Contents lists available at ScienceDirect

# 



### Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

#### Review

## Progress of homogeneous and heterogeneous electro-Fenton treatments of antibiotics in synthetic and real wastewaters. A critical review on the period 2017–2021



#### Enric Brillas

Laboratori d'Electroquímica dels Materials i del Medi Ambient, Secció de Química Física, Facultat de Química, Universitat de Barcelona, Martí i Franquès 1-11, 08028 Barcelona, Spain

#### HIGHLIGHTS

#### GRAPHICAL ABSTRACT

- Homo- and hetero-electro-Fenton, and combined processes, for antibiotic remediation
- Efficient antibiotic removal by homo-EF with a BDD anode at pH 3.0
- Better efficiency of hetero-EF with ironsolid catalysts at pH 3 avoiding iron sludge
- The use of hetero-EF with ironfunctionalized cathodes favors operating up to near neutral pH.
- Combination of EF with absorption, membranes, microbial, and biological processes

#### ARTICLE INFO

Article history: Received 8 December 2021 Received in revised form 9 January 2022 Accepted 10 January 2022 Available online 15 January 2022

Editor: Damià Barceló

Keywords:

Heterogeneous iron functionalized cathodes Heterogeneous iron solid catalysts Homogeneous electro-Fenton Hydroxyl radical Superoxide anion radical Water treatment



#### ABSTRACT

Antibiotics are widely supplied over all the world to animals and humans to fight and heal bacteriological diseases. The uptake of antibiotics has largely increased the average-life expectancy of living beings. However, these recalcitrant products have been detected at low concentrations in natural waters, with potential health risks due to alterations in food chains and an increase in the resistance to bacterial infection, control of infectious diseases, and damage of the beneficial bacteria. The high stability of antibiotics at mild conditions prevents their effective removal in conventional wastewater treatment plants. A powerful advanced oxidation processes such as the electro-Fenton (EF) process is being developed as a guarantee for their destruction by OH generated as strong oxidant. This review presents a critical, exhaustive, and detailed analysis on the application of EF to remediate synthetic and real wastewaters contaminated with common antibiotics, covering the period 2017–2021. Homogeneous EF and heterogeneous EF involving iron solid catalysts or iron functionalized cathodes, as well as their hybrid and sequential treatments, are exhaustively examined. Their fundamentals and characteristics are detailed, and the main results obtained for the removal of the most used antibiotic families are carefully described and discussed. The role of generated oxidizing agents is explained, and the by-products generated, and reaction sequences proposed are detailed.

*Abbreviations:* ACE, Average current efficiency; AO, Anodic oxidation; AO-H<sub>2</sub>O<sub>2</sub>, Anodic oxidation with electrogenerated H<sub>2</sub>O<sub>2</sub>; AOP, Advanced oxidation process; BDD, Boron-doped diamond; BOD<sub>5</sub>, 5-Day biochemical oxygen demand (mg O<sub>2</sub> L<sup>-1</sup>); CF, Carbon felt; CNTs, Carbon nanotubes; COD, Chemical oxygen demand (mg O<sub>2</sub> L<sup>-1</sup>); DSA, Dimensionally stable anode;  $E_{catb}$ , Cathodic potential vs. a reference electrode (V);  $E_{celb}$ . Cell voltage (V);  $E_{Croc}$ . Energy consumption per unit TOC mass (kVh (gTOC)<sup>-1</sup>);  $E_{EO}$ , Electrical energy per order (kWh m<sup>-3</sup> order<sup>-1</sup>); EF, Electro-Fenton; EPR, Electron paramagnetic resonance; FR, Flow rate (L h<sup>-1</sup> or m<sup>3</sup> h<sup>-1</sup>); GC-MS, Gas chromatography-mass spectrometry; GDE, Gas-diffusion electrode, usually of carbonpolytetrafluoroethylene (PTFE) (for H<sub>2</sub>O<sub>2</sub> generation); GF, Graphite felt; Hetero-EF, Heterogeneous electro-Fenton; Homo-EF, Homogeneous electro-Fenton; HOL<sub>2</sub>, Hydroperoxyl radical; HPLC, high-performance liquid chromatography; *I*, Current (mA or A); ICE, Instantaneous current efficiency; *j*, Current density (mA cm<sup>-2</sup>); *k*<sub>1</sub>, Pseudo-first-order rate constant (M<sup>-1</sup> s<sup>-1</sup>); LC-MS, Liquid chromatography-mass spectrometry; MCE, Mineralization current efficiency (%); 'OH, Hydroxyl radical; <sup>1</sup>O<sub>2</sub>, Singlet oxygen; O<sub>2</sub>, Superoxide radical anion; *Q*, Electric consumed charge (Ah L<sup>-1</sup>); SS, Stainless steel; TOC, Total organic carbon (mg C L<sup>-1</sup>); WWTP, Wastewater treatment plant.

E-mail address: brillas@ub.edu.

0048-9697/© 2022 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY license (http://creativecommons.org/licenses/by/4.0/).

1.	Introduction						
2. Search strategy and bibliometric analysis							
3. Fundamentals of electro-Fenton process							
	3.1.	Reactions in divided and undivided systems		. 4			
	3.2.	Electrochemical cells		. 5			
	3.3.	Mechanisms for homogeneous and heterogeneous electro-Fenton.		. 7			
	3.4.	Operating and energetic parameters		. 8			
4.	Treat	ent of antibiotics		. 8			
	4.1.	Homogeneous electro-Fenton		. 8			
		4.1.1. Synthetic solutions		. 8			
		4.1.2. Real wastewaters		16			
	4.2.	Heterogeneous electro-Fenton		19			
		4.2.1. Iron solid catalysts		19			
		4.2.2. Iron functionalized cathodes		23			
	4.3.	Combined electro-Fenton processes.		27			
		4.3.1. Hybrid processes		27			
		4.3.2. Sequential processes		32			
5.	Concl	sions and prospects		34			
CRe	diT aut	orship contribution statement		34			
Decl	Seclaration of competing interest						
Refe	rences			34			
				5.			

#### 1. Introduction

A large variety of antibiotics are supplied to animals and humans to fight and heal bacteriological diseases, thus strongly increasing their average-life expectancy (dos Santos et al., 2021). The widespread use and abuse of antibiotics over all the world causes their release and accumulation at low concentrations (usually  $<10 \ \mu g \ L^{-1}$ ) in many aquatic resources including rivers, lakes, sea water, and even drinking water (Li et al., 2020c; Meijide et al., 2021). The main entry of this pollution into the environment is from wastewaters originated in hospitals, pharmaceutical industries, and houses (also containing the metabolites excreted by animals and humans), with a minor contribution from the inappropriate disposal of expired drugs. Moreover, urban runoff and leaching from agricultural land also contributes to their flow into the groundwater streams (Meijide et al., 2021). The presence of these compounds in water bodies poses serious health risks to animals and humans since they can cause non-negligible alterations in food chains reaching living beings through food or drinking water, as well as increasing the resistance to bacterial infection, control of infectious diseases, and damage of the beneficial bacteria (Liu et al., 2018).

Antibiotics are commonly grouped in families characterized by a similar chemical structure with the same mechanism of action to kill bacteria. Fig. 1 collects the name and chemical structure of the most relevant antibiotics treated in this review. They belong to the families of aminoglycosides (gentamicin), amphenicols (chloramphenicol), β-lactams (amoxicillin), fluoroquinolones (ciprofloxacin, ofloxacin), macrolides (erythromycin), nitroimidazole (metronidazole), sulfonamides (sulfadiazine, sulfamethazine, sulfamethoxazole), and tetracyclines (tetracycline, oxytetracycline). Another important antibiotic such as trimethoprim is not classified in a particular family. Considering the potential harmful effects of antibiotics, recent European Directives 2015/495/EU and 2018/840/EU require to monitor the occurrence, distribution, frequency, and inclusion in risk assessment of active compounds such as amoxicillin and ciprofloxacin. Several methods used to remove antibiotics from wastewaters include biotransformation/ biodegradation and/or adsorption, which applied in conventional wastewater treatment plants (WWTPs). However, these techniques are insufficient to remove these recalcitrant pollutants because they have a low and limited ability for their destruction. For instance, only 40-70% of trimethoprim is abated during its treatment in WWTPs, remaining in the released effluents and re-entering again into the environment (Monteil et al., 2019). More powerful methods are then required to ensure the overall disappearance of antibiotics from waters and wastewaters.

Chlorination and UV irradiation have been used sometimes after the biological treatment, but the oxidizing power of both techniques is not strong enough to degrade most of the pharmaceuticals, their metabolites, or byproducts. Other physical and physicochemical methods such as membrane filtration and coagulation-flocculation have also been used to remove these pollutants, without solving their destruction because either they transfer them from one phase to another or produce concentrates that need to be treated by other methods (Monteil et al., 2019). Much better performances have been obtained with advanced oxidation processes (AOPs), which are specifically designed to efficiently destroy toxic and/or persistent organic pollutants (Brillas and Garcia-Segura, 2020; Brillas, 2021). AOPs refer to a large variety of chemical, photochemical, electrochemical, and photoelectrochemical methods, with the common feature of producing the strong oxidant hydroxyl radical (OH) to remove the organic pollutants. Among them, over the last five years, a hybrid technique of the Fenton treatment with electrochemical technology, the electro-Fenton (EF) process, has been largely developed showing its high ability to destroy not only antibiotics but also other pharmaceuticals, pesticides, and dyes (He and Zhou, 2017; Ganiyu et al., 2018b; Poza-Nogueiras et al., 2018; Brillas, 2021).

This article presents a critical and didactic review over the most relevant research published on the EF treatment of antibiotics in synthetic and real wastewaters, covering the recent period 2017–2021, addressed to broaden the knowledge of scientific young working in this field. First, the fundamentals and characteristics of the different EF processes proposed are detailed to know the main reactions involved to produce the oxidizing agents and the figures-of-merit used to analyze their performance. Further, the application of homogeneous (homo-) and heterogeneous (hetero-) EF, as well as their combined (hybrid and sequential) processes, to antibiotic removal is exhaustively examined. In the case of hetero-EF, the use of iron solid catalysts and iron functionalized cathodes is separately described. The role of the oxidants in each treatment is emphasized and analyzed, also with special didactic attention on the by-products formed and reaction sequences proposed.

#### 2. Search strategy and bibliometric analysis

The Scopus database was taken to search the peer-reviewed literature over the EF process of antibiotics in synthetic and real wastewaters. The following two literature searches were selected: electro-Fenton AND antibiotics and electro-Fenton AND pharmaceuticals. First, publications (reviews and scientific papers) written in English were collected within the period 2017–2021. For each retrieved paper, a list of the authors,



Fig. 1. Name and chemical structure of the most treated antibiotics by the electro-Fenton (EF) process.

title, and abstract was made for individual analysis to be included or excluded in the present review. Other publications such as books, book chapters, and communication in congresses were not considered. The following criteria were used from the reading of the selected papers to decide their possible inclusion:

- (i) Application of homo-and hetero-EF methods to remove antibiotics,
- (ii) study over the degradation and/or mineralization of single or mixed antibiotics in synthetic and real wastewaters,
- (iii) adequate exposition of the experimental setup and experimental conditions used, including the systems for analysis and the determination of the parameters needed to know the performance of the degradation and mineralization processes occurring in the treatment, and
- (iv) appropriate description with an acceptable discussion of the results found, including the removal of the antibiotic, its accurate kinetic

analysis, the efficiency of the decay of the chemical oxygen demand (COD) and/or total organic carbon (TOC) of the wastewater, the effect of main operating variables, the estimation of the energy consumption and/or operating costs, the change of the wastewater toxicity, and the identification of by-products with the proposal of a possible reaction sequence for the antibiotic degradation or mineralization. This review presents 19 figures and 4 tables to support the understanding of these issues for the homo- and hetero-EF processes identified.

The above analysis allowed clarifying the existence of homo-EF, hetero-EF with iron solid catalysts or iron functionalized cathodes, and five hybrid and sequential treatments, which were classified as hybrid EF/absorbent, hybrid EF with membrane, hybrid microbial EF, sequential adsorption-EF, and sequential EF-biological process. The degraded antibiotics were then associated with each treatment, regardless of the reaction matrix used. The present review focus on the description of the fundamentals, characteristics, and application to the destruction of antibiotics for such methods. The oxidation ability of the processes is related to the oxidizing agents produced, whose oxidative ability depends on the operating variables tested, pre-eminently the solution pH, current density (*j*), and electrolyte composition. Relevant importance is also given to the by-products formed since they inform about the change of solution toxicity and the power of the treatment to obtain decontaminated water for reuse.

