SO(_4), pH 3, aeration</td>
<td>≈100% (2 h)</td>
<td>COD: 80% (4 h)</td>
<td>Garrido-Ramírez et al. (2016)</td>
</tr>
<tr>
<td>Benzotriazole / 0.15 mM</td>
<td>ZnFe(_2)O(_4) nanoparticles / 0.067</td>
<td>Carbon/ Graphite</td>
<td>-0.6 V</td>
<td>*UV lamp 15 W, (\lambda= 254) nm, 0.05 M Na(_2)SO(_4), pH 3, AFR 0.13 L min(^{-1})</td>
<td>91.2% (3 h)*</td>
<td>COD: 85.3% (3 h)*</td>
<td>Wu et al. (2013)</td>
</tr>
<tr>
<td>Methyl orange / 50</td>
<td>Magnetite nanoparticles / 1</td>
<td>RuO(_2)-Ti/ CB-PTFE</td>
<td>10 mA cm(^2)</td>
<td>0.05 M Na(_2)SO(_4), pH 3, AFR 1.5 L min(^{-1})</td>
<td>86.6% (1.5 h)</td>
<td>TOC: 32% (1.5 h)</td>
<td>Jiang et al. (2016)</td>
</tr>
</tbody>
</table>

2.1. Magnetite

The potential of magnetite (Fe₃O₄) and its high ability to degrade recalcitrant pollutants compared to conventional iron-supported catalysts derives from the octahedral sites in the magnetite structure that can easily accommodate both Fe²⁺ and Fe³⁺ ions. Fe²⁺ can be reversibly oxidized and reduced back in the same structure. Magnetite has shown exceptional magnetic and electric properties with good structural stability and reusability (Xu and Wang, 2012). It has demonstrated high activity in oxidation processes based on its redox behaviour. Expósito et al. (2007) evaluated natural magnetite, hematite, wüstite, and goethite on electro-Fenton and photoelectro-Fenton processes, using aniline as a pollutant. Among them, wüstite and magnetite exhibited faster mineralization ratios for total organic carbon (TOC) removal, reaching yields higher than 78%. However, authors conclude that, in this process, those two minerals follow essentially a homogeneous catalytic pathway, acting merely as a source of iron ions because the equivalent homogeneous process achieved a similar mineralization of 74%. Anyway, the reported heterogeneous system showed several advantages such as self-regulating the iron ions supply along the process and, in the case of the magnetite, easing the recovery of the catalyst by applying an external magnetic field. Additionally, they highlight that operating with these catalysts the concentration of iron required for electro-Fenton process (range of mg L⁻¹) was much less than in the conventional Fenton’s process (range of g L⁻¹) (Xavier et al., 2015).

Magnetite can be prepared in the laboratory by chemical precipitation using a Fe²⁺ and Fe³⁺ solution in different molar ratios. A 1:2 ratio of Fe²⁺:Fe³⁺ was reported by Kim et al. (2001) as the optimal for the maximum precipitation of magnetite. Nidheesh et al. (2014) evaluated the efficiency of magnetite on the removal of rhodamine B dye from an aqueous solution. In this case, the magnetite was prepared by mixing solutions with various
Fe$^{2+}$:Fe$^{3+}$ molar ratios and the evaluation of kinetic removal of dye indicated that all selected ratios enhanced the dye removal efficiency. The application of an electric field changed this behaviour maintaining the Fe$^{2+}$ concentration in the solution constant by its regeneration at the cathode (Figure 2a). Thus, all the prepared magnetite achieved almost the same dye removal rate with a slight increase when a 2:1 ratio was used, attaining a yield of 97.3% after 3h. In comparison, under the same conditions homogeneous electro-Fenton achieves a similar rhodamine B removal (99.2%) employing 10 mg L$^{-1}$ of Fe$^{2+}$, while in the heterogeneous process 1.63 mg L$^{-1}$ is the maximum Fe$^{2+}$ concentration observed in the bulk solution (Nidheesh et al., 2014; Nidheesh and Gandhimathi, 2014). This fact seems to suggest that the heterogeneous mechanism has a significant role in the degradation process. He et al. (2014b) stated that when using magnetite as a catalyst, both surface-catalysed process and homogeneous reaction take place. The heterogeneous catalysis mechanism involved when using magnetite, in which •OH and •OOH radicals are produced, is illustrated in Figure 2a.
Nidheesh et al. (2014) also evaluated leaching of iron ions from magnetite during electrolysis and found that the concentration of ferric ion in the solution was higher than that of ferrous ion at any stage of electrolysis. During the initial stage, a sudden increase in both ions concentration occurred. Ferrous ion concentration increased up to 30 min of electrolysis time and then decreased, with concentration fluctuations due to the regeneration of ferrous ions from ferric ions. In contrast, the ferric ion concentration increased with electrolysis time indicating that leaching of iron ions from the magnetite occurred as the time elapsed. A reusability study demonstrated that the magnetite efficiency remained the same even after five recycles. These results indicated that, even with leaching of the detected iron, magnetite can be used for longer operation times. Recently, wastewater treatment using Fe₃O₄ magnetic nanoparticles as a catalyst has attracted significant research interest. The most important findings are summarized in the nanoparticles section.
2.2. Pyrite

Pyrite (FeS$_2$) is present in several sediments and hydrothermal deposits and it is one of the most common sulphide minerals and nontoxic semiconductors found on earth (Mozia et al., 2013). Pyrite possesses the dual surface properties of hydrophilicity and hydrophobicity in media with different pH values (Khabbaz and Entezari, 2017). For this reason, both natural and synthesized pyrites have been used for removal of organic pollutants in Fenton processes because of their catalyst potential (Zhang et al., 2014; Khataee et al., 2016). However, few studies have been conducted using pyrite for heterogeneous electro-Fenton treatment of polluted water. Among them, it is relevant the work performed by Oturan’s research group (Table 1). Barhoumi et al. (2015) reported that levofloxacin, a broad spectrum fluoroquinolone antibiotic, was successfully degraded by heterogeneous electro-Fenton using a pyrite mineral catalyst from a mine in Jendouba (Tunisia). The pyrite powder in suspension supplied Fe$^{2+}$ as a catalyst due to self-regulation of iron ions in solution (Figure 2a) and regulated the pH and iron in the presence of O$_2$, based on the following reactions:

\[
2 \text{FeS}_2 + 7 \text{O}_2 + 2 \text{H}_2\text{O} \rightarrow 2 \text{Fe}^{2+} + 4 \text{SO}_4^{2-} + 4 \text{H}^+ \quad (12)
\]

\[
2 \text{FeS}_2 + 15 \text{H}_2\text{O}_2 \rightarrow 2 \text{Fe}^{3+} + 14 \text{H}_2\text{O} + 4 \text{SO}_4^{2-} + 2 \text{H}^+ \quad (13)
\]

\[
\text{FeS}_2 + 14 \text{Fe}^{3+} + 8 \text{H}_2\text{O} \rightarrow 15 \text{Fe}^{2+} + 2 \text{SO}_4^{2-} + 16 \text{H}^+ \quad (14)
\]

Solution’s pH and supplied Fe$^{2+}$ were reduced and augmented, respectively, by the amount of added pyrite. Thus, in a suspension of 1.0 g L$^{-1}$ pyrite, the solution acquired a pH of 3.0 with 0.2 mM Fe$^{2+}$, which are the optimum operational conditions for the classical electro-Fenton using the same experimental conditions as El-Ghenemy et al. (2014). Similarly, Ammar et al. (2015) determined the acidification of the solution based on the dissolution of pyrite surface by reaction (Eq. (12)). This was related to the pyrite loading and the release of a greater amount of H$^+$ when the pyrite concentration increased.
causing the pH to decrease. The pH profiles showed that after 20 minutes the reactions had reached an equilibrium state, resulting in stationary pH values for each pyrite concentration used. In addition, the released Fe\(^{2+}\) concentration had a pseudo-linear relationship with the pyrite concentration after 30 minutes at pH 3. Thus, the Fe\(^{2+}\) concentration increased 7.5 times (from 0.14 to 1.05 mM) while pyrite loading increased 12 times (from 0.5 g L\(^{-1}\) to 6 g L\(^{-1}\)) (Labiadh et al., 2015). In the same way, the enhancement of tetracycline and dye poly R-478 degradation by electro-Fenton-pyrite with a BDD anode compared to conventional anodic oxidation or H\(_2\)O\(_2\) electroggeneration processes has been observed (Barhoumi et al., 2017; Bouzayani et al., 2017).