From the above criteria, 10 recent review articles were identified. Most of these reviews reported a general description on the remediation of organics including some antibiotics from waters by EF (He and Zhou, 2017; Liu et al., 2018; Poza-Nogueira et al., 2018; Meijide et al., 2021), even making emphasis over the use of carbonaceous cathodes (Yu and Breslin, 2020; Nair et al., 2021). Three more specific papers were centered on the general degradative behavior of hybrid microbial EF, also called bio-EF, over organics with mention of antibiotics (Monteil et al., 2019; Li et al., 2020a; Sathe et al., 2022). Only a very short review of dos Santos et al. (2021) presented a general application of electrochemical technologies to the remediation of antibiotics, in which the EF process was also considered. The analysis was completed by selecting 93 scientific articles from 2017 to 2021. Fig. 2a shows that they corresponded to a percentage of 44.0% for homo-EF (41 articles), 17.3% for hetero- EF with iron solid catalyst (16 articles), 23.7% for hetero-EF with iron functionalized cathodes (22 articles), and 8.6% for hybrid (8 articles) and 6.4% sequential (6 articles) EF processes. The homo-EF process was then majority investigated in this scenario. Regarding the publication year, the number of reviews and scientific papers (102 in total) increased significantly in 2020 and 2021, as can be seen in Fig. 2b, thus showing the upgrading interest of this technology for antibiotic remediation. So, 9.7% of articles were published in 2017, 13.5% in 2018, 16.5% in 2019, 27.3% in 2020, and 33.0% in 2021. Practically all the scientific articles were devoted to the treatment of synthetic solutions, 85 in total, and only 7 articles gave information over the degradative behavior of real wastewaters. Much more research is necessary to be made with real wastewaters to know the actual oxidation ability of EF in complex organic and inorganic aqueous matrices for its feasible application at industrial level. The destruction of 32 antibiotics was covered by the scientific articles (see Fig. 2c), 12 of them with several compounds, preferentially related to the fluoroquinolone family (26.4%), followed by those corresponding to sulfonamides (21.8%), tetracyclines (17.3%), β-lactams (12.7%), amphenicols (7.3%), macrolides (3.6%), aminoglycosides (2.7%), and nitroimidazoles (2.7%). Moreover, 5.5% of the treated antibiotics did not belong to a defined family. The more studied antibiotics were ciprofloxacin (18.2%) and tetracycline (14.5%).

#### 3. Fundamentals of electro-Fenton process

This section is devoted to describing the basic operating principles of EF to remove antibiotics and other organic pollutants from wastewaters. The reactions involved, electrochemical cells, action mechanisms, and operating parameters are separately and briefly detailed.

#### 3.1. Reactions in divided and undivided systems

The key reactions of the EF process are the cathodic electrogeneration of  $H_2O_2$  and the subsequent 'OH production from Fenton's reaction. The weak oxidant  $H_2O_2$  with a reduction standard potential ( $E^\circ$ ) of 1.76 V/SHE is usually generated at a carbonaceous cathode (Nair et al., 2021) upon continuous injection of  $O_2$  gas or air directly to the solution or at the cathode surface in gas-diffusion electrodes (GDE) according to reaction (1). Other cathodic reactions involve the H<sup>+</sup> (or water) reduction to H<sub>2</sub> gas via reaction (2) and the reduction of the Fe<sup>3+</sup> ion formed in Fenton's reaction to regenerate the Fe<sup>2+</sup> catalyst via reaction (3) (Brillas et al., 2021).

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \tag{1}$$

$$2H^+ \rightarrow H_2$$
 (2)



**Fig. 2.** Bibliometric analysis of the literature. (a) Percentage of applied treatments. (b) Percentage of publications by year (c) Percentage of treated antibiotic families.

$$\mathrm{F}\mathrm{e}^{3+} + \mathrm{e}^{-} \to \mathrm{F}\mathrm{e}^{2+} \tag{3}$$

The amount of  $H_2O_2$  generated at the cathode depends on the relative rate of reactions (1) and (2) and can be easily enhanced by specific electrocatalysts added to the carbonaceous electrode (Sirés and Brillas, 2021). This situation is much less important using GDE cathodes that have a much greater  $H_2O_2$  production than conventional cathodes, limited by the  $O_2$  solubility in the aqueous medium. The carbonaceous cathodes also possess a good ability for Fe<sup>2+</sup> regeneration from reaction (3), although it is much smaller for the GDEs because of their more effective  $H_2O_2$  electrogeneration.

Once  $H_2O_2$  is accumulated in the medium, it can react with Fe<sup>2+</sup> added in low catalytic concentration via a Fenton system to form two main oxidants, 'OH with  $E^{\circ} = 2.80$  V/SHE and hydroperoxyl radical (HO<sub>2</sub>) with  $E^{\circ} =$ 1.65 V/SHE. The latter radical is called superoxide anion radical ( $O_2^-$ ) when it is deprotonated at pH > 4.9. Other less reactive oxygen species like singlet oxygen  $({}^{1}O_{2})$  can be produced as well (Zhu et al., 2022). Organics are then preferentially attacked by the stronger oxidant 'OH. Table 1 summarizes the main chemical reactions with their corresponding absolute rate constants  $(k_2)$  involved in a Fenton system, which can be separated in four steps, namely initiation (reaction (4)), catalysis with  $Fe^{2+}$  regeneration (reactions (5)-(8)), propagation (reactions (9)-(12)) and inhibition (reactions (13)-(20)) (Oturan et al., 2009). Reaction (4) is the well-known Fenton's reaction that originates large quantities of 'OH at optimum pH ca. 3. The Fenton-like reaction (5) is so slow compared to (4) that practically does not regenerate  $Fe^{2+}$ . This differentiates the behavior of a Fenton reagent, where H<sub>2</sub>O<sub>2</sub> and Fe<sup>2+</sup> act as reagents until consumption, vs. EF, in which Fe<sup>2+</sup> is regenerated from reaction (3), thus being more efficient because it maintains the rate of 'OH generation from Fenton's reaction (4). In the propagation steps, it is noticeable the reactions (11) and (12) of this radical with aliphatic (RH) and aromatic (ArH) pollutants. While the former molecule is dehydrogenated, the second one is hydroxylated at higher constant rate. This different reactivity explains the slow decay in the mineralization rate of aromatic antibiotics since they are converted into small carboxylic acids that are more hardly oxidizable, as will be discussed below.

Other catalysts can be used in EF such as the  $Cu^{2+}$  ion. Reaction (21) shows the Fenton-like oxidation of  $Cu^+$  to  $Cu^{2+}$  with release of the oxidant OH (Brillas, 2020).

$$Cu^{+} + H_2O_2 \rightarrow Cu^{2+} + {}^{\bullet}OH + OH^{-}$$
<sup>(21)</sup>

All the above homogeneous reactions take place in the homo-EF process within the reaction medium. When the hetero-EF treatment is considered with iron solid catalysts or iron functionalized cathodes, the same heterogeneous reactions are proposed but with the participation of surface  $Fe^{2+}$  and  $Fe^{3+}$ , designed as  $\equiv Fe^{2+}$  and  $\equiv Fe^{3+}$ , respectively. For instance, the heterogeneous Fenton's reaction with production of heterogeneous 'OH is expressed as follows (Ganiyu et al., 2018b):

$$\equiv Fe^{2+} + H_2O_2 \rightarrow \equiv Fe^{3+} + {}^{\bullet}OH + OH^-$$
(22)

#### Table 1

Absolute second-order rate constant for the main chemical reactions involved in a Fenton system at pH ca. 3 (Oturan et al., 2009).

Reaction	$k_2 (M^{-1} s^{-1})$	Number
Initiation		
$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + OH + OH^-$	55	(4)
Catalysis with $Fe^{2+}$ regeneration		
$H_2O_2 + Fe^{3+} \rightarrow Fe^{2+} + HO_2^{-} + H^{+}$	$3.1 \times 10^{-3}$	(5)
$Fe^3 + HO_2 \rightarrow Fe^2 + O_2 + H$	$2 \times 10^{-7}$	(6)
$\mathrm{Fe}^{3+}$ + $\mathrm{O}_2^{-} \rightarrow \mathrm{Fe}^{2+}$ + $\mathrm{O}_2$	$5 \times 10'$	(7)
$Fe^{3+} + O_2^{-} + 2 H_2O \rightarrow Fe^{2+} + 2 H_2O_2$	$1.0 \times 10^{7}$	(8)
Propagation		
$H_2O_2 + OH \rightarrow H_2O + HO_2$	$3.3 \times 10^{7}$	(9)
$HO_2 \rightleftharpoons H^+ + O_2$	4.8 <sup>a</sup>	(10)
$RH + OH \rightarrow R + H_2O$	$10^{7}-10^{9}$	(11)
ArH + 'OH $\rightarrow$ ArHOH'	$10^{8} - 10^{10}$	(12)
Inhibition		
$Fe^{2+}$ + $OH \rightarrow Fe^{3+}$ + $OH^-$	$4.3 \times 10^8$	(13)
$\mathrm{Fe}^{2+} + \mathrm{HO}_2^{\cdot} + \mathrm{H}^+ \rightarrow \mathrm{Fe}^{3+} + \mathrm{H}_2\mathrm{O}_2$	$1.2 \times 10^{6}$	(14)
$O_2^{\cdot} + HO_2^{\cdot} + H^+ \rightarrow H_2O_2 + O_2$	$9.7 \times 10^{7}$	(15)
$HO'_2 + HO'_2 \rightarrow H_2O_2 + O_2$	$8.3 \times 10^{5}$	(16)
$HO_2 + OH \rightarrow H_2O + O_2$	$7.1 \times 10^{9}$	(17)
$O_2^- + OH \rightarrow OH^- + O_2$	$1.0 \times 10^{10}$	(18)
$O_2^{-}$ + $OH$ + $H_2O \rightarrow H_2O_2$ + $OH^-$ + $\frac{1}{2}O_2$	$9.7 \times 10^{7}$	(19)
$OH + OH \rightarrow H_2O_2$	$5.2 \times 10^9$	(20)

<sup>a</sup> Equilibrium constant.

In a divided cell,  $H_2O_2$  electrogeneration and oxidation from the Fenton system takes place in the catholyte placed in the cathode compartment, and the anodic reactions do not influence the behavior of the EF process. This system is used in the hybrid microbial EF with electricity production. However, it presents as main drawback the voltage penalty of the separator between the two cell compartments, and to obtain more cost-effective treatments, two- or three-electrode undivided cells are chosen for homoand hetero-EF, as well as the other combined processes when a current or a cathodic potential ( $E_{cat}$ ), respectively, is provided to the system. Under these conditions, the anodic reactions from the wastewater components notably influence the process performance and need to be studied to justify its oxidation ability.

H<sub>2</sub>O<sub>2</sub> and water are always oxidized at the surface of the anode M by reactions (23) and (24), respectively (Boye et al., 2002). The oxidation of the former compound causes the decay of its concentration in the medium and produces more amount of the weak oxidant HO2. In contrast, water oxidation finally releases O2 gas with formation of heterogeneous M(OH) as intermediate. Note that these radicals are only reactive near the anode surface and then, have different oxidation power over organics than those homogeneously produced in the Fenton system. The anode material exerts a strong influence over the amount of M('OH) generated. Two kinds of anodes are used, so-called active and non-active (Martínez-Huitle and Brillas, 2021). The active anodes (Pt, dimensionally stable anodes (DSA)) have low ability for water oxidation and produce low quantities of M ('OH). In contrast, the non-active anodes (boron-doped diamond (BDD), sub-stoichiometric Ti<sub>4</sub>O<sub>7</sub>, PbO<sub>2</sub>) can oxidize more largely water giving more quantity of reactive M('OH). The BDD anode is considered the best electrode for this purpose (Oturan et al., 2017).

$$\mathrm{H}_{2}\mathrm{O}_{2} \to \mathrm{HO}_{2}^{\bullet} + \mathrm{H}^{+} + \mathrm{e}^{-} \tag{23}$$

$$M + H_2O \rightarrow M(^{\bullet}OH) + H^+ + e^-$$
(24)

The anions of the salts present in the wastewater can also be oxidized to originate reactive species. The most ubiquitous medium in EF contains high amounts of  $SO_4^{2-}$  to enhance its conductivity. This ion can be easily transformed into sulfate radical anion (SO<sub>4</sub>) by reaction (25), which is a strong oxidant, even with higher oxidation power than 'OH or M('OH) in alkaline medium (Brillas, 2022). Cl<sup>-</sup> is another ion widely used as electrolyte. It can be converted into active chlorine (Cl<sub>2</sub>/HClO/ClO<sup>-</sup>) via reactions (26) and (27), followed by consecutive oxidation to the toxic and undesirable  $ClO_3^-$  and  $ClO_4^-$  ions by reactions (28) and (29) (Brillas, 2020). These ions need to be removed from the treated wastewater before disposal. Active chlorine reacts with organic pollutants in competence with 'OH or M ('OH) giving rise to chloroderivatives than can be even more toxic and recalcitrant than the parent molecule (Poza-Nogueira et al., 2018).

$$\mathrm{SO}_4^{2-} \to \mathrm{SO}_4^{\bullet-} + \mathrm{e}^- \tag{25}$$

$$2\text{Cl}^- \to \text{Cl}_2(\text{aq}) + 2\text{e}^- \tag{26}$$

$$Cl_2(aq) + H_2O \rightarrow HClO + Cl - + H$$
 (27)

$$HClO + 2H_2O \rightarrow ClO_3^- + 5H^+ + 4e^-$$
 (28)

$$ClO_3^- + H_2O \rightarrow ClO_4^- + 2H^+ + 2e^-$$
 (29)

#### 3.2. Electrochemical cells

The characteristics of the electrochemical cell (form, volume, electrode dimension and position, stirring or liquid flow rate (FR), etc.) affect the performance of the homo-EF and hetero-EF treatments of antibiotics. Stirred tank reactors and flow systems at bench scale have been used by the researchers, usually with small wastewater volumes (< 500 mL) and electrode area (< 80 cm<sup>2</sup>). In this scenario, only the oxidation power of the

systems can be assessed, but no information enough is given over its feasible application at industrial scale. Further work should be addressed to investigate the treatments in pilot plants, making techno-economic studies to benchmark these technologies in front other available AOPs (Garcia-Segura et al., 2020). Flow systems with higher versatility and scalability should be used for this purpose.

Fig. 3a presents a scheme of an electrochemical system with stirred tank reactor equipped with a conventional carbonaceous cathode (Heidari et al.,

2021). The applied current is controlled by a power supply and  $O_2$  or air is continuously bubbled into the solution for  $H_2O_2$  electrogeneration. Stirring is needed for solution homogenization and to facilitate the mass transport of reagents toward the electrodes. The two electrodes are usually of the same size, in parallel, with a small gap (< 2–3 cm), but Fig. 3a shows the case of a larger carbon felt (CF) cathode that covers all the inner wall of the cell to have more electroactive area. A similar stirred tank reactor can be seen in Fig. 3b when using a GDE cathode (Brillas et al., 2021). In this



**Fig. 3.** Schemes of experimental setups for the homo- and hetero-EF treatments of antibiotics in aqueous media. (a) Stirred tank reactor with a carbon-felt cathode covering the inner wall of the cell (adapted from Heidari et al. (2021)). (b) Stirred tank reactor with a gas-diffusion electrode (GDE) as cathode (adapted from Brillas (2021)). (c) Recirculation flow-by system (adapted from Serra-Clusellas et al. (2021)). (d) Recirculation flow-through system (adapted from Moratalla et al. (2021)).

case,  $O_2$  or air is directly injected to the dry and inner face of the GDE to release  $H_2O_2$  to the solution from its outer face. Fig. 3c and d depict the sketches of two flow recirculation arrangeClusellas et al., 2021), whereas Fig. 3d shows a flow-through cell with the liquid crossing the two parallel electrodes (Moratalla et al., 2021).

3.3. Mechanisms for homogeneous and heterogeneous electro-Fenton

ments. The liquid passes by the electrochemical cells with small electrodes from a reservoir thanks to a pump with a FR regulated by a rotameter. A power supply and a gas feeder are necessary as well. Both electrochemical reactors differ from the kind of flow applied. In Fig. 3c, a flow-by cell with the liquid passing between the two parallel electrodes is used (Serra-

Based on the reactions pointed out in Section 3.1, several authors have schematized the mechanisms for the homo- and hetero-EF processes of antibiotics for a better visualization.



**Fig. 4.** Suggested schematic mechanisms for: (a) the homo-EF treatment of amoxicillin in aqueous sulfate matrix using a stirred tank reactor with a  $Ti|RuO_2$ -IrO<sub>2</sub> anode and a multi-walled carbon nanotubes and carbon black co-modified graphite felt cathode (MWCNTs-CB/GF) (adapted from Pan et al. (2020)), and (b) the homo-EF-like process of tetracycline and other pharmaceuticals, like the antidepressant amitriptyline represented here, in sulfate medium with a stirred tank reactor equipped with a boron-doped diamond (BDD) anode and a carbon fiber brush cathode, with addition of triphosphate (TPP) ligand (adapted from Olvera-Vargas et al. (2019)).

Fig. 4a highlights the mineralization of amoxicillin to CO<sub>2</sub> by conventional homo-EF (Pan et al., 2020). O2 is reduced at the cathode to form  $H_2O_2$  and this species reacts with  $Fe^{2+}$  to produce the oxidant 'OH from Fenton's reaction (4). Fe<sup>2+</sup> regeneration from cathodic Fe<sup>3+</sup> reduction is remarked, and the anodic oxidation of the antibiotic is stated, without indicating the participation of M('OH). Fig. 4b shows the proposed mechanism for the mineralization of tetracycline and other drugs by a homo-EF-like process with a stirred tank reactor with a BDD anode, a carbon fiber brush cathode, and triphosphate (TPP) as ligand of Fe<sup>2+</sup> (Olvera-Vargas et al., 2019). In this way, a soluble  $Fe^{2+}$ -TPP complex is formed that is oxidized to a soluble  $\mathrm{Fe}^{3+}$ -TPP one by  $\mathrm{H_2O_2}$  generated at the carbon fiber brush cathode from O<sub>2</sub> reduction, thus generating the oxidant 'OH. The Fe<sup>2+</sup>-TPP complex is regenerated again from Fe<sup>3+</sup>-TPP reduction at the cathode. The oxidative role of the heterogeneous BDD('OH) generated by the BDD anode is highlighted as well. Note that a near neutral pH of 6 was used, very far from the optimum pH 3 of Fenton's reaction (4).

A curious mechanism for the mineralization of levofloxacin and trimethoprim upon a hetero-EF process with a solid Pd-Fe<sub>3</sub>O<sub>4</sub> catalyst is depicted in Fig. 5 (Zhou et al., 2018). In the electrolysis, O<sub>2</sub> and M(OH) are produced at the DSA anode of Ti|RuO<sub>2</sub>-IrO<sub>2</sub>, and H<sub>2</sub> and H<sub>2</sub>O<sub>2</sub> at the carbon-felt cathode. The H<sub>2</sub> and O<sub>2</sub> gases evolved are embedded into the Pd nanoparticles to originate reactive 'H as additional reductor and more amount of H<sub>2</sub>O<sub>2</sub>. This species then reacts with the =Fe<sup>2+</sup> species at the Fe<sub>3</sub>O<sub>4</sub> surface giving rise to heterogeneous 'OH that destroys the antibiotics.

Fig. 6 shows two mechanisms for the mineralization of ciprofloxacin by hetero-EF process with different iron functionalized cathodes. Fig. 6a accounts for a stirred tank reactor with a Pt anode combined with a meso-NiMn<sub>2</sub>O<sub>4</sub>|CF cathode (Sun et al., 2019). The surface Fe<sup>3+</sup>/Fe<sup>2+</sup>, Mn<sup>3+</sup>/Mn<sup>2+</sup>, and Ni<sup>3+</sup>/Ni<sup>2+</sup> couples help to the heterogeneous 'OH generation from the H<sub>2</sub>O<sub>2</sub> released from the cathode. The formation of O<sub>2</sub> is remarked, alongside its conversion into H<sub>2</sub>O<sub>2</sub>. However, this scheme disregards the expected generation of M('OH) from the anode. A similar behavior can be observed in Fig. 6b for a functionalized ferrocene|graphene encapsulated carbon felt array cathode (Divyapriya et al., 2018b). The Fe(III) and Fe(II) forms of ferrocene cycle to produce 'OH and HO<sub>2</sub> from the electrogenerated H<sub>2</sub>O<sub>2</sub>, and the antibiotic is mineralized via destruction of intermediates and accumulation of inorganic ions.

#### 3.4. Operating and energetic parameters

A set of general operating and energetic parameters are used to analyze the performance of the degradation and mineralization stages of each antibiotic treatment. Table 2 summarizes 13 parameters determined by the authors and identified in this review (Monteil et al., 2019; Brillas et al., 2021; Meijide et al., 2021). The evolution of these parameters is usually presented as figures-of-merit as function of the time or the electric consumed charge (*Q*) in the publications. Apart from them, the change in toxicity during the treatment is sometimes reported. Four parameters can be defined to determine the degradative behavior of the process. The simplest one is the change of the normalized concentration of the antibiotic during the assay, defined as the  $c/c_0$  ratio by Eq. (30). The kinetic analysis of this term generally obeys a pseudo-first-order reaction that allows calculating the corresponding constant rate ( $k_1$ ) according to Eq. (31). The normalized concentration is many times given as percentage of concentration removal or % degradation through Eq. (32). Finally, for comparative purposes, the electrical energy per order ( $E_{EO}$ ) is estimated from Eq. (33) as energetic parameter for the antibiotic removal.

A higher number of 9 parameters characterizes the mineralization process. The most determined parameters are the normalized COD and TOC, expressed as Eq. (34) and (35), respectively, or the corresponding percentages of COD and TOC removal given by Eq. (36) and (37). Note that the true parameter to analyze the mineralization performance is TOC that provides the amount of C atoms that are lost as  $CO_2$  during the trial. In contrast, COD informs about the removal of oxidizable products, and it is useful, as a first approach, for the mineralization analysis of complexes aqueous matrices. The above parameters allow calculating those related to the efficiency namely the instantaneous current efficiency (ICE) from Eq. (38), average current efficiency (% MCE) from Eq. (40). Two energetic parameters are also established for the overall treatment, the energy consumption per unit volume (EC) and the energy consumption per unit TOC mass (EC<sub>TOC</sub>) from Eq. (41) and (42), respectively.

#### 4. Treatment of antibiotics

In this section, the most interesting results obtained for the treatment of antibiotics by homo-EF, hetero-EF, and hybrid and sequential processes are consecutively detailed and analyzed. The description is made by antibiotic families because of their common chemical reactivity.

#### 4.1. Homogeneous electro-Fenton

As stated above, homo-EF has been the most studied process for antibiotic remediation. It has been checked for synthetic and real wastewaters, which will be separately analyzed below. Table 3 lists the best results found for selected homo-EF treatments, indicating the system with the anode/cathode used and the experimental conditions applied.

#### 4.1.1. Synthetic solutions

The performance of antibiotic removal by homo-EF has been checked for several families including amphenicols, aminoglycosides,  $\beta$ -lactams, fluoroquinolones, macrolides, sulfonamides, and tetracyclines. The majority of these studied have been made in synthetic sulfate media with pure water, and they considered the influence of operating parameters, the role of oxidizing agents generated, and the by-products originated.



Fig. 5. Suggested schematic mechanism for the hetero-EF process of levofloxacin and trimethoprim with a solid Pd-Fe<sub>3</sub>O<sub>4</sub> catalyst in sulfate medium using a stirred tank reactor with a Ti $|RuO_2$ -IrO<sub>2</sub> anode and a carbon felt cathode. Adapted from Zhou et al. (2018).





**Fig. 6.** (a) Suggested schematic mechanism for the hetero-EF process of ciprofloxacin with a functionalized meso-Ni $Mn_2O_4$  carbon felt cathode in sulfate medium using a stirred tank reactor with a Pt anode (adapted from Sun et al. (2019)). (b) Proposed mechanism for the hetero-EF of ciprofloxacin with a functionalized ferrocene| graphene encapsulated carbon felt array cathode in sulfate matrix using a semi cylindrical shape reactor with a rotating carbon-felt disc anode (adapted from Divyapriya et al. (2018b)).

Unfortunately, no techno-economic studies have been reported, a pending subject that should be done in the next future research.

Arhoutane et al. (2019c) reported the removal of 200 mL of a solution containing 0.1 mM of the amphenicol gentamicin in 0.050 M Na<sub>2</sub>SO<sub>4</sub> and 0.1 mM Fe<sup>2+</sup> at pH 3.0 using a stirring Pt/CF tank reactor like of Fig. 3a. The trials were centered in the study of the effect of *j* from 60 to 300 mA cm<sup>-2</sup> lasting 240 min. They found that only a 60% of the antibiotic was removed at *j* = 60 mA cm<sup>-2</sup> in 20 min, whereas total degradation was achieved for *j* ≥ 100 mA cm<sup>-2</sup>. The antibiotic decay obeyed a pseudo-firstorder kinetics, with increasing *k*<sub>1</sub>-values of 0.045, 0.202, and 0.315 min<sup>-1</sup> with raising *j* values of 60, 100, and 300 mA cm<sup>-2</sup> (see Table 3). This positive effect of *j* is a common feature in all the EF processes, which is ascribed to the increase in rate of all electrode reactions such as reactions (1) and (24), thereby enhancing the amounts of H<sub>2</sub>O<sub>2</sub> and M('OH) generated, with the consequent production of more 'OH from Fenton's reaction (4) thar can be maintained by the acceleration of reaction (3). This tendency was also reflected in the COD decay at 240 min, which reached increasing values of 50%, 86%, and 97% for the above *j*-values. It is also noticeable the high increase up to a value of 5 of the 5-day biochemical oxygen demand (BOD<sub>5</sub>)/COD ratio at *j* = 100 mA cm<sup>-2</sup>, indicating that the resulting wastewater can subsequently be biologically detoxified. Four cyclic and two aliphatic derivatives were identified by LC-MS/MS.