The effect of different operating parameters, such as the applied current, the catalyst concentration, and the nature of the anode material on the degradation of several pollutants have also been studied. In sulfamethazine mineralization, Barhoumi et al. (2016) found that the use of a BDD anode in a pyrite-catalysed electro-Fenton process led to greater mineralization efficiency than the use of a Pt anode. However, they remarked that this system using Pt achieved TOC abatement and mineralization current efficiency (MCE) results comparable to those obtained by a homogeneous process using BDD. These findings highlight the potential of pyrite as a catalyst for the oxidation of organics by electro-Fenton process even with the use of other anodes different from BDD, such as Pt, for the generation of M(\(^{•}\)OH) and paves the way for using cheaper anodes with a similar efficiency. The degradation of vanillic acid by electro-Fenton pyrite was evaluated using a Pt/carbon-felt cell (Ouiriemmi et al., 2017). Application of an electric current (50-300 mA) led to an increase in the degradation rate, which was more pronounced at low currents (≤ 100 mA) compared to higher current (300-500 mA). The progressive slowdown of reaction rate as the current rises is due to the continuous acceleration of parasitic reactions favouring the non-oxidative consumption of \(^{•}\)OH, the
reduction of $\text{H}_2\text{O}_2$, evolution of $\text{H}_2$ at the cathode, and the self-destruction of $\text{M(HO}^*\text{)}$ at the anode (Sirés et al., 2014).

All published articles seem to confirm the superiority of the heterogeneous electro-Fenton-pyrite process over conventional processes and its slightly superior performance over heterogeneous electro-Fenton. According to several authors (Ammar et al., 2015; Labiadh et al., 2015; Barhoumi et al., 2017; Bouzayani et al., 2017), this is mainly due to the pyrite ability for the spontaneous self-regulation of soluble $\text{Fe}^{2+}$ and pH, reaching values around 3, creating the optimal conditions for the Fenton reaction. Therefore, pyrite provides an environmentally friendly alternative since it can be recovered and reutilized. However, it has been noticed that the parameters controlling iron leaching, an important phenomenon for this process, have not been analysed in the literature. Hence, this issue should be addressed in the future.

2.3. Goethite

Goethite ($\alpha$-FeOOH) is a widespread soil mineral. It is one of the most stable iron oxides due to its orthorhombic structure, a hexagonally close-packed array of $\text{O}^2-$ and $\text{OH}^-$ anions with $\text{Fe}^{3+}$ at the centre of the octahedral (Liu et al., 2014). It is known as an effective catalyst due to its abundance, high catalytic activity, wide range of operating pH, controllable leaching of iron into the solution, large surface area, and high surface hydroxyl content (Wang et al., 2015). There are several examples, in which goethite has been used as Fenton’s catalyst (Lu et al., 2002; Pereira et al., 2012; Mesquita et al., 2016; Lin et al., 2017). The goethite Fenton’s reaction mechanism established by Lin and Gurol (1998) is presented in Figure 2b. The reactions were initiated by the formation of a precursor surface complex of $\text{H}_2\text{O}_2$ with the oxide surface, $\equiv\text{FeIII-OH}$. The surface species of $\text{H}_2\text{O}_2$ are represented by $\equiv\text{H}_2\text{O}_2$, and the progression of the reaction may undergo a reversible electron transfer, which is a ground-state electron transfer from ligand-to-metal
within a surface complex. The electronically excited state can be deactivated through the
dissociation of the peroxide radical. The reduced iron, being a reductant, can react with
either H₂O₂ or oxygen, but the last one is much slower than the other reaction. The HO₂●
and HO● produced during the reaction may react with Fe(III) and Fe(II) sites on the
surface. The HO₂● and HO● generated in the system may also react with adsorbed ≡H₂O₂
and these radicals may react with each other, terminating the reactions.

The use of goethite for electro-Fenton treatment has been rarely reported. Sankara-
Narayanan et al. (2003) determined that the use of goethite as a catalyst did not
significantly improve process efficiency. However, Sánchez-Sánchez et al. (2007)
obtained almost total aniline mineralization in a wide range of experimental conditions
when the usual ferrous ion source was substituted with goethite. They pointed out that
under optimum standard electro-Fenton conditions, the heterogeneous process yielded a
95% of mineralization using only 2 ppm of soluble iron, while 55 ppm were necessary
for the homogeneous one. Expósito et al. (2007) compared the behaviour of goethite with
magnetite, hematite and wüstite on electro-Fenton and photoelectro-Fenton processes for
the degradation of aniline. They determined that although wüstite and magnetite exhibited
the fastest mineralization ratios for TOC removal yields, goethite exhibited the highest
TOC removal yield value (90.2%). Due to the low solubility of goethite, iron ions
concentration in the solution at the end of the experiment was lower compared to the other
minerals. This fact explains why the process is slower and also the high mineralization
extent, since the negligible Fe³⁺ concentration avoids the formation of complexes with
short linear organic diacids, which are hardly mineralized. Regarding photoelectro-
Fenton, this process did not improve the mineralization efficiency, since goethite forms
an opaque suspension that blocks the UV light transmission. Similarly, Meijide et al.
(2017; 2018) determined that goethite had good catalyst stability and reusability by its inclusion into a polyvinyl alcohol (PVA)-alginate matrix.

In all cases, one of the main drawbacks of this process, the long reaction time required for complete pollutant mineralization, that could be avoided by optimization of the pH and the applied current density.

Another alternative studied related to the use of goethite in the electro-Fenton process was its inclusion on the cathode. Thus, activated carbon-supported nano-FeOOH catalysts were prepared by the air oxidation of ferrous hydroxide suspension method (Zhang et al., 2012). They determined that under weak acidic and external electric field conditions, the supported nano-FeOOH catalyst undergoes proton-promoted dissolution and electrochemical reductive dissolution processes, which facilitate $\text{Fe}^{3+}/\text{Fe}^{2+}$ transformation and produce a beneficial enhancement of the heterogeneous/homogeneous electro-Fenton reaction rates. By using this cathode, the oxidation of pollutant takes place not only through the heterogeneous Fenton’s reaction on the catalyst/solution interface, but also through the homogeneous Fenton’s reaction in bulk solution due to iron liberation from the supported nano-FeOOH.

### 3. Iron supporting materials

Iron- and iron oxide-loaded materials can be efficient catalysts to promote the presence of the Fenton’s mixture in solution and to avoid the use of dissolved iron salts. Several materials have been used as efficient supports for iron and iron oxides and various methods to fix them into the material have been used. In these cases, the nature and properties of the support play a crucial role in the modulation of the activity in catalytic sites (Navalon et al., 2011). Thus, a good supporting material should have the following properties: i) chemically inert and promotes strong surface chemical-physical binding
with the iron species without altering their properties and reactivity; ii) high specific surface area; iii) good adsorption capacity for iron and the organic compounds to be degraded; iv) favours liquid-solid phase separation, and v) amenable to simple reactor design with low mass transfer limitations (Babuponnusami and Muthukumar, 2014). These properties allow for resistance to the strain caused in bulk medium and flow systems, from particle to particle, and particle-fluid mechanical interactions in the reactor environment, avoiding the detachment of iron species from the support (Pozzo et al., 1997).

In the next sections, a review of several studies in which the catalytic activity of the reaction system and the stability of the catalysts were enhanced by binding iron species onto appropriate support materials, such as neutral organic polymers, ion exchange membranes or resins, and inorganic materials are described.

### 3.1. Organic polymers

Several polymers have been used to attach iron into matrixes. Rosales et al. (2012a) demonstrated that iron could be effectively entrapped in a biopolymer matrix such as alginate without significant reduction in reactivity. The porosity of alginate beads allows solutes to diffuse into the beads and come into contact with the entrapped material. Several applications of this technique used to develop heterogeneous Fenton-based processes have been reported (Barreca et al., 2014; Li et al., 2014; Hammouda et al., 2016a; 2016b; 2016c; Quadrado and Fajardo, 2017; Cruz et al., 2017). Table 1 describes studies in which this catalyst was applied in electro- and photoelectro-Fenton processes. In this sense, investigation performed by the Sanromán’s research team on iron alginate beads is remarkable. They have applied this catalyst to the heterogeneous electro-Fenton treatment of pollutants such as dyes, ionic liquids, pesticides, and winery wastewater (Iglesias et al., 2013b; 2014; 2015b; Bocos et al., 2016a; Poza-Nogueiras et al., 2018)
using different reactor configurations (Rosales et al., 2012a; Iglesias et al., 2013c). Iglesias et al. (2014) found that degradation of pesticide imidacloprid was successfully achieved by using iron loaded on alginate beads, attaining good results at neutral pH (90% degradation in 200 min). However, they pointed out that reactions are more favourable at pH 3, since at higher pH values H$_2$O$_2$ decomposes into H$_2$O and O$_2$ and the oxidation potential of the hydroxyl radicals is reduced. Regarding the reusability of the iron alginate beads, Rosales et al. (2012a) determined that after three batches, the required time for obtaining the maximum dye decolourisation increased from 30 min in the first one to 1 h in the second and third cycles. Similarly, Hammouda and collaborators (Hammouda et al., 2016a; 2016b; 2016c) evaluated the effectiveness of heterogeneous Fenton and electro-Fenton for the degradation of indole using iron loaded alginate beads as a reusable catalyst. They determined that the specific surface area of the beads employed was 9.32 m$^2$ g$^{-1}$ and that the catalyst could be reused at least four cycles in an electro-Fenton process, achieving in all cases a degradation efficiency near 100% in 1 h.