The treatment of the aminoglycoside chloramphenicol has been reported by Hu et al. (2020). A three-electrode tank reactor with a Pt anode, a N,O-co-doped biomass porous carbon cathode, and a SCE electrode reference was used. The co-doping of the biomass cathode helped to improve the H<sub>2</sub>O<sub>2</sub> generation. O<sub>2</sub>-saturated solutions with 50 mg L<sup>-1</sup> antibiotic in 0.050 M Na<sub>2</sub>SO<sub>4</sub> and 1.0–2.0 mM Fe<sup>2+</sup> at pH 1.0–5.0 and  $E_{cat}$  from -0.3 to -0.7 V for 80 min, were electrolyzed. The main parameter affecting the antibiotic removal was the  $E_{cat}$ -value since it regulates the quantity of electrogenerated H<sub>2</sub>O<sub>2</sub>. After 80 min of electrolysis at the optimum condition of 1.0 mM Fe<sup>2+</sup>, pH 3.0, i.e., the optimum value for

#### Table 2

Operating and energetic parameters used to quantify the degradation and mineralization performance of the homo- and hetero-EF treatments of antibiotics in aqueous matrices (Monteil et al., 2019; Brillas et al., 2021; Meijide et al., 2021).

Symbol (units)	Equation	Symbol meaning	Number
Degradation Normalized concentration			
c/c <sub>0</sub>	<i>c</i> / <i>c</i> <sub>0</sub>	<i>c</i> : Target concentration at time <i>t</i> (mg L <sup><math>-1</math></sup> ) <i>c</i> <sub>0</sub> : Initial target concentration (mg L <sup><math>-1</math></sup> )	(30)
Pseudo-first-order rate constant for antibiotic $k_1$ (s <sup>-1</sup> , min <sup>-1</sup> ) Percentage of concentration removal	$\frac{1}{\ln (c_0 / c)} = k_1 t$	t: Electrolysis time (s, min)	(31)
% degradation	$\frac{100 \ (c_0 - c)}{c_0}$		(32)
Electrical energy per order EEO (kWh m <sup>-3</sup> order <sup>-1</sup> )	$\frac{E_{cell} t}{Vlog} \frac{t}{(c_0/c)}$	<i>E</i> <sub>cell</sub> : Cell voltage (V) <i>I</i> : Current (A) <i>t</i> : Electrolysis time (h) <i>V</i> : Solution volume (L)	(33)
Mineralization			
COD/COD <sub>0</sub>	$COD / COD_0$	COD: COD concentration at time $t (mg O_2 L^{-1})$ COD <sub>0</sub> : Initial COD concentration (mg O_2 L <sup>-1</sup> )	(34)
Normalized total organic carbon (TOC) TOC/TOC <sub>0</sub>	TOC / TOC <sub>0</sub>	TOC: TOC concentration at time t (mg C L <sup><math>-1</math></sup> ) TOC <sub>0</sub> : Initial TOC concentration (mg C L <sup><math>-1</math></sup> )	(35)
Percentage of COD removal % COD removal	100 (COD <sub>0</sub> -COD)		(36)
Percentage of TOC removal % TOC removal	<u>100 (TOC_0-TOC)</u>		(37)
Instantaneous current efficiency ICE	$\frac{F V(COD_{t+D_t}-COD_t)}{8t t}$	<i>F</i> : Faraday's constant (96.485C mol <sup>-1</sup> ) <i>V</i> : Solution volume (L) COD <sub>t+At</sub> = COD concentration at time $t + \Delta t (\text{mg O}_2 \text{ L}^{-1})$ COD <sub>t</sub> = COD concentration at time $t (\text{mg O}_2 \text{ L}^{-1})$ 8: Equivalent of oxygen (mg) $\Delta t$ : Increment of electrolysis time (s)	(38)
Average current efficiency ACE	$\frac{F V(COD_0 - COD)}{8I t}$	<i>t</i> : Electrolysis time (s)	(39)
Percentage of mineralization current efficien % MCE	$\frac{n F V(TOC_0 - TOC)}{4.32 \times 10^5 m I t}$	<i>n</i> : Number of electrons exchanged for total theoretical mineralization <i>m</i> : Number of carbon atoms of target pollutant <i>t</i> : Electrolysis time (h)	(40)
Energy consumption per unit volume EC (kWh $m^{-3}$ )	$rac{E_{cell}I t}{V}$	<i>E</i> <sub>cell</sub> : Cell voltage (V) <i>t</i> : Electrolysis time (h)	(41)
Energy consumption per unit TOC mass $EC_{TOC}$ (kWh (g TOC) <sup>-1</sup> )	$\frac{E_{coll}I t}{V(TOC_0 - TOC)}$	t: Electrolysis time (h)	(42)

Fenton's reaction (4) that generates the main oxidant 'OH, and  $E_{cat} = -0.5$  V, total degradation was reached (see Table 3). The cathode showed a good reusability after 4 consecutive treatment cycles, and 12 aromatic by-products were detected, allowing proposing a reaction sequence for chlor-amphenicol degradation. Zhang et al. (2020a) presented a comparative study over the separated removal of 50 µM chloramphenicol and 50 µM thiamphenicol in 0.050 M Na<sub>2</sub>SO<sub>4</sub> solutions using a three-electrode tank reactor with a Pt anode, a N-doped porous carbon cathode, and a SCE electrode. The trials lasting 60 min were made with 50 mL of air-saturated solutions with 1.0 mM Fe<sup>2+</sup> as catalyst, at pH 3.0, and  $E_{cat} = -0.5$  V, giving rise to 98% degradation in 10 min and 90–93% TOC removal in 120 min for both antibiotics (see Table 3). After 8 consecutive cycles, the cathode showed a similar electroactivity.

The homo-EF process has been tested by many β-lactams such as amoxicillin (Oturan et al., 2017; Pan et al., 2020; Zhang et al., 2021), ampicillin (Vidal et al., 2019), cefalexin (Zhang et al., 2019), and cefoperazone (Wang et al., 2021a). Oturan et al. (2017) presented a brilliant work on the effect of the anode over the treatment of 0.1 mM amoxicillin in synthetic pharmaceutical wastewater. Four anodes, namely BDD, sub- stoichiometric Ti<sub>4</sub>O<sub>7</sub>, Pt, and DSA, were comparatively tested in a cell like of Fig. 3a with a CF cathode. Air-saturated solutions of 250 mL with 0.1 mM Fe<sup>2+</sup> at pH 3.0 and 23 °C were tested for 360 min, also aiming to clarify the influence of *I* from 10 to 120 mA. It was confirmed that non-active BDD and Ti<sub>4</sub>O<sub>7</sub> anodes with higher M('OH) generation were more effective for homo-EF than active Pt and DSA ones. Operating at I = 120 mA, total antibiotic removal was attained after 5 min for the three former anodes and after 10 min for DSA. The corresponding  $k_1$ -values were 0.62 min<sup>-1</sup> for BDD and Ti<sub>4</sub>O<sub>7</sub>, 0.61 min<sup>-1</sup> for Pt, and 0.052 min<sup>-1</sup> for DSA. Results given in Table 3 make in evidence the superior mineralization performance of the BDD anode, achieving 90% TOC abatement with a 7.5% MCE and an EC<sub>TOC</sub> = 0.68 kWh (g TOC)<sup>-1</sup>. The solution detoxification was confirmed, and 6 carboxylic acids were detected by HPLC, along with released SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, and NH<sub>4</sub><sup>+</sup> ions.

Pan et al. (2020) reported the effect of pH from 3.0 to 9.0 and *j* from 3 to 15 mA cm<sup>-2</sup> on the homo-EF process of 300 mL of air-saturated solutions with 10 mg L<sup>-1</sup> of amoxicillin with 0.050 M Na<sub>2</sub>SO<sub>4</sub> and 0.5 mM Fe<sup>2+</sup> at 25 °C lasting 120 min. A stirred tank reactor was used with 2 parallel electrodes, a DSA of Ti|RuO<sub>2</sub>-IrO<sub>2</sub> anode and a large surface cathode of graphite felt (GF) coated with a multiwalled CNTs onto carbon black (MWCNTs-CB). Fig. 7a depicts the high H<sub>2</sub>O<sub>2</sub> content, up to near 10 mM, accumulated in the medium at pH 3.0 and *j* = 12 mA cm<sup>-2</sup> for 120 min using the coated cathode, which decreased gradually up to approximately 7.3 mM at pH 9.0. On the contrary, Fig. 7b shows the opposite trend of the degradation of the antibiotic solution that rose from 85% to 93% when pH varied from 3.0 to 9.0 upon AO-H<sub>2</sub>O<sub>2</sub> (without Fe<sup>2+</sup>) at such *j*-value. This tendency is attributable to the progressive loss of the oxidation power of M ('OH) and the increasing power of SO<sup>+</sup><sub>4</sub> formed from reaction (25) that prevails in alkaline medium. A different behavior can be observed in Fig. 7c for

#### Table 3

Selected results obtained for the homogeneous electro-Fenton treatment of several antibiotics in synthetic and real wastewaters.

Antibiotic	System (anode/cathode)	Experimental remarks	Best results	Ref.
Synthetic solutions Aminoglycosides				
Gentamicin	Like of Fig. 3a (Pt/CF <sup>a</sup> )	200 mL of 0.1 mM antibiotic in pure water, 0.050 M $Na_2SO_4,$ 0.1 mM $Fe^{2+},$ pH 3.0, $j^{\rm b}$ 60–300 mA cm $^{-2}.$ 240 min.	Degradation: 60% at 60 mA cm <sup>-2</sup> and 100% at 100 and 300 mA cm <sup>-2</sup> in 20 min. $k_1^{c} = 0.045$ , 0.202, and 0.315 min <sup>-1</sup> , respectively. COD removal at 240 min: 50%, 86%, and 97%, respectively. Increase of BDO <sub>5</sub> /COD up to 5 at 100 mA cm <sup>-2</sup> . 6 by-products identified by LC-MS/MS.	Arhoutane et al. (2019c)
Ampnenicois Chloramphenicol	Three-electrode tank reactor (Pt/N,O-BPC <sup>d</sup> ) and SCE reference	O <sub>2</sub> -saturated solution with 50 mg L <sup>-1</sup> antibiotic in pure water, 0.050 M Na <sub>2</sub> SO <sub>4</sub> , 1.0–2.0 mM Fe <sup>2+</sup> , pH 1.0-5.0, $E_{cat}^{e} = -0.3$ to $-0.7$ V, 80 min.	100% degradation at 1.0 mM Fe <sup>2+</sup> , pH 3.0, and $E_{cat} = -0.5$ V. Low influence of Fe <sup>2+</sup> content and pH. Good reusability. 12 by-products detected by LC-MS. Reaction sequence	Hu et al. (2020)
Chloramphenicol Thiamphenicol	Three-electrode tank reactor (Pt/NPC <sup>f</sup> ) and SCE reference	,50 mL of air-saturated solution with 50 $\mu$ M of separated antibiotic in pure water, 0.050 M Na <sub>2</sub> SO <sub>4</sub> , 1.0 mM Fe <sup>2+</sup> , pH 3.0, $E_{cat} = -0.5$ V, 120 min.	98% degradation of all antibiotics in 10 min. 90–93% TOC removal of all antibiotics in 120 min. Good cathode reusability.	Zhang et al. (2020a)
Amoxicillin	Fig. 3a (BDD, Ti <sub>4</sub> O <sub>7,</sub> Pt, DSA/CF)	250 mL of air-saturated solution with 0.1 mM antibiotic in synthetic pharmaceutical water, 0.050 M Na <sub>2</sub> SO <sub>4</sub> , 0.1 mM Fe <sup>2+</sup> , pH 3.0, $I^{\rm h}=$ 10–120 mA, 23 °C, 360 min.	Total degradation at 120 mA: 5 min (BDD, Ti <sub>4</sub> O <sub>7</sub> , Pt) and 10 min (DSA). $k_1 = 0.62 \text{ min}^{-1}$ (BDD, Ti <sub>4</sub> O <sub>7</sub> ), 0.61 min <sup>-1</sup> (Pt), and 0.52 min <sup>-1</sup> (DSA). % TOC removal, % MCE, EC <sub>TOC</sub> (kWh (g TOC <sup>-1</sup> )) at 360 min: 91, 7.5, 0.62 for BDD, 90, 7.5, 0.68 for Ti <sub>4</sub> O <sub>7</sub> , 81, 6.3, 4.5 for Pt, and 57, 5.9, 5.3 for DSA. Solution detoxification. Detection of 6 carboxylic acids by HPLC, SO <sub>4</sub> <sup>2-</sup> , NO <sub>3</sub> <sup>-</sup> , and NH <sub>4</sub> <sup>+</sup> .	Oturan et al. (2017)
	Like of Fig. 3a (Ti  RuO <sub>2</sub> -IrO <sub>2</sub> /MWCNTs-CB <sup>i</sup>   GF <sup>j</sup> )	300 mL of air-saturated solution with 10 mg L <sup>-1</sup> antibiotic in pure water, 0.050 M Na <sub>2</sub> SO <sub>4</sub> , 0.5 mM Fe <sup>2+</sup> , pH 3.0–9.0, 25 °C, $j = 3$ –15 mA cm <sup>-2</sup> , 120 min.	Degradation after 25 min at 12 mA cm <sup>-2</sup> : 43% (AO-H <sub>2</sub> O <sub>2</sub> , pH 5.5), 100% (EF, pH 3.0 and 5.5). $k_1$ : 0.031, 0.191, and 0.144 min <sup>-1</sup> , respectively. TOC removal at 120 min: 9%, 48%, and 45%, respectively. 12 by-products identified by LC-MS. Reaction sequence proposed.	Pan et al. (2020)
	Cubic cell (BDD, DSA/SS <sup>k</sup> )	2 L of air-saturated solution with 10 mg $L^{-1}$ antibiotic in pure water, 0.050 M Na <sub>2</sub> SO <sub>4</sub> , optimization by RSM <sup>1</sup> .	<ul> <li>97% degradation upon optimum conditions with</li> <li>BDD: 26.17 mg L<sup>-1</sup>, FeSO<sub>4</sub>·7H<sub>2</sub>O, pH 2.29,</li> <li><i>I</i> = 366.08 mA, 30 min.</li> <li>Pseudo-first-order decay.</li> <li>50% removal of acute toxicity.</li> <li>7 bv-products detected by LC-MS.</li> </ul>	Zhang et al. (2021)
Ampicillin	Like of Fig. 3b (BDD/GDE <sup>m</sup> )	250 mL of 10–100 mg L <sup>-1</sup> , 10 and 50 μg L <sup>-1</sup> antibiotic in pure water, 0.050 M Na <sub>2</sub> SO <sub>4</sub> , 1 mM Fe <sup>2+</sup> , pH 2.8, $j = 5$ mA cm <sup>-2</sup> , 30 °C, 120 min.	Degradation and TOC removal: 68% and 67% for AO-H <sub>2</sub> O <sub>2</sub> , 73% and 56% for EF. $k_1 = 1.07 \times 10^{-2}$ and 9.1 $\times 10^{-3}$ s <sup>-1</sup> , respectively. Detected 6 cyclic derivatives by LC-MS/MS, 6 carboxylic acids by HPLC, NO <sub>3</sub> <sup>-</sup> , and NH <sub>4</sub> <sup>+</sup> .	Vidal et al. (2019)
Ciprofloxacin	Three-electrode tank reactor (Pt/GO-LCD <sup>n</sup> ) and Ag AgCl reference	150 mL of air-saturated solution with 3 mg L <sup>-1</sup> antibiotic in pure water, 0.050 M Na <sub>2</sub> SO <sub>4</sub> , 2 mM Fe <sup>2+</sup> , pH 3.5–9.0, $E_{cat} = -1.5$ V, 180 min.	Degradation and $k_1 (min^{-1})$ : 99% and 0.026 (pH 3.5), 92% and 0.014 (pH 7.0), and 78% and 0.008 (pH 9.0). Low reusability.	Divyapriya et al. (2018c)
	Like of Fig. 3a (Ti  RuO <sub>2</sub> -IrO <sub>2</sub> /GF)	500 mL of air-saturated solution with 50 mg L <sup>-1</sup> antibiotic in pure water, 0.050 M Na <sub>2</sub> SO <sub>4</sub> , 2:1 or 1:1 $Mn^{2+}/Fe^{2+}$ , 0.1 mM Fe <sup>2+</sup> , or acid mine drainage, pH 3.0, $I = 100$ -400 mA, 480 min.	In pure water: 2:1 Mn <sup>2+</sup> /Fe <sup>2+</sup> at 400 mA: 96% degradation in 30 min, 94% TOC removal and 16% MCE in 480 min. With 0.1 mM Fe <sup>2+</sup> , 74% degradation. With acid mine drainage: 89% degradation in 60 min. 11 intermediates detected by LC-MS. Reaction sequence proposed.	Huang et al. (2021a)
	Like of Fig. 3a (Pt/graphene aerogel)	50 mL of air-saturated solution with 50 mg L <sup>-1</sup> antibiotic in pure water, 0.050 M Na <sub>2</sub> SO <sub>4</sub> , 0.2–1.6 mM Fe <sup>2+</sup> , pH 3.0–9.0, $j = 5$ –30 mA, 120 min.	Total degradation at 0.8 mM Fe <sup>2+</sup> , pH 3.0, and 30 mA cm <sup>-2</sup> in 90 min. 91% TOC removal in 120 min. 12% MCE in 90 min. 11 by-products detected by LC-MS. Reaction sequence proposed.	Wang et al. (2021b)
Ofloxacin	Like of Fig. 3a (Pt/CF)	200 mL of air-saturated solution with 0.03–0.20 mM antibiotic in pure water, 0.050 M Na <sub>2</sub> SO <sub>4</sub> or 0.1 M NaCl, 0.2 mM Fe <sup>2+</sup> , pH 2.0–4.0, $I = 200$ mA, 300 min.	$      COD decay for 0.20 mM antibiotic at pH 3.0: 65\% \\ with NaCl and 81\% with Na_2SO_4 (ICE: 12\%). \\ COD decay for 0.20 mM antibiotic in Na_2SO_4: 69\% \\ (pH 2.0) and 74\% (pH 4.0). $	Yahya et al. (2020)
Macrolides Erythromycin	Fig. 3c (BDD/GDE)	1 L of 10 mg L <sup>-1</sup> antibiotic in pure water, 0.050 M Na <sub>2</sub> SO <sub>4</sub> , 10 mg L <sup>-1</sup> Fe <sup>2+</sup> , pH 2.8–7.0, FR ° = 20 L h <sup>-1</sup> , 25 °C, $j_{anod} = 5-10$ mA cm <sup>-2</sup> , $Q = 0.32-0.64$ Ah L <sup>-1</sup> .	TOC removal: 24% at 10 mA cm <sup><math>-2</math></sup> and 0.64 Ah L <sup><math>-1</math></sup> , 38% at 5 mA cm <sup><math>-2</math></sup> and 0.32 Ah L <sup><math>-1</math></sup> . 23 intermediates detected by LC-QTOF-MS. Reaction sequence proposed.	Serra-Clusellas et al. (2021)

(continued on next page)

#### Table 3 (continued)

Antibiotic	System (anode/cathode)	Experimental remarks	Best results	Ref.
Sulfonamides				
Sulfamethazine	Fig. 3a (Pt/CS <sup>p</sup> , CF, SS)	250 mL of air-saturated solution with 0.2 mM antibiotic in pure water, 0.050 M Na <sub>2</sub> SO <sub>4</sub> , 0.2 mM Fe <sup>2+</sup> , pH 3.0, $I = 50-500$ mA, 480 min.	Increasing degradation for all systems up to 400 mA. Total degradation and $k_1$ at 400 mA: 10 min and 0.61 min <sup>-1</sup> (CS), 40 min and 0.11 min <sup>-1</sup> (CF), 60 min and 0.07 min <sup>-1</sup> (SS). % TOC decay and % MCE after 480 min at 300 mA: 63 and 3.7 (CS), 56 and 2.5 (CF), and 37 and 1.4 (SS).	Sopaj et al. (2020)
Tetracyclines	Like of Fig. 20 (Til	400 mL of oir activated solution with 90 mg L <sup><math>-1</math></sup>	02% degradation at 00 min	Chan at al (2010a)
Tetracycline	RuO <sub>2</sub> -IrO <sub>2</sub> /CF)	antibiotic in pure water, 0.050 M Na <sub>2</sub> SO <sub>4</sub> , 0.1 mM $Fe^{2+}$ , pH 3.0, room temperature, $I = 60$ mA, 480 min.	$k_1 = 0.065 \text{ min}^{-1}.$ TOC removal, MCE, and EC <sub>TOC</sub> at 480 min; 82%, 2.8%, and 0.19 kWh (g TOC) <sup>-1</sup> . 9 by-products detected by LC-MS. Reaction sequence	Gien et al. (2019a)
	Like of Fig. 3a (Pt/NPC-CNTs <sup>q</sup>  ACFs <sup>r</sup> )	150 mL of air-saturated solution with 50 mg L <sup><math>-1</math></sup> antibiotic in pure water, 0.050 M Na <sub>2</sub> SO <sub>4</sub> , 0.4 mM Fe <sup>2+</sup> , pH 3.0, 25 °C, $j = 20$ mA cm <sup><math>-2</math></sup> , 120 min.	Total degradation with the prepared cathode, 72% using the raw ACFs. 96% TOC removal with the prepared cathode, 9.6% using the raw ACFs. Detection of 'OH as oxidant.	Tao et al. (2020)
Real wastewaters				
β-lactams Penicillin G	Like of Fig. 3a (Ti)	150 mL of air-saturated solution with 50 mg $L^{-1}$	98% degradation. Two consecutive pseudo-first-order	Gonzaga et al.
	RuO <sub>2</sub> -IrO <sub>2</sub> /CF)	antibiotic in urine, 0.5 mM Fe <sup>2+</sup> , pH 3.0, 25 °C, j = 120 mA cm <sup>-2</sup> , 480 min.	rate constants. 60% COD and 50% TOC decays. Abatement of urea, uric acid, and creatinine. Detection of ClO <sup>-</sup> , ClO <sub>3</sub> <sup>-</sup> , ClO <sub>7</sub> <sup>-</sup> , and chloramines	(2021)
Fluoroquinolones				
Ciprofloxacin	Like of Fig. 3a (ZnO-CeO <sub>2</sub> /CF)	65 mL of 50 mg L <sup>-1</sup> antibiotic in sewage, 0.050 M Na <sub>2</sub> SO <sub>4</sub> , 0.1 mM Fe <sup>2+</sup> , pH 3.0–7.0, $E_{cell} = 4$ V, 120 min.	<ul><li>99% degradation. 81% TOC removal Good</li><li>reusability.</li><li>9 by-products identified by LC-MS. Reaction sequence</li><li>proposed.</li></ul>	Liu et al. (2020b)
Sulfonamides	vi (1) 11 -			D (10010)
Sulfadiazine	Flow filter-press cell in continuous (DSA/graphene)	Air-saturated solution with 0.5–10 mg L <sup>-1</sup> antibiotic in WWTP effluent, 0.005–0.20 M Na <sub>2</sub> SO <sub>4</sub> , pH 7.1, 0.4 mM Fe <sup>2+</sup> , FR = 50 L h <sup>-1</sup> , 25 °C, $I = 50$ mA, 120 min.	Best degradation for 0.05 M Na <sub>2</sub> SO <sub>4</sub> : ~ 100% by flow-through, 55–69% by flow-by. Similar degradation for all antibiotics contents by flow-through. Good reusability. 10 by-products identified by GC–MS. Reaction sequence proposed.	Ren et al. (2019)
Tetracyclines				
Tetracycline	Like of Fig. 3a (Ti RuO <sub>2</sub> -IrO <sub>2</sub> , BDD/carbon brush)	400 mL of air-saturated pharmaceutical wastewater (initial TOC 40 mg L <sup>-1</sup> ), 0.050 M K <sub>2</sub> SO <sub>4</sub> , 3.33 mM Fe <sup>2+</sup> , 10 mM TTP <sup>s</sup> , pH 6.0, $j = 2-6$ mA cm <sup>-2</sup> , 360 min.	At 4.67 mA cm <sup>-2</sup> with Ti RuO <sub>2</sub> -IrO <sub>2</sub> , total degradation in 20 min. 90% TOC removal in 360 min. 88% TOC removal with 0.2 mM Fe <sup>2+</sup> at pH 3.0. Using BDD, 98% TOC removal with Fe <sup>2+</sup> -TPP at pH 6.0. Detection of 3 carboxylic acids by HPLC, Cl <sup>-</sup> , NO <sub>3</sub> <sup>-</sup> , and NH <sub>4</sub> <sup>+</sup> .	Olvera-Vargas et al. (2019)
	Like of Fig. 3a (Ti RuO <sub>2</sub> -IrO <sub>2</sub> , BDD/carbon fiber)	500 mL of air-saturated pharmaceutical wastewater (initial COD 1250 mg L <sup>-1</sup> ), 0.050 M K <sub>2</sub> SO <sub>4</sub> , 0.2 mM Fe <sup>2+</sup> , pH 3.0, $j = 0.83$ -8.33 mA cm <sup>-2</sup> , 360 min.	At 6.25 mA cm <sup>-2</sup> , COD and TOC removal: 100% and 100% with BDD, and 72% and 64% with Ti  $RuO_2$ -IrO_2. For AO-H <sub>2</sub> O <sub>2</sub> with BDD, 97% TOC removal. Detection of 6 carboxylic acids by HPLC, Cl <sup>-</sup> , ClO <sub>3</sub> ClO <sub>4</sub> <sup>-</sup> , NO <sub>3</sub> <sup>-</sup> , and NH <sub>4</sub> <sup>+</sup> .	Olvera-Vargas et al. (2021)

<sup>a</sup> CF: Carbon felt.