Lately, hydrogels have attracted much interest as superabsorbent polymers due to their hydrophilic group. They can absorb large quantities of water as well as toxic or carcinogenic heavy metals such as Fe, Pb, Cd, and Ni, even at relatively low concentrations (Sahiner, 2008; Liu et al., 2008; Zhou et al., 2009). Bocos et al. (2014) synthetized polyacrylamide hydrogels, evaluating the influence of parameters like concentration of initiator, cross-linking, and monomer on the properties of the hydrogel and its ability to adsorb iron using different ratios of Fe$^{2+}$:Fe$^{3+}$. Results indicated that the swelling due to water was higher using hydrogels made with 0.05% of cross-linking. However, the amount of iron adsorbed into the hydrogel (22 mg g$^{-1}$) was the same at different cross-linking concentrations and Fe$^{2+}$:Fe$^{3+}$ ratios. Best results were obtained when hydrogels were loaded with a 1:2 molar ratio of Fe$^{2+}$:Fe$^{3+}$, which is consistent with
data reported by Souza et al. (2013). Using this catalyst, the superiority of heterogeneous electro-Fenton over homogeneous and anodic oxidation in the degradation of several pollutants has been verified. In addition, the applicability and durability of this catalyst was demonstrated by operation in four consecutive batches of 2 h, yielding a decolourization efficiency greater than 96% at the end of all cycles, showing the last batch a slight reduction in the decolourization rate.

3.2. Inorganic materials

Zeolites are hydrated aluminosilicate minerals that can be synthesized by reacting sodium aluminate with sodium silicate. They have many different crystalline structures with large open pores in a regular arrangement. The catalysts can be obtained by synthetic zeolite impregnation of ferric ions followed by calcination (Noorjahan et al., 2005) or by ion exchange with sodium in zeolite which is replaced with ferric ions (Rache et al., 2014). Recently, Zeolite Socony Mobile-5 (ZSM-5) has attracted attention due to its high stability, large surface area (243.93 m² g⁻¹), and outstanding porosity. The Fe²⁺/Fe³⁺ complexes produced on the surface of ZSM-5 can react with H₂O₂ to initiate the Fenton’s catalytic cycle (Ahmad et al., 2015). Lately, Rostamizadeh et al. (2018) determined that the optimum operational conditions of prepared Fe-ZSM-5 are iron impregnation at 1% and pH 3.0. This condition showed high decolourization efficiency (>95%) in three batches of 30 min.

Li et al. (2011) evaluated the electro-Fenton oxidation of neutral coking wastewater after biological processing, using a graphite anode and iron-zeolite Y catalyst prepared by the method reported by Neamtu et al. (2004). They determined that the production of hydroxyl radicals took place mainly on the Fe-Y catalyst surface from decomposition of H₂O₂. By addition of Fe-Y into the electrochemical system, chemical oxygen demand (COD) removal efficiency of the electro-Fenton process increased to 49% compared to
the 23% that was achieved applying only a combination of anodic and cathodic indirect oxidation. Furthermore, they verified that the catalyst adsorption was not the major contributor to COD removal (since it only accounts for 9% of the removal). However, Iglesias et al. (2015a) reported that the reusability of Fe-Y zeolite was not appropriate because this catalyst is a powder, 8% of catalyst weight was lost after three cycles. In order to enhance its recyclability, Fe-Y zeolite was embedded in alginate. The new catalyst was efficiently used in the electro-Fenton treatment of the pesticides imidacloprid and chlorpyrifos in an aqueous medium and showed high recyclability, yielding a removal higher than 93% in all the three cycles of 3 h tested.

Due to the high production costs of synthetized iron-zeolite catalysts, the use of natural zeolites has been explored (Arimi, 2017). Natural zeolite may provide two benefits: the removal of iron from polluted aqueous solutions and the generation of Fe-zeolite that can be used as an iron heterogeneous catalyst in Fenton-based processes (Fernández de Dios et al., 2014). After iron adsorption, its homogenous distribution on the clay particle permits the electro-Fenton process to occur in successive cycles without the addition of Fenton’s agents. This catalyst was successfully applied to degrade reactive black 5 and phenanthrene. In the case of the dye, recyclability was test during three batches of 90 min and the decolourization removal showed a slight decrease from near 97% in the first cycle to near 88% in the third one. Its operational stability was verified by physicochemical characterization, showing that the zeolites maintain their structure and retain their iron content.

A comparison of nine materials evaluated as iron supports showed that iron sepiolite was the best catalyst; a real textile wastewater was successfully treated with this catalyst (Rodríguez et al., 2010). Similarly, Iglesias et al. (2013a) evaluated the potential of iron-loaded sepiolite as a catalyst in the electro-Fenton oxidation of organic pollutants in
textile effluents. They confirmed the application of sepiolite for iron adsorption and the utility of iron-loaded sepiolite as an effective heterogeneous catalyst for the degradation of organic dyes, determining that the main mechanism involved was the dye adsorption onto the sepiolite, followed by a rapid degradation by the Fenton reaction.

Bentonite is a typical absorbent clay with the ability to fix iron into its structure. Qiao et al. (2015) studied three kinds of iron-bentonite: Fe$_3$O$_4$-Bent, Fe$_2$O$_3$-Bent and Fe$^0$-Bent as catalysts in the heterogeneous electro-Fenton phenol degradation at pH 6.24. Evaluation of iron leaching behaviours during the degradation of phenol indicated that both homogeneous and heterogeneous electro-Fenton reactions were involved in the degradation. The results showed that Fe$^0$-Bent was the most efficient catalyst under natural conditions reaching a maximum of 92.48% and 67.48% removal of phenol and COD, respectively. Recently, this research group synthesized an iron-modified bentonite using a rapid and completely green method with aqueous green tea extracts as both the reducing and capping agents (Qiao et al., 2016). They determined the superiority of this heterogeneous system over the homogeneous system for removal of orange II dye.

In this frame, kaolin clay is widely used as a catalyst support due to its low cost, good adsorption capacity, and environmentally friendly structure. He et al. (2014a) determined that the iron content of their prepared FM-kaolin-450 was 3.47%. Thus, Fe$_2$O$_3$ modified kaolin is a promising candidate as a heterogeneous catalyst for the electro-Fenton process. The catalytic activity of Fe$_2$O$_3$ modified kaolin was tested in the electro-catalytic oxidation of methylene blue and enoxacin, a fluoroquinolone antibiotic (Ma et al., 2009; Özcan et al., 2017). To evaluate the importance of the heterogeneous reaction in the production of HO•, Özcan et al. (2017) determined the iron concentrations leached from the added Fe$_2$O$_3$ modified kaolin. The results showed an initially small amount (∼0.056 ppm) of dissolved iron in solution that reached its highest value (∼0.336 ppm) at 30 min.
After 30 min, the iron concentrations decreased slowly and finally reached a plateau (∼0.224 ppm). They concluded that leached iron concentrations are very low according to the added amount of iron (16.8 ppm) in homogeneous systems and \( \text{HO}^\bullet \) are mainly produced in the electrolysis medium of the heterogeneous reaction instead of in the homogeneous reaction.

### 3.3. Ion-exchange resins and membranes

Several metals can be removed from wastewater using ion-exchange resins or membranes. These materials can be used as support to synthetize iron catalysts. Fernandez et al. (2000) demonstrated that the degradation of azo dye orange II by the photo-assisted Fenton could be effectively catalysed by a Nafion cation-transfer membrane exchanged with iron ions in the presence of \( \text{HO}^\bullet \). The sulfonate groups on the surface of the Nafion film tightly anchored the iron ions so that no iron ions were detected in the solution. However, the system using iron-Nafion films is too expensive for practical industrial application. Thus, a suitable catalyst support with functions similar to Nafion film, but less expensive, is needed. Ramírez et al. (2010) noted that it is possible to remove orange II dye from solution using a heterogeneous photoelectro-Fenton process with different resins as iron supporting materials (Table 1). In this study, amberlite, purolite, and Nafion were doped with 59, 65 and 45 mg Fe g\(^{-1}\), respectively. TOC results indicated that the process can be used with any of these iron supporting materials. The dissolved iron concentration in the solution was time dependent, but the authors indicate that the levels leached from the catalysts were lower than 10% of the initial iron content.