- <sup>b</sup> *j*: Current density.
   <sup>c</sup> k<sub>1</sub>: Pseudo-first-order rate constant for antibiotic decay.
- <sup>d</sup> BPC: Biomass porous carbon.
- <sup>e</sup>  $E_{cat}$ : Cathodic potential. <sup>f</sup> NPC: N-doped porous carbon.
- <sup>h</sup> I: Current.
- <sup>i</sup> MWCNTs-CB: Multiwalled carbon nanotubes-carbon black.
- <sup>j</sup> GF: graphite felt.
- <sup>k</sup> SS: Stainless steel.
- <sup>1</sup> RSM: Response surface methodology.
- <sup>m</sup> GDE: Gas diffusion electrode.
- $^{\rm n}\,$  GO-LCD: Graphene oxide-liquid crystal display.
- ° FR: Flow rate of liquid.
- <sup>p</sup> CS: Carbon sponge.
- <sup>q</sup> CNTs: Carbon nanotubes.
- <sup>r</sup> ACFs: Active carbon fibers.
- <sup>s</sup> TPP: Triphosphate.



**Fig. 7.** Effect of pH on: (a) accumulated  $H_2O_2$  concentration in 300 mL of an air-saturated 0.050 M Na<sub>2</sub>SO<sub>4</sub> solution at 25 °C using a stirred tank reactor with a Ti|RuO<sub>2</sub>-IrO<sub>2</sub> anode and a MWCNTs-CB/GF cathode by applying a current density (*j*) of 12 mA cm<sup>-2</sup>, (b) the percent of degradation of 100 mg L<sup>-1</sup> amoxicillin upon the above conditions by anodic oxidation with electrogenerated  $H_2O_2$  (AO- $H_2O_2$ ), and (c) the comparative percent of amoxicillin degradation by AO- $H_2O_2$  and homo-EF with 0.50 mM Fe<sup>2+</sup> with the above system or replacing the cathode by a graphite felt (GF). (d) Percentage of TOC removal for the above assays. Adapted from Pan et al. (2020).

the antibiotic degradation with the homo-EF process when OH is generated from Fenton's reaction (4) since it was completely removed in 25 min at pH of 3.0 and 5.5 at the optimum *j* of 12 mA cm<sup>-2</sup>, with  $k_1$ -values of 0.191 and 0.144 min<sup>-1</sup>, respectively (see Table 3). In contrast, slower degradation was determined for the raw GF due to its much lower H<sub>2</sub>O<sub>2</sub> production. This behavior was reflected in the TOC removal presented in Fig. 7d, where the greater mineralization of 48% and 45% was achieved after 120 min at pH 3.0 and 5.5, respectively. This means that the coated cathode is useful in the pH range 3.0–5.5, although yielded low mineralization. A total of 8 aromatic and 4 cyclic derivatives were identified by LC-MS, and a reaction sequence for degradation was suggested.

Zhang et al. (2021) published a work dealing with the homo-EF treatment of 2 L of air-saturated solutions with 10 mg  $L^{-1}$  of amoxicillin in 0.050 M Na<sub>2</sub>SO<sub>4</sub> using a cubic cell with a BDD or DSA anode and an inefficient SS cathode for H2O2 generation, as pointed out above. The degradation was optimized by response surface methodology (RSM), which revealed, as expected, that BDD was the best anode yielding 97% degradation with 26.17 mg L<sup>-1</sup> of FeSO<sub>4</sub>·7H<sub>2</sub>O as catalyst, at pH 2.29, and a I =366.08 mA for 30 min. It is also confirmed a 50% removal of acute toxicity under these conditions. Fig. 8 shows the reaction sequence proposed for amoxicillin (1) mineralization from the 7 by-products identified by LC-MS by these authors, complemented by 6 carboxylic acids detected by HPLC by Kalantary et al. (2018) with hetero-EF with a nano-Fe<sub>3</sub>O<sub>4</sub> solid catalyst. The initial attack of 'OH over 1 gives 3 primary derivatives, the hydroxylated compound 2 and the opening of the  $\beta$ -lactam groups to the compounds 3 and 4. Further breaking of 2 leads to compound 5, whereas the successive cleavage of the opened  $\beta$ -lactam groups of **3** and **4** produces the compound 6, which is demethylated to compound 8. Moreover, decarboxylation of 4 gives the compound 7. Subsequent oxidation of the aromatic and cyclic groups of the above compounds caused their cleavage leading to small carboxylic acids such as succinic, malic, maleic, and acetic, which evolve to oxalic and formic acids as final by-products since they are directly converted into  $CO_2$  (Brillas, 2021). It should be noteworthy that all these acids form very stable iron complexes that are slowly and more easily destroyed by heterogeneous M(OH) than homogeneous OH (Brillas, 2021, 2022). This is the main reason why the BDD anode with the highest oxidation power is the best electrode for homo-EF.

In the treatment of ampicillin, Vidal et al. (2019) used a stirred BDD/ GDE stirred tank reactor like of Fig. 3b. The assays were carried out with 250 mL of 10–100 mg L<sup>-1</sup> or 10 and 50 µg L<sup>-1</sup> of antibiotic in 0.050 M Na<sub>2</sub>SO<sub>4</sub> with 1 mM Fe<sup>2+</sup>, at pH 2.8, j = 5 mA cm<sup>-2</sup>, and 30 °C during 120 min. For 100 mg L<sup>-1</sup> and 50 µg L<sup>-1</sup>, antibiotic, TOC was reduced by 68% and 67% for AO-H<sub>2</sub>O<sub>2</sub>, and 73% and 56% for homo-EF, with  $k_1$ -values of 1.07 × 10<sup>-2</sup> and 9.1 × 10<sup>-3</sup> s<sup>-1</sup>, respectively (see Table 3). The loss of efficiency with decreasing antibiotic content is due to the presence of less organic load that favors the acceleration of the inhibition or parasitic reactions of 'OH (Brillas, 2021). LC-MS and HPLC allowed identifying 6 cyclic byproducts and 6 carboxylic acids. The release of NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> ions was confirmed as well.

The fluoroquinolone ciprofloxacin has been the most checked antibiotic for homo-EF process (Chen et al., 2017; Li et al., 2017a, 2017b; Rani et al., 2017; Villegas-Guzman et al., 2017; Divyapriya et al., 2018c; Pourzamani et al., 2018; Mi et al., 2019, 2020; Huang et al., 2021a; Wang et al., 2021b), Levofloxacin (Liu et al., 2017), ofloxacin (Yahya et al., 2020), and nalidixic acid (Zarei et al., 2019) have been considered as well. Divyapriya et al. (2018c) used a three-electrode cell with a Pt anode, a cathode of graphene oxide-liquid crystal display, and an Ag|AgCl reference electrode to confirm the optimum pH near 3 for the degradation of 150 mL of an



Fig. 8. Proposed reaction sequence for amoxicillin mineralization by homo-EF (adapted from Zhang et al. (2021)). Final carboxylic acids were identified by Kalantary et al. (2018) from hetero-EF with nano-Fe<sub>3</sub>O<sub>4</sub> solid catalyst in sulfate medium.

air-saturated solution with 3 mg  $L^{-1}$  antibiotic and 0.050 M  $\rm Na_2SO_4$  with 2 mM Fe<sup>2+</sup> by applying an  $E_{cat} = -1.5$  V for 180 min. Results of Table 3 make in evidence that 99% of degradation was achieved at pH 3.5 ( $k_1 =$  $0.026 \text{ min}^{-1}$ ) in front of 78% at pH 9,0 ( $k_1 = 0.008 \text{ min}^{-1}$ ). An interesting work of Huang et al. (2021a) focus the co-catalytic action of Mn<sup>2+</sup> and Fe<sup>2+</sup> in the homo-EF process. The trials were made with a stirred tank reactor like of Fig. 3a with a Pt anode and a chemically modified GF cathode containing 500 mL of 50 mg  $L^{-1}$  of ciprofloxacin in 0.050 M Na<sub>2</sub>SO<sub>4</sub> at pH 3.0. Fig. 9a shows that after 30 min at I = 400 mA, 74% degradation was attained with a classical 0.10 mM  $Fe^{2+}$  catalyst, which rose to 89% and 96% with a mixture of 1:1 and 2:1  $Mn^{2+}/Fe^{2+}$  ratio. This enhancement can be associated with the production of more 'OH from the Fenton-like reaction related to the Mn<sup>3+</sup>/Mn<sup>2+</sup> couple. With the 2:1 co-catalyst mixture, TOC was reduced by 94% with 16% MCE after 480 min of electrolysis, as can be seen in Fig. 9b. The good effectiveness of this mixture was corroborated by studying the effect of I on the process performance. Fig. 9c and d highlight the increase in degradation and TOC with raising I from 100 to 400 mA, as expected by the greater production of 'OH owe to the acceleration of the electrode reactions. Effective electrolysis was also found with a natural acid mine drainage rich in  $Mn^{2+}$  and  $Fe^{2+}$ , yielding a lower degradation of 96% in 60 min. LC-MS analysis of treated solutions detected 11 aromatic derivatives, which were sorted in a degradation sequence. In other study with a cell equipped with a Pt anode and a graphene aerogel anode, Wang et al. (2021b) determined that 0.8 mM  $Fe^{2+}$ , pH 3.0, and j =30 mA cm<sup>-2</sup> were the best conditions to completely degrade 50 mg L<sup>-1</sup> of ciprofloxacin from 50 mL of an air-saturated solution with 0.050 M Na<sub>2</sub>SO<sub>4</sub> after 90 min of treatment. About 91% of TOC was reduced in 120 min with 12% MCE in 90 min (see Table 3). From the by-products identified by LC-MS, the mineralization sequence of Fig. 10 was proposed.

Ciprofloxacin (1) can be initially attacked by OH to release the piperazine group yielding the compound **2**, which is subsequently defluorinated to the compound **3**. A second path is feasible by the partial cleavage of the piperazine group giving the compound **4**, which is further oxidized to compounds **5–7**. The oxidation of these by-products originates simpler aromatic derivatives like  $\alpha$ -aminophenol and 1,2,4-trihydroxybenzene, which were transformed into small linear-aliphatic acids like maleic and malonic before overall mineralization.

In the case of ofloxacin, Yahya et al. (2020) reported the effect of 0.050 M Na<sub>2</sub>SO<sub>4</sub> or 0.1 M NaCl on the homo-EF treatment of 200 mL of air-saturated solutions with 0.03–0.20 mM antibiotic in the presence of 0.2 mM Fe<sup>2+</sup> at pH 2.0–4.0 with a Pt/CF cell like of Fig. 3a by applying a I = 200 mA during 300 min. It was found that with 0.20 mM antibiotic at pH 3.0, the formation of active chlorine from Cl<sup>-</sup> oxidation by reactions (26)–(28) was detrimental since it reacted more slowly than 'OH with the parent molecule. Thus, COD was abated by 65% with NaCl and more largely, by 81% with Na<sub>2</sub>SO<sub>4</sub> with 12% ICE. The optimum pH of 3.0 was confirmed again since in Na<sub>2</sub>SO<sub>4</sub>, 69% COD reduction was attained at pH 2.0 and 74% at pH 4.0 (see Table 3).

The remediation of the macrolide erythromycin has been investigated by Serra-Clusellas et al. (2021) using the flow-through plant of Fig. 3c with a BDD anode and a GDE cathode. A solution of 1 L containing 10 mg L<sup>-1</sup> antibiotic, 0.050 M Na<sub>2</sub>SO<sub>4</sub>, and 10 mg L<sup>-1</sup> Fe<sup>2+</sup> at pH 2.8–7.0 recirculated a flow rate (FR) of 20 L h<sup>-1</sup> and 25 °C. However, they applied so low *j*-values (low 'OH production) that only a 24% of TOC was removed at pH 3.0, 10 mA cm<sup>-2</sup>, and Q = 0.64 Ah L<sup>-1</sup>, whereas increased to 38% at 5 mA cm<sup>-2</sup> and Q = 0.32 Ah L<sup>-1</sup> (see Table 3). A high number of 23 intermediates were detected by LC-QTOF-MS analysis and a feasible reaction sequence was suggested.



**Fig. 9.** (a) Variation of the percentage of ciprofloxacin degradation with electrolysis from the homo-Fenton degradation of 500 mL of 50 mg L<sup>-1</sup> antibiotic in 0.050 M Na<sub>2</sub>SO<sub>4</sub> and either 0.10 mM Fe<sup>2+</sup> or several Mn<sup>2+</sup>/Fe<sup>2+</sup> ratios as co-catalysts at pH 3.0. The assays were carried out with a stirred tank reactor equipped with a Ti/RuO<sub>2</sub>-IrO<sub>2</sub> anode and a chemically modified GF cathode at *I* = 400 mA. (b) Percentage of TOC removal and mineralization current efficiency for the above trial with 2:1 Mn<sup>2+</sup>/Fe<sup>2+</sup>. Effect of *I* over the percentages of (c) degradation and (d) TOC removal for the solution treated in (b). Adapted from Huang et al. (2021a).

Regarding the sulfonamides, only one work of Sopaj et al., (2020) has been reported over sulfamethazine destruction in 0.050 M Na<sub>2</sub>SO<sub>4</sub> using a cell like of Fig. 3a equipped with a Pt anode and a cathode either of carbon sponge (CS), CF, or SS. An air-saturated solution of 250 mL with 0.2 mM antibiotic and 0.2 mM Fe<sup>2+</sup> at pH 3.0 was electrolyzed by applying a *I* range of 50–500 mA. The degradation rate increased progressively from 50 to 400 mA, whereupon no higher antibiotic abatement was found because the excess of 'OH produced was consumed by its parasitic reactions. The cathode affected largely the degradation rate as function of H<sub>2</sub>O<sub>2</sub> electrogenerated since higher production of this species gave faster abatement. So, total degradation increased in the order: 10 min for CS ( $k_1 =$ 0.61 min<sup>-1</sup>) < 40 min for CF ( $k_1 = 0.11 \text{ min}^{-1}$ ) < 60 min for SS ( $k_1 =$ 0.07 min<sup>-1</sup>). The same trend was followed for TOC decay and MCE after 480 min of electrolysis at 300 mA, with maximum values of 63% and 3.7%, for the best CS cathode, respectively (see Table 3).

More information is available over the behavior of tetracyclines, centered in tetracycline Chen et al., 2019a; Ganzenko et al., 2020; Tao et al., 2020; Zhou et al., 2021) and oxytetracycline Lai et al., 2020; Hasani et al., 2021). The work of Chen et al. (2019a) was performed with a conventional DSA anode of Ti|RuO<sub>2</sub>-IrO<sub>2</sub> and a CF cathode in a cell like of Fig. 3a using 400 mL of an air-saturated solution with 80 mg L<sup>-1</sup> antibiotic, 0.050 M Na<sub>2</sub>SO<sub>4</sub>, and 0.1 mM Fe<sup>2+</sup> at pH 3.0 by providing a *I* of 60 mA. A rather poor performance was found because 93% degradation with  $k_1 = 0.065 \text{ min}^{-1}$  at 90 min was attained, and after 480 min, 82% of TOC was removed with 2.8% MCE and EC<sub>TOC</sub> = 0.19 kWh (g TOC)<sup>-1</sup>. These authors detected 9 by-products by LC-MS and proposed a reaction sequence for tetracycline degradation. In contrast, Tao et al. (2020) tested a N-doped porous CNTs coating an active carbon fiber as a large surface cathode that produces much higher quantities of H<sub>2</sub>O<sub>2</sub> in a similar cell with a Pt anode and obtained total degradation and an excellent 96% TOC reduction for 150 mL of an air-saturated solution with 50 mg L<sup>-1</sup> tetracycline using 0.4 mM Fe<sup>2+</sup> at pH 3.0 upon a j = 20 mA cm<sup>-2</sup> for 120 min (see Table 3). These results confirm the large influence of electrocatalytic ability of the cathode to electrogenerate H<sub>2</sub>O<sub>2</sub> with the consequent 'OH production from Fenton's reaction (4) over the homo-EF performance.

Other authors have considered the treatment of unclassified antibiotics such as p-aminosalicylic acid, (Oturan et al., 2018, 2021), cetofaxime (Lei et al., 2020), and pyrazinamide (Arhoutane et al., 2019b). Oturan et al. (2021) reported an interesting work dealing with the homo-EF process of 230 mL of an air-saturated solution of 0.10 mM p-aminosalicylic acid in 0.050 M Na<sub>2</sub>SO<sub>4</sub> solution at pH 3.0 using a stirred tank reactor like of Fig. 3a with 5 alternative anodes (DSA, Pt, Ti<sub>4</sub>O<sub>7</sub>, PbO<sub>2</sub>, BDD) and 5 alternative cathodes (CF, CS, carbon graphite, SS, Ti). Fig. 11a makes in evidence the greater H<sub>2</sub>O<sub>2</sub> accumulation in the medium (without antibiotic), up to 67 mg L<sup>-1</sup>, after 180 min of electrolysis at I = 100 mA using the Pt/CF system. For the best CF cathode in the presence of the antibiotic and  $0.10 \text{ mM Fe}^{2+}$ , the BDD anode yielded a faster antibiotic decay than the other anodes (see Fig. 11b), with total removal at 15 and 10 min for Ivalues of 50 and 500 mA, respectively (see Fig. 11c). Similarly, Fig. 11d corroborates the higher oxidation power of the process when BDD is compared with the other anodes, yielding 78% TOC removal at 360 min. Greater I leads to a faster mineralization, but with lower MCE and higher  $EC_{TOC}$ . This behavior can be observed in Fig. 11e and f, which show that the best results were found for the lower I of 50 mA for BDD, reaching the maximum MCE of 4.8% and the lower  $EC_{TOC} = 0.62 \text{ kWh} (\text{g TOC})^{-1}$ .

Comparative treatments with several antibiotics have been described by Murillo-Sierra et al. (2018). These authors treated 130 mL of a mixture of 50.0 mg  $L^{-1}$  sulfamethoxazole + 11.1 mg  $L^{-1}$  trimethoprim in 0.050 M



Fig. 10. Suggested reaction sequence for ciprofloxacin mineralization in sulfate medium by homo-EF. Adapted from Wang et al. (2021b).

Na<sub>2</sub>SO<sub>4</sub> with 0.5 mM Fe<sup>2+</sup> was tested in a stirred BDD/GDE cell like of Fig. 3b at j = 33.33 mA cm<sup>-2</sup> and found that trimethoprim ( $k_1 = 0.55 \text{ min}^{-1}$ ) was more rapidly abated than sulfamethoxazole ( $k_1 = 0.37 \text{ min}^{-1}$ ), clearly demonstrating the different reactivity of the different antibiotic families in front of the oxidant OH.

The above findings allow establishing that the best conditions for the homo-EF process of antibiotics are attained at pH 3.0, i.e., the optimum pH for Fenton's reaction (4), and with a BDD anode, whereas CF, CS, and some prepared carbonaceous cathodes with extended electroactive surface, can be alternative cathodes. However, comparative studies with different antibiotics are needed to clarify their reactivity respect to 'OH.

#### 4.1.2. Real wastewaters

Much less attention has received the homo-EF treatment of real wastewaters, centered on the  $\beta$ -lactam Penicillin G in urine (Gonzaga et al., 2021), the fluoroquinolone ciprofloxacin in sewage (Liu et al., 2020b), the sulfonamide sulfadiazine in a WWTP effluent (Ren et al., 2019), and tetracycline in pharmaceutical wastewater (Olvera-Vargas et al., 2019, 2021). The main results for these works are summarized at the end of Table 3.

Gonzaga et al. (2021) used a stirred Ti|RuO<sub>2</sub>-IrO<sub>2</sub>/CF tank reactor like of Fig. 3a to degrade 50 mg L<sup>-1</sup> Penicillin G in urine by adding 0.2 mM Fe<sup>2+</sup> at pH 3.0. It is noticeable that at j = 12 mA cm<sup>-2</sup>, the antibiotic



**Fig. 11.** (a) Change of accumulated  $H_2O_2$  concentration with electrolysis time for 230 mL of an air-saturated 0.050 M Na<sub>2</sub>SO<sub>4</sub> solution at pH 3.0 and 23 °C using a stirred tank reactor with a Pt anode and five alternative cathodes at a current (*I*) of 100 mA. (b) Percentage of degradation for the above solution containing 0.10 mM *p*-aminosalicylic acid and 0.10 mM Fe<sup>2+</sup> by homo-EF process with different anodes and a carbon-felt cathode at the same *I*. (c) Effect of *I* on the percent of degradation achieved for the BDD/carbon felt cell. (d) Percentage of TOC removal, (e) mineralization current efficiency, and (f) energy consumption per unit TOC mass for the previous assays with different anodes and a carbon-felt cathode. Adapted from Oturan et al. (2021).

underwent two consecutive kinetic decays, the first one, more rapid, due to the attack of the antibiotic by 'OH formed from Fenton's reaction (4) and the slower second one to the removal of the Fe(III)-Penicillin G complex originated. Only 60% COD and 50% TOC abatements were obtained after 480 min of electrolysis because of the parallel oxidation of the components of urine. So, important removal of urea, uric acid, and creatinine was determined, disclosing the power of the process to oxidize these organic pollutants. Additionally, they confirmed the formation of  $ClO^-$ ,  $ClO_3^-$ ,  $ClO_4^-$ , and chloramines from the oxidation of  $Cl^-$  present in the aqueous matrix following reactions (26)–(29).

The effectiveness of the homo-EF process over the remediation of real wastewaters has been well-proved for ciprofloxacin in sewage using either a stirred ZnO-CeO<sub>2</sub>/CF tank reactor (Liu et al., 2020b) or a flow system in

continuous treating sulfadiazine in a WWTP effluent with a filter-press DSA/graphene cell (Ren et al., 2019). In both cases, Na<sub>2</sub>SO<sub>4</sub> was added to the wastewater to increase its conductivity. Liu et al. (2020b) determined up to 99% degradation and 81% TOC decay after 120 min of electrolysis of 65 mL of 50 mg L<sup>-1</sup> antibiotic with 0.1 mM Fe<sup>2+</sup> at pH 3.0–7.0, and cell voltage ( $E_{cell}$ ) of 4 V. They identified 9 by-products by LC-MS and suggested a reaction sequence for the antibiotic degradation. A more interesting investigation has been presented by Ren et al. (2019), who demonstrated that at neutral pH of 7.1 with 0.050 M Na<sub>2</sub>SO<sub>4</sub>, 0.4 mM Fe<sup>2+</sup>, and FR = 50 L h<sup>-1</sup>, total degradation was reached by operating in flow-through regime at a low I = 50 mA, regardless of the antibiotic concentration between 0.5 and 10 mg L<sup>-1</sup> checked. In contrast, only 55–69% degradation was achieved using the flow-by regime, which is the most

ubiquitous method tested in flow filter-press cells. The regime of the flow cell then needs to be deeper investigated in future work to confirm the best method for the homo-EF process. Additionally, these authors detected 10 derivatives by GC–MS, proposing a reaction degradation sequence.

Olvera-Vargas et al. (2019) reported the homo-EF-like treatment of tetracycline in a pharmaceutical wastewater involving the TPP ion as ligand of Fe<sup>2+</sup> and Fe<sup>3+</sup> (see Section 3.3). The iron-TPP complexes formed were highly soluble in water and stable. Fig. 12a shows the overall removal in 20 min of 0.034 mM antibiotic in 400 mL of an air-saturated solution with 3.33 mM Fe<sup>2+</sup> and 10 mM TTP at pH 6.0 using a stirred tank reactor like of Fig. 3a with a Ti|RuO<sub>2</sub>-IrO<sub>2</sub> anode and a carbon fiber brush cathode at j = 4.67 mA cm<sup>-2</sup>. This rapid destruction of the molecule confirms the excellent power of the Fe(III)-TPP/Fe(II)-TPP couple to produce OH from a Fenton-like reaction similar to (4). The pharmaceutical wastewater contained other 3 drugs (no antibiotics) and Fig. 12b shows that at 360 min of electrolysis, good TOC removal of approximately 85% was obtained with 10–30 mM TPP and 3.33 mM Fe<sup>2+</sup>. Providing j-values  $\geq$  44.67 mA cm<sup>-2</sup>, no higher TOC abatements were obtained due to the increase in rate of the parasitic reactions of OH, as can be seen in Fig. 12c. Fig. 12d highlights that the oxidation ability of the homo-EF-like process was largely improved using an alternative and more powerful BDD anode, allowing 98% TOC decay, much greater than 88% found by homo-EF with the same amount of Fe<sup>2+</sup>. Several by-products were quantified. Fig. 12e shows the generation of final carboxylic acids like oxamic,



**Fig. 12.** (a) Time course of the normalized tetracycline concentration ( $c_0 = 0.037$  mM) for 400 mL of an air-saturated solution with a mixture of other four pharmaceuticals containing 3.33 mM Fe<sup>2+</sup> and 10 mM TTP at pH 6.0 treated by homo-EF-like process using a stirred tank reactor with a Ti|RuO<sub>2</sub>-IrO<sub>2</sub> anode and a carbon fiber brush cathode by applying a j = 4.67 mA cm<sup>-2</sup>. (b) Effect of the TPP content with a 3:1 TPP/Fe<sup>2+</sup> ratio on TOC removal of the above mixture (TOC<sub>0</sub> = 40 mg L<sup>-1</sup>) at j = 2.0 mA cm<sup>-2</sup>. (c) Influence of j on TOC removal of the mixture with 3.33 mM Fe<sup>2+</sup> and 10 mM TTP at pH 6.0. (d) Percent of TOC removal for conventional homo-EF with 0.050 M K<sub>2</sub>SO<sub>4</sub> and 0.2 mM Fe<sup>2+</sup> at pH 3.0, and the same solution as in (c) but using a BDD anode at pH 6.0, by applying in both cases a j = 4.67 mA cm<sup>-2</sup>. Evolution of (e) generated carboxylic acids and (f) released inorganic ions during the assay given in (a). Adapted from Olvera-Vargas et al. (2019).

oxalic, and more largely formic, which were completely removed from the medium. Fig. 12f depicts the evolution of released Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, and NH<sub>4</sub><sup>+</sup> ions. The main drawback of TPP as ligand is that it must be extracted from the medium to obtain a clean water before disposal. Later, the same authors (Olvera-Vargas et al., 2019) used the same electrolytic systems to remediate 500 mL of an air-saturated pharmaceutical wastewater with initial COD of 1250 mg L<sup>-1</sup> after addition of 0.050 M K<sub>2</sub>SO<sub>4</sub> and 0.2 mM Fe<sup>2+</sup> at pH 3.0 by applying *j*-values of 0.83–8.33 mA cm<sup>-2</sup> for 360 min. Operating at 6.25 mA cm<sup>-2</sup> upon homo-EF conditions, good 100% COD and TOC abatements were obtained with BDD in front of 72% and 64% determined with Ti|RuO<sub>2</sub>-IrO<sub>2</sub>. The high oxidation power of BDD was confirmed from the 97% TOC removal found by AO-H<sub>2</sub>O<sub>2</sub> (without Fe<sup>2+</sup>) with this anode. A total of 6 carboxylic acids were identified by HPLC, alongside the release of Cl<sup>-</sup>, ClO<sub>3</sub><sup>-</sup>, ClO<sub>4</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>, and NH<sub>4</sub><sup>+</sup>.