In particular, desorption tests indicated that the iron concentration in the solution was 1.1 mg L\(^{-1}\) for purolite, while it was 4.8 mg L\(^{-1}\) and 4.7 mg L\(^{-1}\) for amberlite and Nafion membrane, respectively. Despite these positive results, there was a reasonable doubt if it was actually a heterogeneous process or if there was a contribution from the iron
dissolved from the resins. To evaluate this possibility, recently, this research group (García-Rodríguez et al., 2017) studied the relative contribution of homogeneous and heterogeneous Fenton’s processes in the treatment of the same dye solutions at pH 3 and 7 using an ion exchange resin Amberlite IR-120 as iron support. They found that the iron dissolution is strongly depended on pH and a mixed homogeneous and heterogeneous Fenton’s process takes place. In these studies, the leached iron ions were found to re-adsorb on the catalyst surface maintaining good catalyst stability. This confirmed the utility of ion exchange amberlite and purolite resins, as less expensive iron supporting materials than Nafion. Feng et al. (2004) determined that the sulfonate groups on the surface of an acidic ion exchange resin, SAIER, anchor the iron ions with little iron leaching into the solution and that this resin is a valuable catalyst alternative.

4. Nanoparticles

Heterogeneous Fenton and electro-Fenton processes have been improved by application of iron nanomaterials (Hansson et al., 2012; Munoz et al., 2015). At nano-scales (particles with a diameter <100 nm) the physical and chemical properties are very different from those of the same material at larger particle sizes. The activity and selectivity of catalyst nanoparticles are strongly dependent on their size, shape, and surface structure, as well as on their bulk and surface composition (Rosales et al., 2017). The small particle size increases the proportion of atoms located at the surface increasing the possibility for the atoms to adsorb, interact, and react with other atoms and molecules (Crane and Scott, 2012). However, it is important to mention that the use of nanoparticles in water treatments should be done cautiously, since their subsequence separation may be an issue and the potential toxicity of these materials in the environment is still mostly unknown (Ray et al., 2009; Anjum et al., 2016).
The issue of recovering the nanocatalyst can be addressed by employing ferromagnetic materials, which can be easily and economically separated with the application of a magnetic field. In heterogeneous electro-Fenton the use of ferromagnetic nanoparticles, such as nano zero-valent iron (nZVI), magnetite (Fe$_3$O$_4$), and maghemite ($\gamma$-Fe$_2$O$_3$), have the potential to degrade a wide range of organic compounds (Table 1). Munoz et al. (2015) noted that the study of magnetic nanomaterials for remediation began around 2008 and continues unabated. Although initially these materials were applied to Fenton’s process, their uses have been extended to different AOPs.

Magnetite nanoparticles with different morphologies (tubes, wires, films, spheres, rods, and other novel structures) can be produced by a variety of synthetic routes, including coprecipitation, thermal decomposition, hydrothermal reactions, sol-gel, wet-chemical, microemulsion, and electrochemical procedures (Prakash et al., 2004; Peng et al., 2006; Matta et al., 2007; Ardo et al., 2015; Es'haghzade et al., 2017). Evaluation of results using nanomagnetite indicates that it is necessary to study each process because the effect of the process variables depends on the type of nanoparticle used and its properties.

One of the classic methods used to synthesize magnetite nanoparticles is by coprecipitation. For example, Jiang et al. (2016) made magnetite nanoparticles by coprecipitation of Fe$^{2+}$ and Fe$^{3+}$ in a basic solution and these nanoparticles were used as a catalyst in azo dye methyl orange degradation by heterogeneous electro-Fenton. In this study, they determined that higher current density and aeration rate facilitated dye degradation. The electro-Fenton process did not require a high dosage of magnetite nanoparticles (1 g L$^{-1}$) and was effective over a wide pH range (2 - 9.5), although best results were attained under acidic conditions (reaching 94.7% degradation in 1.5 h at pH 2 while only 68.6% at pH 9.5). This finding can be attributed to the inhibition of the homogeneous Fenton’s process because of the reduction of H$_2$O$_2$ concentration and
dissolved concentration of iron in the solution (Seyed Dorraji et al., 2015). Thus, by using 1 g L\(^{-1}\) Fe\(_3\)O\(_4\) under the current density of 10 mA cm\(^{-2}\), the leaching was less than 3.5 and 0.5 mg L\(^{-1}\) of iron at pH 3 and 5, respectively. These results suggest that homogeneous reaction plays an important role in the heterogeneous catalysis using magnetite nanoparticles.

Nowadays, green technology is commonly implemented in the synthesis of catalysts (Rosales et al., 2017). Es'haghzade et al. (2017) synthesized magnetite nanoparticles with spherical structure and cubic crystals (40-45 nm) through a facile green and inexpensive electrochemical method. The effects of several operational factors like pH range, dye concentration, Fe\(_3\)O\(_4\) loading, current intensity, and electrolyte were investigated in the heterogeneous electro-Fenton decolourisation of acid red 14 and acid blue 92 dyes. The high level of colour removal obtained in a wide range of pH values and their recyclability after easy magnetic separation illustrated the superior catalytic potential of these nanoparticles.

Another alternative is the use of nanostructured allophane clays supported with iron oxide (Fe-allophane) with presence of both Fe\(^{3+}\) and Fe\(^{2+}\) species on the surface (Garrido-Ramírez et al., 2013) which were used for the oxidation of atrazine. It was concluded that heterogeneous electro-Fenton system showed higher efficiency towards the oxidation of atrazine than the heterogeneous Fenton one. This was mainly due to the continuous and simultaneous electro-regeneration of iron species (Fe\(^{3+}/\)Fe\(^{2+}\)) and electro-generation of H\(_2\)O\(_2\) by the oxygen reduction process. The degradation of atrazine profiles showed a typical behaviour, with complete degradation at pH 3.0 and reduced efficiency (\(\sim 76\%\)) at more neutral pH, attributed to the greater decomposition of H\(_2\)O\(_2\) in parasitic reactions at higher pH values. In addition, bimetallic (Fe-Cu) allophane nanoclays were synthesized using a two-step wet impregnation method with different Fe/Cu ratios and compared with
the catalytic activities Fe-allophane and Cu-allophane nanoclays catalysts for phenol degradation (Garrido-Ramírez et al., 2016). COD removal was less than 47% for Cu-allophane and 65% for Fe-allophane, whereas for the bimetallic allophane nanoclays the COD removal decreased with the amount of copper oxide in the catalyst, achieving an 80% COD removal with Fe$_{5.4}$Cu$_{0.6}$ catalyst. These results showed a synergistic effect of the Fe$^{3+}$ and Cu$^{2+}$ ions present in the bimetallic allophane nanoclays. This effect was caused by the formation of small copper oxide particles stabilized by iron oxide species.

In the bimetallic allophane nanoclays, the leaching of iron and copper into the solution was less than 1.25 mg L$^{-1}$ and 0.638 mg L$^{-1}$, respectively, indicating high stability of the bimetallic allophane catalysts. Similarly, benzotriazole was degraded by a heterogeneous photoelectro-Fenton process using ZnFe$_2$O$_4$ nanoparticles as the catalyst prepared by co-precipitation (Wu et al., 2013). These results highlight the feasibility of a heterogeneous photoelectro-Fenton process.

Several authors have reported that the reusability of nanoparticles can be limited due to gradually decreasing activity during consecutive runs. Catalyst deactivation may have several causes including reduction of the catalyst specific area, poisoning of the active catalytic sites by adsorbed organic species, conglomeration of nanoparticles, and the loss of supernatants during nanoparticle rinsing (Zhang et al., 2009; Xu and Wang, 2012). To reduce this negative effect, nanoparticles have been deposited onto the surface of unique two-dimensional graphene or graphene oxide in order to increase the surface area. Exfoliated graphene oxide (GO) sheets can be used to anchor Fe$_3$O$_4$ nanoparticles, forming a GO–Fe$_3$O$_4$ nanocomposite catalyst, which exhibits a highly heterogeneous electronic structure determined by the interplay of the oxygenated functional groups (Zubir et al., 2014; Akerdi et al., 2017). This technique provides new alternatives for the development of cathodes with properties that will be discussed below.
Another method for minimizing the negative effects of nanoparticle use is the incorporation of iron nanoparticles in hydrogels. This avoids their conglomeration into aggregates, which reduces their reactivity, and allows easy separation and recovery from the treated water. Hammouda et al. (2015) synthesized magnetite nanoparticles embedded with iron in alginate beads. They concluded that this catalyst offers simplicity, low cost, good structural stability, easy recovery, and stable catalytic activity in three reaction cycles of 2 h. However, they concluded that catalyst could not be reused after the forth cycle. They highlighted that the operating conditions must be carefully chosen to prevent excessive iron leaching and competing degradation of the organic component of the beads. Specifically, it has been pointed out that leaching increases at low pH and high H$_2$O$_2$ concentration, the later parameter affecting the beads oxidative degradation. Nevertheless, the amount of the active species leached from the catalyst into the solution during the Fenton’s process was low after three reuses, which is minimal compared to some industrial heterogeneous catalysts. Likewise, nZVI was entrapped in a PVA-alginate matrix, and successfully used in the photoelectro-Fenton process to degrade phenol (Babuponnusami and Muthukumar, 2013). PVA consists of many hydroxyl groups, which generally form complexes with metal ions (Kieber et al., 2005). Thus, Fe$^{2+}$ forms a complex with organic compounds and the use of these PVA-alginate beads reduces or avoids the problems associated with the release of iron into wastewater (Bai et al., 2009). The concentration of nZVI in the alginate beads was varied from 0.1 to 0.6 g L$^{-1}$. At high concentrations, a Fe$^{2+}$ leakage of 3% was detected and the observed frequency of alginate bead fractures was 2%, confirming bead stability. Babuponnusami & Muthukumar (2013) determined that the removal rate constant was proportional to the nZVI and H$_2$O$_2$ dosage and inversely proportional to the initial phenol concentration and initial pH of the solution. The detection of residual H$_2$O$_2$ concentration throughout the
experiments confirmed the continuous production of $\text{H}_2\text{O}_2$ by the photoelectro-Fenton process.

5. Modified cathodic materials

$\text{H}_2\text{O}_2$ production is closely related to the nature of the cathode and anode and their selection is an important step in the electro-Fenton and derived processes. Cathode modification has been explored by diverse authors (Table 2). Several materials have been used, such as polymers, metal oxides or nanoparticles, which can improve cathode properties and increase the electric conductivity (Rosales et al., 2012b). In addition, the inclusion of metals in the carbon matrix electrode can act as a heterogeneous catalyst with the ability to react with electrogenerated $\text{H}_2\text{O}_2$.

5.1. Metallic materials

The development of a metal-cathode was the focus of several studies. Ai et al. (2007) used Fe@Fe$_2$O$_3$ nanowires mixed with multiwall carbon nanotubes and fixed them to tetrafluoroethylene (PTFE) as an oxygen-fed gas diffusion cathode for degradation of rhodamine B at neutral pH. They demonstrated that the electro-Fenton process using this cathode was effective under a wide pH range, although at pH 3 dye removal was slightly higher (99.6% compared to the 91.5% attained at neutral pH). Nevertheless, authors highlighted that working at neutral pH is preferable for recycling the Fe@Fe$_2$O$_3$ nanowires. Cyclic voltammetry experiments showed that the main reactions took place on the cathode and indicated that this kind of cathode is promising for Fenton’s reactions in wastewater treatment. Considering the simplicity of this process, several Fe@Fe-oxides functionalized cathodic materials such as Fe@Fe$_2$O$_3$/carbon felt (Li et al., 2009; Zhuang et al., 2010) or pyrrhotite-coated graphite-cathode by conductive silver paste (Li et al., 2010b) were made and functioned as a releasing iron reagent to initiate a
heterogeneous Fenton's reaction. Do et al. (2017) integrated magnetite particles into the cathode by washcoating metal foams (FeCrAl alloy foam) with magnetite powder. In this electrode type, the surface of metal foam was corrugated so that washcoating of oxide particles onto the surface was facilitated. The porous support (90% of porosity with an average pore of 800 µm) maximizes reaction efficiency by increasing the exposed surface area of the cathode and reducing the mass transport limitations. Comparing the performance of this cathode with a homogeneous electro-Fenton process using graphite and stainless steel as cathodes, authors ascertained that methylene blue degradation rate was much higher with the magnetite wash coated foam (ca. 96% versus ca. 73% and 33%, respectively, in 30 min). They explained this fact as a consequence of a more efficient generation of the •OH radical due to the proximity of the generated H₂O₂ and the source of iron ions, both present around the cathode. Similarly, polytetrafluoroethylene/ferromagnetic nanoparticle/carbon black (PTFE/MNP/CB)-modified graphite felt was successfully used as a cathode for the mineralization of rhodamine B dye by the electro-Fenton process (Tian et al., 2016). This kind of electrode can be used to simplify the operation of the electro-Fenton system. An effective tubular membrane cathode coated by heterogeneous Fe₂O₃ nanoparticles with carbon black was fabricated and successfully used for flutriafol degradation. These tubular membrane electrodes are characterized by a greater number of electroactive sites and enhanced mass transfer that increases the efficiency of the degradation process (Xu et al., 2017). Mass transport improvement can be ascribed to the use of a peristaltic pump and the tubular shape of the electrodes, which prevents the pollutant from bypassing the electrode surface (Zhang et al., 2016).
Table 2. Summary of modified cathodic materials

<table>
<thead>
<tr>
<th>Modified Cathode</th>
<th>Anode</th>
<th>Operational conditions</th>
<th>Pollutant / mg L&lt;sup&gt;-1&lt;/sup&gt;</th>
<th>Maximum degradation</th>
<th>Maximum mineralization / MCE</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe@Fe&lt;sub&gt;3&lt;/sub&gt;O&lt;sub&gt;4&lt;/sub&gt;/CNTs</td>
<td>Pt</td>
<td>0.05 M Na&lt;sub&gt;2&lt;/sub&gt;SO&lt;sub&gt;4&lt;/sub&gt;, 1.2 V, neutral pH, AFR 5 L min&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>Rhodamine B / 1.04·10&lt;sup&gt;-4&lt;/sup&gt; M</td>
<td>91.5% (2 h)</td>
<td>-</td>
<td>Ai et al. (2007)</td>
</tr>
<tr>
<td>Fe@Fe&lt;sub&gt;3&lt;/sub&gt;O&lt;sub&gt;4&lt;/sub&gt;/ACF</td>
<td>Pt</td>
<td>0.05 M Na&lt;sub&gt;2&lt;/sub&gt;SO&lt;sub&gt;4&lt;/sub&gt;, -1.2 V , pH 6.2, AFR 5 L min&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>Rhodamine B / 5</td>
<td>74.1% (2 h)</td>
<td>-</td>
<td>Li et al. (2009)</td>
</tr>
<tr>
<td>Pyrrhotite/graphite</td>
<td>CF</td>
<td>1 M KCl, 4.2 W m&lt;sup&gt;-2&lt;/sup&gt; (MFC), pH 2.7, aerated</td>
<td>Landfill leachate / 1022 COD</td>
<td>77% (45 d)</td>
<td>COD: 78% (45 d)</td>
<td>Li et al. (2010b)</td>
</tr>
<tr>
<td>Magnetite/FeCrAl</td>
<td>Graphite</td>
<td>0.05 M Na&lt;sub&gt;2&lt;/sub&gt;SO&lt;sub&gt;4&lt;/sub&gt;, 2 V, pH 3</td>
<td>Methylene Blue / 10</td>
<td>99.9% (1 h)</td>
<td>-</td>
<td>Do et al. (2017)</td>
</tr>
<tr>
<td>PTFE/MNP/CB-GF</td>
<td>Pt</td>
<td>0.05 M Na&lt;sub&gt;2&lt;/sub&gt;SO&lt;sub&gt;4&lt;/sub&gt;, 50 A m&lt;sup&gt;-2&lt;/sup&gt;, pH 3, AFR 1 L min&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>Rhodamine B / 0.1 mM</td>
<td>92.6% (30 min)</td>
<td>TOC: 89.5% (4.5 h) / MCE: 4.6% (4.5 h)</td>
<td>Tian et al. (2016)</td>
</tr>
<tr>
<td>Tubular CB/PTFE-Fe&lt;sub&gt;3&lt;/sub&gt;O&lt;sub&gt;4&lt;/sub&gt; NPs</td>
<td>Tubular Ti-RuO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>0.05 M Na&lt;sub&gt;2&lt;/sub&gt;SO&lt;sub&gt;4&lt;/sub&gt;, 13.0 A m&lt;sup&gt;-2&lt;/sup&gt;, pH 6.7</td>
<td>Flutriafol / 100</td>
<td>74.5% (30 min)</td>
<td>-</td>
<td>Xu et al. (2017)</td>
</tr>
<tr>
<td>Fe/AC</td>
<td>Pt</td>
<td>0.05 M Na&lt;sub&gt;2&lt;/sub&gt;SO&lt;sub&gt;4&lt;/sub&gt;, -0.9 V, pH 3, O&lt;sub&gt;2&lt;/sub&gt; flow *Idem previous conditions + UV lamp 75 mW cm&lt;sup&gt;-2&lt;/sup&gt;, λ = 365 nm</td>
<td>Methyl Orange / 10</td>
<td>96% (30 min)</td>
<td>TOC: 88% (30 min)</td>
<td>Bañuelos et al. (2015)</td>
</tr>
<tr>
<td>FeOOH/GF</td>
<td>Graphite</td>
<td>0.05 M Na&lt;sub&gt;2&lt;/sub&gt;SO&lt;sub&gt;4&lt;/sub&gt;, 2 V, pH 6.8, AFR 1.5 L min&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>Rhodamine B / 5</td>
<td>62.5% (2 h)</td>
<td>95.4% (2 h)</td>
<td>Sun et al. (2015)</td>
</tr>
<tr>
<td>Fe-ChI/Ni</td>
<td>Pt</td>
<td>0.05 M Na&lt;sub&gt;2&lt;/sub&gt;SO&lt;sub&gt;4&lt;/sub&gt;, 0.01 A, pH 6.2, AFR 1.7 L min&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>Rhodamine B / 5</td>
<td>93% (2 h)</td>
<td>-</td>
<td>Fan et al. (2010)</td>
</tr>
<tr>
<td>Fe-ChI/Ni</td>
<td>BDD</td>
<td>0.01 M Na&lt;sub&gt;2&lt;/sub&gt;SO&lt;sub&gt;4&lt;/sub&gt;, 5 V, pH 2, AFR 0.02 L min&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>Poly R-478 / 80</td>
<td>100% (2 h)</td>
<td>TOC: 72.0% (2 h)</td>
<td>Bocos et al. (2016b)</td>
</tr>
<tr>
<td>CNT + CNT-COOFe&lt;sup&gt;2+&lt;/sup&gt;</td>
<td>CNT</td>
<td>0.01 M Na&lt;sub&gt;2&lt;/sub&gt;SO&lt;sub&gt;4&lt;/sub&gt;, -1.0 V, pH 6.3, O&lt;sub&gt;2&lt;/sub&gt; flow</td>
<td>Oxalate / 0.2 5 mM</td>
<td>93% (1.5 h)</td>
<td>TOC: 74% (1.5 h)</td>
<td>Gao et al. (2015)</td>
</tr>
<tr>
<td>Ferrite-carbon aerogel</td>
<td>BDD</td>
<td>0.1 M Na&lt;sub&gt;2&lt;/sub&gt;SO&lt;sub&gt;4&lt;/sub&gt;, 10 mA cm&lt;sup&gt;-2&lt;/sup&gt;, pH 6, O&lt;sub&gt;2&lt;/sub&gt; flow 0.33 L min&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>Metalaxyl / 500</td>
<td>73% (1 h)</td>
<td>TOC: 98% (4 h) / MCE: 28% (4 h)</td>
<td>Wang et al. (2013)</td>
</tr>
<tr>
<td>Modified Cathode</td>
<td>Anode</td>
<td>Operational conditions</td>
<td>Pollutant / mg L⁻¹</td>
<td>Maximum degradation</td>
<td>Maximum mineralization / MCE</td>
<td>Reference</td>
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<td>----------------------------------</td>
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</tr>
<tr>
<td>Fe₃O₄@Fe₂O₃/ACA</td>
<td>BDD</td>
<td>0.05 M Na₂SO₄, 10 mA cm², pH 3, O₂ flow 0.33 L min⁻¹</td>
<td>Imidacloprid / 236.7</td>
<td>90% (30 min)</td>
<td>TOC: 90% (1 h)</td>
<td>Zhao et al. (2012)</td>
</tr>
<tr>
<td>CO₂- and N₂-activated FeCuC aerogel</td>
<td>BDD</td>
<td>0.05 M Na₂SO₄, 0.01 A, pH 3, O₂ flow 0.1 L min⁻¹</td>
<td>Methylene Blue / 50</td>
<td>98% (30 min)</td>
<td>TOC: 82% (1 h) COD: 83% (1 h)</td>
<td>Zhao et al. (2016)</td>
</tr>
<tr>
<td>Zeolite/Cu(15)-β zeolite</td>
<td>Carbon</td>
<td>0.1 M NaCl, -0.1 V</td>
<td>Reactive Black 5 / 20</td>
<td>40% (3 h)</td>
<td>COD: 15% (3 h)</td>
<td>Oliver-Tolentino et al. (2014)</td>
</tr>
<tr>
<td>CoFe-LDH/CF</td>
<td>Pt</td>
<td>0.05 M Na₂SO₄, -0.04 A, pH 3, AFR 1 L min⁻¹</td>
<td>Acid Orange II / 0.1 mM</td>
<td>≥95% (10 min)</td>
<td>TOC: 97% (8 h)</td>
<td>Ganiyu et al. (2017)</td>
</tr>
<tr>
<td>ERGO/CB metal-free</td>
<td>Pt</td>
<td>0.05 M Na₂SO₄, 2.86 mA cm², pH 6</td>
<td>BPA / 20</td>
<td>100% (20 min)</td>
<td>TOC: 74.6% (30 min) / MCE: 30.7% (30 min)</td>
<td>Dong et al. (2016)</td>
</tr>
</tbody>
</table>

Electrochemical techniques such as Pt electrodeposition on carbon vulcan material using a rotating disk-slurry electrode (RoDSE) (Santiago et al., 2010) was employed by Bañuelos et al. (2015) to electrochemically prepare bulk iron/carbon as cathode material. This system avoided complicated cleaning processes and agglomerations, reducing the cost and preparation time of electrodes for water treatment applications. In the developed cathode they detected a relatively uniform distribution of iron oxides and zero valent iron. This fact, as well as the activation of the surface with H$_2$SO$_4$, enhanced the H$_2$O$_2$ cathodic generation in comparison with the conventional cathode. Its efficiency was evaluated for electro- and photoelectro-Fenton degradation of methyl orange dye. The highest degradation level was seen when the cathode with the greatest amount of electrodeposited iron (1973 mg kg$^{-1}$) was used: 96% of discoloration in the electro-Fenton process and 98% in photoelectro-Fenton. These results were better than those of homogeneous (72% and 90%) and iron-supported exchange resin (52% and 71%) processes. Recently, this group (García-Rodríguez et al., 2016) evaluated the electrocatalytic activity of three carbon materials (carbon cloth, carbon felt, and carbon sponge) in which the iron was electrodeposited on their surface for degradation of the same dye by heterogeneous electro-Fenton process. The largest amount of generated H$_2$O$_2$ was achieved with the carbon felt showing a greater and faster degradation of the dye, due to its greater catalytic activity, uniform distribution of iron, more efficient TOC removal, and lower cost of material. These results are consistent with those reported by Popescu et al. (2018) in which graphite felt, taffeta carbon fibre, and unidirectional carbon fibre were evaluated as cathode materials on the electro-Fenton degradation of the pesticide pyrimethanil. In this study, the superior performance of H$_2$O$_2$ electro-generation by the unidirectional carbon fibre cathode was explained by the fact that its fibre wire structure (50,000 filaments per strand) provided a large specific surface area and great number of
mesoporous pores allowing O₂ to be easily electro-reduced on the surface to generate additional H₂O₂.

Another alternative was studied by Sun et al. (2015) who developed an *in situ* procedure to utilize ferrous iron, contained in acidic mine drainage, using an air-cathode fuel cell. Three types of iron oxide/graphite felt (GF) were obtained (FeOOH/GF, Fe₂O₃/GF and Fe₃O₄/GF), by regulating the calcining conditions, and their catalytic activities were evaluated at neutral pH using rhodamine B as the target pollutant. The results suggested a higher electro-Fenton catalytic activity with Fe₃O₄/GF and this was attributed to the presence of Fe²⁺ and octahedral sites in the Fe₃O₄ structure. The process can be described as completely surface-catalysed without participation of soluble iron species. Iron oxides maintained their structures along the degradation process, exhibiting good stability and recycling characteristics.

In this framework, several composite electrodes were prepared and used in the electro-Fenton process. Fan et al. (2010) synthesized iron-chitosan/nickel|activated carbon fibre|iron-chitosan/nickel (Fe-CHI/Ni|ACF|Fe-CHI/Ni) sandwich film cathode for removal of rhodamine B. The use of this sandwich film cathode allowed controlling the H₂O₂ supply and ferrous ions in reasonable ratios. Fe-CHI was used as the iron reagent to release Fe²⁺ more quickly and allow for catalytic cycling (Fe²⁺ → Fe³⁺ → Fe²⁺). This was a more attractive scheme than that achieved by Fe@Fe₂O₃, which uses a different iron cycling pathway (Fe⁰ → Feⁿ⁺ → Fe₂O₃). Results obtained by these authors indicate that the homogeneous mechanism is the responsible for the catalytic action in this process.

Similarly, Bocos et al. (2016b) applied the interesting properties of chitosan as a metal stabilizer to develop a cathode of nickel foam coated with iron-chitosan solutions. Electrochemical impedance spectroscopy analysis of the coated electrodes was made and there was a relationship between the chitosan molecular weight and the resistance. In
addition, to promote the generation of H₂O₂ due to the reactions related on nickel foam (Eqs. (15) and (16)), the coating procedure was modified and only half of the submerged surface of the electrode was covered with chitosan.

\[
\text{Ni} + 2\text{O}_2 \rightarrow \text{Ni}^{2+} + 2(\text{O}_2^-) \quad (15)
\]

\[
(\text{O}_2^-) + \text{e}^- + 2\text{H}^+ \rightarrow \text{H}_2\text{O}_2 \quad (16)
\]

Different electrodes were tested on the decolourization and mineralization of poly R-478 and lissamine green B by electro-Fenton treatment and it was found that the total coated nickel foam was significantly less efficient than half-coated surface (73% decolourization with the former cathode, near 100% with the latter for poly R-478 degradation within 2 h), since it was possible to increase the production of HO• and the oxidation reactions in the system. In addition, this electrode showed favourable behaviour in successive batches (lissamine green B degradation higher than 93% after five cycles of 90 min) and continuous fluidized bed electro-Fenton reactor (attaining more than 95% decolourization for residence times of 45 and 90 min). Stable high decolourization levels were achieved without operational problems and negligible iron concentration was found in the solution at the end of the experiments.

5.2. Carbon nanotubes and derivatives

Carbon nanotubes (CNTs) have unique properties such as high surface area, geometry, high electrical conductivity, relative chemical inertness, and mechanical strength (Šljukic et al., 2006). Thus, CNT cathodes are effective and efficient for the in situ generation of H₂O₂ and the oxidized CNT contains surface carboxylate groups with the potential to strongly chelate Fe²⁺ and favour the generation of HO• (Divyapriya et al., 2016). Based on this fact, a recently developed electrochemical CNT filter has been applied to design a new cell configuration. Gao et al. (2015) developed a 4-layer CNT-based membrane stack (~200 μm thickness) for sequential flow-through electro-Fenton process. This flow
system consisted of the following stages: i) a CNT network cathode for \( \text{H}_2\text{O}_2 \) generation, ii) a CNT-COOFe\(^{2+}\) cathode for chemical production of HO\(^*\) and OH\(^-\) and \textit{in situ} iron regeneration, iii) a porous PVDF or PTFE insulating separator, and iv) a CNT filter anode for the remaining intermediate oxidation intermediates. Compared to conventional electro-Fenton studies, this flow system allowed operation at neutral pH, since the iron was bound to the electrode. The multifunctional prepared membrane-electrode stack allowed for convective mass transport and \textit{in situ} Fe\(^{2+}\) electroregeneration that reduced the iron leaching.

Interestingly, Vishnu and Kumar (2016) proposed the use of multiwalled CNTs containing an iron impurity (2.1% w/w) to modify a glassy carbon electrode (GCE/MWCNT-Fe*). In the presence of electrogenerated \( \text{H}_2\text{O}_2 \), the intrinsic iron impurity present in MWCNT-Fe* followed the Fenton’s reaction to oxidize benzene on its surface.

5.3. Aerogel

Aerogels are ultralight materials in which the liquid component of the gel has been replaced with a gas obtaining a solid with extremely low density. Aerogels have potential for use in the development of new electrodes, due to properties such as high electrical conductivity, good corrosion resistance, high mechanical robustness, thermal stability, large surface area, and porosity (Ren et al., 2016).

Ferrite-carbon aerogel monoliths with different iron/carbon ratios have been synthesized directly from metal-resin precursors accompanied by phase transformation (Wang et al., 2013). The main objective was to obtain a uniform and stable bulk ferrite carbon hybrid aerogel cathode that combines the aerogel properties and the catalytic activity by inclusion of metal ions into the framework of the hybrid aerogel. Electrogenerated \( \text{H}_2\text{O}_2 \) on ferrite-carbon aerogel (with an iron content of 5% w/w) was decomposed to \( \cdot\text{OH} \) and
its yield remarkably increased in comparison to the levels obtained when electrodes of lower iron concentration were applied to metalaxyl degradation by electro-Fenton process. The comparison of this process with homogeneous electro-Fenton process at different pH values, disclosed that in the heterogeneous process around 98% TOC decay was maintained operating between pH 3 - 6, while in the homogeneous process (with Fe$^{2+}$ 1 mM), the level was reduced from 85% at pH 3 to 70% at pH 6. Furthermore, better results were obtained compared to those using an iron oxide supported electrode (Fe@Fe$_2$O$_3$/CA): 73% removal achieved in 1 h with the ferrite-carbon aerogel cathode, while 4 h were necessary with the Fe@Fe$_2$O$_3$/CA. Similarly, Zhao et al. (2012) developed a composite iron oxide activated carbon aerogel containing hematite and magnetite (Fe$_3$O$_4$@Fe$_2$O$_3$/ACA) as a cathode. This cathode was more efficient at degrading imidacloprid than an activated carbon aerogel used in conventional electro-Fenton with Fe$^{2+}$, and worked effectively over a wide pH range (3 to 9) without sacrificing efficiency (ca. 90% TOC removal in all the range, while for homogeneous process it dropped from ca. 90% at pH 3 to ca. 30% at pH 9). These results are related to the nature of carbon aerogel that possesses high surface area (2410 m$^2$ g$^{-1}$) and increased porosities (formed of both micropores and mesopores) that favours the electrogeneration of H$_2$O$_2$ and metal fixation. They concluded that the oxidation mechanisms of electro-Fenton process with this cathode at different pH ranges were different. Thus, in acidic solutions, it followed a Haber-Weiss mechanism and the dissolved iron ions and surface Fe(II) sites immediately reacted with H$_2$O$_2$ to generate HO$^*$. In basic media, the mechanism involved the formation and deactivation of H$_2$O$_2$ complex with surface Fe(III) sites and the catalytic decomposition of H$_2$O$_2$ with Fe(II) sites, producing both superoxide anions (O$_2^*/$HO$_2^*$) and HO$^*$. 
5.4. Bimetallic materials

As previously noted, several studies have demonstrated the synergistic effect of the Fe$^{3+}$ and Cu$^{2+}$ ions simultaneously present in bimetallic allophane nanoclays (Garrido-Ramírez et al., 2016). Based on this concept, several multi-metallic cathodes have been developed. Zhao et al. (2016) fabricated a novel iron-copper-carbon (FeCuC) aerogel, using an environmentally friendly technique, by one-step process from metal-resin precursors and activated with CO$_2$ and N$_2$. The enhanced mineralization efficiency of this cathode was mostly due to ultradispersed metallic Fe-Cu nanoparticles embedded in a 3D carbon matrix in which Cu$^0$ acted as a reduction promoter for interfacial electron transfer. In addition, the CO$_2$-N$_2$ treatment enhanced the accessibility to the aerogel pores. This fact enlarged the porosity and regenerated the ultradispersed zerovalent iron with reductive carbon, resulting in low leaching of iron (<0.1 ppm) within the acidic solution.

The effect of Cu was also determined by Oliver-Tolentino et al. (2014), who reported electrocatalytic production of HO$^\bullet$ on the surface of a zeolite modified electrode employing Cu-Zeolites (ZSM5 and β) with different theoretical ionic exchange (15 and 100%). They suggested that HO$^\bullet$ was produced by a combined effect of the acidic properties of zeolite and copper acting as a redox mediator on the electrode surface via an electrocatalytic mechanism, and they demonstrated that the catalyst with 15% ionic exchange had the highest catalytic activity.

Another bimetallic cathode, hierarchical CoFe-layered double hydroxide (CoFe-LDH) grown on carbon-felt (CoFe-LDH/CF), was developed by Ganiyu et al. (2017) and used for heterogeneous electro-Fenton mineralization of acid orange II dye. This cathode was prepared by an in-situ solvothermal growth process. Its structure, morphology, and CoFe-LDH loading on the carbon felt were related to the temperature and time used on the hydrothermal treatment. The best conditions were an initial Co/Fe molar concentration
ratio of 25:12.5 maintained at 90 °C for 7 h. This cathode exhibited high catalytic activity and extended the pH range of the process from 2 to 7.1. Thus, TOC removal with a CoFe-LDH/CF cathode was 1.7 and 3.5 times greater than a homogeneous system with Fe²⁺/Co²⁺ at pH 5.8 and 7.1 respectively. Authors noted that the high efficiency could have resulted from: i) reactions occurring at the surface of the cathode avoiding the precipitation of iron sludge and expanding the working pH, ii) enhanced generation of H₂O₂ due to improved electroactive surface area of the cathode, and iii) co-catalytic effects of the Co²⁺ that promoted regeneration and additional production of Fe²⁺ and HO⁻.

5.5. Non-metallic cathode modification

To avoid possible metal ion pollution of treated water due to the leaching of iron during the electro-Fenton process, Dong et al. (2016) evaluated the generation of oxygen-containing radicals via H₂O₂ decomposition through direct oxygen reduction by using a metal-free catalyst cathode such as electrochemically reduced graphene oxide (ERGO)-modified gas diffusion electrode (GDE). They concluded that ERGO-modified GDE cathodes, obtained after reduction treatment times of 60 and 120 min, enabled the complete degradation of a bisphenol A solution (20 mg L⁻¹) in a neutral pH environment under a constant current density of 2.86 mA cm⁻². This modified cathode appears to be a promising material for the development of metal-free EAOP for wastewater treatment under mild conditions.

6. Other applications of heterogeneous electro-Fenton

Heterogeneous electro-Fenton is used in other applications such as the regeneration of adsorbents like granular activated carbon or clays. For example, Bañuelos et al. (2013) performed the regeneration of granular activated carbon, previously adsorbed with toluene, by electro-Fenton using the ion-exchange resin catalyst, Purolite C-100, loaded
with iron. In this context, iron loaded activated carbon was used for the degradation of m-cresol by heterogeneous electro-Fenton process (Bounab et al., 2015) demonstrating that the mechanism was an initial adsorption on activated carbon loaded with iron followed by a rapid degradation on its surface. Based on this result, a cathode sandwich of granular activated and fibre carbon was prepared showing that the remediation of pharmaceutical effluents can take place in two steps: adsorption and oxidation (Bocos et al., 2015a). Trellu et al. (2016b) examined a similar multi-step process, using a carbon sponge as cathode. This technique led to a fast initial adsorption of hydrophobic humic acids that reacted with HO\(^\bullet\) produced in bulk from electro-Fenton reactions.

Among adsorbents, CNTs are frequently used for water purification. Naghizadeh (2016) reported the feasibility of regeneration of humic acid-exhausted CNTs using electro-Fenton process. Their results indicated that regeneration efficiency at low concentrations of H\(_2\)O\(_2\) (0.05 M) is higher than at high concentrations. In addition, the regeneration efficiency increases with the current until 0.1 mA and then decreases at higher current, which may be due to iron particles and aggregates deposition onto the CNTs pores. Adsorbent specific surface area diminished ca. 13% after five regeneration cycles, causing an efficiency decrease from 98% to 87%. A tubular electro-Fenton cell comprising a microtube made of multi-walled CNTs (MWCNT-GDE) has been implemented in a cyclic water treatment process (Roth et al., 2016). In this process, a model pollutant, acid red 14 dye, was firstly removed from wastewater by adsorption on the MWCNT-GDE used as the cathode. In the subsequent phase, the pollutant was electrochemically degraded by electro-Fenton process.

Other adsorbents such as clays have shown similar efficiency. Díez et al. (2017) studied the potential of two natural phyllosilicate clays, illite and montmorillonite, as adsorbents for the removal of the ionic liquid 1-butyl, 2,3-dimethyl imidazolium chloride. The clay
regeneration was performed by Fenton-based processes, using the catalytic action of the iron naturally present in both clays. Both adsorbents were treated in the fluidized bed reactor by electro-Fenton process. Illite was completely regenerated, but the desorption equilibrium was a limiting factor in the removal process of montmorillonite. Similar results were obtained after the adsorption of lissamine green B dye on kaolinite. This reduced the dye content by 80% when electro-Fenton process was carried out with graphite electrodes at a constant potential difference of 5 V and pH 3 (Rosales et al., 2009).

Fenton-based processes can be used in the treatment of polluted soils. Inclusion of the reactive agents into the soil can be accomplished by soil flushing, electric field action “electrokinetic flushing”, or by direct addition of the agents into the soil. Thus, heterogeneous catalysis based on Fenton’s reaction can be in situ accomplished in the soil and the treatment can be used for removal of hydrophobic organoxenobiotics such as polycyclic aromatic hydrocarbons, petroleum hydrocarbons, and pesticides in long-term contaminated soils (Trellu et al., 2016a). In this technology, the in situ generation of HO• takes place from the decomposition of H₂O₂. This occurs by the catalytic action of iron present in the soil, which was included and mobilised along the soil by means of the electric field action (Pazos et al., 2013; Ng et al., 2014; Seo et al., 2015). The influence of variables such as H₂O₂ dosage, iron soil concentration, and porosity on the electro-Fenton process on soil (the so-called electrokinetic-Fenton), have been determined by experiments using kaolinite spiked with rhodamine B (Popescu et al., 2017). This model system was selected for easy monitoring of the oxidation reactions across the soil bed (Figure 3). The results indicate that the highest H₂O₂ dosage (7.5-10%) provided a faster colour removal rate. A slight influence of iron concentration in the soil was detected at the range of concentrations used (3000 - 6000 ppm) in these experiments. In other studies
(Bocos et al., 2015b; Sandu et al., 2016; 2017), this technology was applied to polluted soils. The results also show that it is possible to reduce the negative environmental effects and confirm the utility of electrokinetic-Fenton treatment as a suitable technique for the remediation of historically polluted sites.

Figure 3. Electrokinetic-Fenton degradation of a model soil polluted with rhodamine B. Operational conditions: \([\text{H}_2\text{O}_2] = 1\ \text{M}, [\text{RhB}] = 120\ \text{mg of dye g}^{-1}\ \text{of soil}, [\text{Fe}] = 420\ \text{ppm}, [\text{Citric acid}] = 0.1\ \text{M}, [\text{Na}_2\text{SO}_4] = 0.1\ \text{M}, V = 2.5\ \text{V cm}^{-1}, \text{pH} = 2.

7. Conclusion

Electro-Fenton is an efficient method for degradation of recalcitrant organic contaminants in wastewater. The studies reported in this review show that the use of a heterogeneous catalyst improves Fenton’s reactions due to their higher activity under a broad range of pH conditions and, in contrast with soluble iron salts, provides the possibility of catalyst reusability. The main conclusions of this review are the following:
- Iron minerals such as pyrite, magnetite, and goethite are abundant, inexpensive materials with high activity. Their reaction mechanisms have been established and several successful examples are described. All information leads us to conclude that these materials should be considered as low-cost iron catalysts.

- Iron- and iron oxide-loaded materials have proved to be efficient catalysts. The nature and properties of the carrier play a crucial role in the modulation of the activity at catalytic sites. Among the various preparation methods, fixation by entrapment in hydrogels or metal adsorption appear to be the most promising, easy, and cost effective technologies for synthesis of the heterogeneous catalysts.

- Improvements in physicochemical properties of the catalyst, such as decreasing particle size, pore diameter, and increasing surface area, can be achieved by the utilization of nanoparticle catalysis. In addition, the use of magnetic nanoparticles eased their separation from the reaction medium and their reuse. Thus, the use of new nanoparticles facilitates the application of heterogeneous catalysts to electro-Fenton process, but the potential toxicity of these materials should be further investigated.

- Modification of the cathode by inclusion of metal oxides or nanoparticles improves its properties. The cathode acts as heterogeneous catalyst with the ability to react with electrogenerated H₂O₂ and provide new material to develop more effective reactor designs.

- In most cases, some iron leaching occurs but the leaked iron concentrations are typically very low.

- It is not always determined whether the HO• are mainly produced in the medium from the heterogeneous mechanism, the homogeneous reaction, or a combination
of both effects. More research should be performed in this field in order to clarify the mechanism that takes place in the different processes.

- Although good results have been reported within a wide pH range, it is worth noting that most studies attained better results operating at pH near 3. This fact is attributed to the parasitic \( \text{H}_2\text{O}_2 \) decomposition into \( \text{H}_2\text{O} \) and \( \text{O}_2 \) as pH increases. Additionally, some authors noted that acidic medium increases iron leaching; therefore, a greater contribution of homogeneous reaction at pH near 3 may explain the higher performances achieved.

- The extension of heterogeneous electro-Fenton to other environmental problems suggests that this system could be a solution for the regeneration of adsorbents and the \textit{in situ} remediation of polluted soils.

In our view, heterogeneous catalysis for electro-Fenton process is a promising research field in which investigation efforts should be aimed to pave the way for a future scaling up of the process. In order to achieve such an objective, the spotlight should be put on: i) assessing the costs involved in the process, comparing them with its homogeneous counterpart, ii) improving and assessing catalyst lifetime (in most existing studies only three reusability cycles are performed), and iii) determining the homogeneous/heterogeneous contribution in the catalytic mechanism depending on the operating parameters.

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