#### 4.2. Heterogeneous electro-Fenton

Hetero-EF processes have been developed to solve two key drawbacks of homo-EF, the generation of iron sludge that needs further treatment and the enlargement of the operating pH up to near neutral values. Two approaches have been proposed to attain these purposes, namely using iron solid catalysts or iron functionalized cathodes, whose characteristics and the best results obtained for antibiotic remediation are described below.

#### 4.2.1. Iron solid catalysts

A large variety of iron solid catalysts have been checked for the hetero-EF treatment of antibiotics, showing a good oxidation ability, and avoiding, in most cases, iron sludge, although they were slightly chemically solubilized or adsorbed by-products that reduced their electrocatalytic activity. Table 4 summarizes the best results reported in the literature for such treatments.

The remediation of gentamicin with a Cu,Fe-nano-layered double hydroxide catalyst in sulfate medium has been described by Ghasemi et al. (2019). The hetero-EF process was studied in a conventional stirred Pt/ graphite tank reactor like of Fig. 3a containing 100 mL of an air-saturated solution with 20 mg L<sup>-1</sup> antibiotic and 1 g L<sup>-1</sup> catalyst, at pH 3–12, and I = 400 mA. Although the quicker degradation was attained at pH 3 with 93% reduction in 100 min, an excellent removal of 88% was found at pH 6, disclosing the good oxidation power of the catalyst at near neutral pH. In contrast, only 25% of the pollutant was degraded by AO-H<sub>2</sub>O<sub>2</sub> (without catalyst) at pH 6 (see Table 4). In the hetero-EF process, a high COD reduction of 86% was obtained at pH 6 in 300 min, with a good reusability of the catalyst. Using scavenger, 'OH and O<sub>2</sub>' were identified as the main oxidants. NO<sub>3</sub><sup>-</sup> and NO<sub>2</sub>were detected as released ions.

The destruction of the  $\beta$ -lactams amoxicillin with nano-Fe<sub>3</sub>O<sub>4</sub> (Kalantary et al., 2018), cefalexin with chalcopyrite (Droguett et al., 2020, cefazolin with mineral iron-based natural catalysts (Heidari et al., 2021), meropenem with goethite (Moratalla et al., 2021), and nafcillin with chalcopyrite (Campos et al., 2020), all in sulfate medium, has been reported. The work of Kalantary et al., (2018) was centered on the degradation of 200 mL of a solution with 20 mg  $L^{-1}$  amoxicillin and 1 g  $L^{-1}$ catalyst at pH 3.0 with a stirred Pt/GF tank reactor like of Fig. 3a at I =300 mA. After 90 min of electrolysis, 98% degradation was attained with  $k_1 = 0.058 \text{ min}^{-1}$ , showing the catalyst a good reusability (see Table 4). GC-MS analysis of electrolyzed solution allowed detecting 9 by-products, from which a feasible reaction sequence was proposed. Droguett et al. (2020) used the cell of Fig. 3b with a Ti|IrO<sub>2</sub> anode and a GDE cathode to treat 100 mL of 50 mg  $L^{-1}$  cefalexin with 1 g  $L^{-1}$  catalyst at pH 3.0 by providing a j = 50 mA cm<sup>-2</sup>. Note that chalcopyrite (CuFeS<sub>2</sub>) loses a small amount of surface Fe<sup>2+</sup> and Cu<sup>2+</sup> ions that regulate the solution pH to approximately 3. Under these conditions, the antibiotic was completely degraded in 30 min with  $k_1 = 3.12 \times 10^{-3} \text{ s}^{-1}$ , and after 300 min of electrolysis, TOC was reduced by 43%, with a 2% MCE, and a high  $EC_{TOC}$  =  $8.67 \text{ kWh} (\text{g TOC})^{-1}$  (see Table 4). Despite the loss of surface material, the catalysts presented a good reusability. A total of 18 by-products were identified by LC-ESI-MS and HPLC.

The flow-through system of Fig. 3d with a 3D Ti|IrO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub> anode and a carbon black||PTFE cathode was used by Moratalla et al. (2021) to study the removal of 50 mg L<sup>-1</sup> meropenem with 10.8 g goethite at pH 3.0 in a pressurized synthetic urine solution at FR = 140 L h<sup>-1</sup>, by applying a j = 5 mA cm<sup>-2</sup> up to Q = 0.83 Ah L<sup>-1</sup>. An enhancement of the degradation rate was found with raising the solution pressure with  $k_1$ -values of  $3.3 \times 10^{-3}$  min<sup>-1</sup> for 0 bar,  $4.5 \times 10^{-3}$  min<sup>-1</sup> for 1.0 bar),  $5.0 \times 10^{-3}$  min<sup>-1</sup> for 2.0 bar, and  $5.7 \times 10^{-3}$  for 3.0 bar (see Table 4). However, the treatment was not useful for mineralization since a very poor TOC decay was determined at 1.0 bar. 11 intermediates were identified by LC-MS and HPLC.

The oxidation of ciprofloxacin was tested with 200 mL of an airsaturated solution with 30 mg L<sup>-1</sup> antibiotic, 0.050 M Na<sub>2</sub>SO<sub>4</sub>, and 1.5 g L<sup>-1</sup> of CeO<sub>2</sub>|N,P-carbon catalyst, with a stirred Pt/CF tank reactor like of Fig. 3a by applying an  $E_{cell} = 4$  V for 180 min (Han et al., 2022). The best performance was achieved at pH 3.0, with 95% degradation, 57% TOC decay, 6.2% MCE, and EC<sub>TOC</sub> = 0.43 kWh (g TOC)<sup>-1</sup> (see Table 4). The process was slower at pH 4–6 giving rise to 90% antibiotic abatement. A good reusability was found for the catalyst and again, 'OH and O<sub>2</sub>' were found as the main generated oxidants. Eleven by-products were identified by LC-MS and a reaction degradation sequence was suggested.

Tetracycline has been removed by several iron solid catalysts (Barhoumi et al., 2017a, 2017b; Liu et al., 2020a; Niaei and Rostamizadeh, 2020). A first interesting study of Barhoumi et al. (2017a) focus the treatment of 230 mL of an air-saturated solution with 20 mg  $L^{-1}$  antibiotic, 0.050 M Na<sub>2</sub>SO<sub>4</sub>, and 0.5–2.0 g  $L^{-1}$  chalcopyrite as catalyst or 0.2 mM Fe<sup>2+</sup> (homo-EF), at pH 3.0 using a stirred tank reactor with a BDD or Pt anode and a CF cathode at I = 100-500 mA. As pointed out above, chalcopyrite acted as a buffer keeping the solution pH close to 3 during all the electrolysis. Fig. 13a depicts the rapid removal of the antibiotic using BDD, completely disappearing between 5 and 12 min with decreasing the catalyst content from 2.0 to 0.5 g L<sup>-1</sup> at I = 300 mA, because of the lower electrocatalytic ability of the system. These decays followed a pseudo-first-order kinetics with increasing  $k_1$ -values of 0.383, 0.561, and  $0.719 \text{ min}^{-1}$  for raising catalyst concentrations of 0.5, 1.0, and 2.0 g L<sup>-1</sup>, respectively (see Table 4). The process was enlarged with a Pt anode, with lesser oxidation power than BDD, and total degradation varied between 10 and 16 min, with corresponding smaller  $k_1$ -values of 0.183, 0.230, and 0.350 min<sup>-1</sup>, as can be observed in Fig. 13b. Fig. 13c and d show the similar effect of I on TOC decay using BDD and Pt anodes, respectively, achieving overall mineralization after 240 min of electrolysis at 500 mA with 6% MCE. Similar results were obtained by homo-EF with 0.2 mM Fe<sup>2+</sup> for the BDD anode, but with the advantage that the treated solution contained less content of this ion in the hetero-EF assay, without any precipitation of iron sludge. The release of  $\text{NO}_3^\sim$  and  $\text{NH}_4^+$  ions was detected, alongside the production of 6 final carboxylic acids whose evolution for the heteroand homo-EF assays with BDD at I = 300 mA are presented in Fig. 13e and f, respectively. From the intermediates identified by LC-MS, the reaction sequence for tetracycline (1) mineralization of Fig. 14 is proposed. The initial attack of 'OH yields the hydroxylation of its C(2) to form the compound 2 or the demethylation of the dimethylamino group to originate the compound 3. Subsequent carboxylation of the dimethylamino group of  ${f 2}$  leads to compound  ${f 4}$ , whereas overall demethylation of the methylamino group of 3 followed by the cleavage of the lateral benzene ring originates the compounds 5 and 6. Subsequent leakage of the condensed benzenic rings of the above primary by-products gives a mixture of the benzene derivatives 7-11, which are then broken and oxidized to the ultimate succinic, malic, malonic, oxamic, oxalic, and formic acids. A second work of the same group reported an analogous study of tetracycline remediation using pyrite as catalyst (Barhoumi et al., 2017b). This natural catalyst (FeS<sub>2</sub>) also allows the regulation at pH 3 by solving small quantities of surface material. Results given in Table 4 reveal that the hetero-EF process with this catalyst was slower than with chalcopyrite, probably because in the latter case, Cu<sup>2+</sup> ion was also released to the medium with the consequent production of additional 'OH from reaction (21), along with that generated

#### Table 4

Selected results found for the heterogeneous electro-Fenton process with iron solid catalysts of several antibiotics in synthetic and real wastewaters.

beleeted results found	for the neterogeneo	as ciccus renton process with non sond catalysis of	several antibioties in synthetic and real wastewaters.	
Antibiotic	System, solid catalyst (anode/cathode)	Experimental remarks	Best results	Ref.
Synthetic solutions Aminoglycosides Gentamicin	Like of Fig. 3a Cu-Fe-NLDH <sup>a</sup> (Pt/graphite)	100 mL of air-saturated solution with 20 mg L <sup>-1</sup> antibiotic in pure water, 0.050 M Na <sub>2</sub> SO <sub>4</sub> , 1 g L <sup>-1</sup> catalyst, pH 3–12, 25 °C, $I = 400$ mA, 300 min.	93% and 88% degradation at pH 3 and 6, respectively, in 100 min. Using AO-H <sub>2</sub> O <sub>2</sub> , 25% at pH 6. 86% COD reduction after 300 min at pH 6. Good reusability. 'OH and O <sup>2</sup> <sub>2</sub> as main oxidants. $NO_3^-$ and NO <sub>2</sub> detected.	Ghasemi et al. (2019)
β-lactams Amoxicillin	Like of Fig. 3a Nano-Fe <sub>3</sub> O <sub>4</sub>	200 mL of 20 mg L <sup><math>-1</math></sup> antibiotic in pure water, 0.050 M Na <sub>2</sub> SO <sub>4</sub> , 1 g L <sup><math>-1</math></sup> catalyst, pH 3.0, $I = 300$ mA,	98% degradation. $k_1 = 0.058 \text{ min}^{-1}$ . Good reusability. 9 by-products detected by GC–MS. Reaction sequence	Kalantary et al. (2018)
Cefalexin	(Pt/GF) Fig. 3b Chalcopyrite (Ti IrO <sub>2</sub> /GDE)	90 min. 100 mL of a solution with 50 mg L <sup>-1</sup> antibiotic in pure water, 0.050 M Na <sub>2</sub> SO <sub>4</sub> , 1 g L <sup>-1</sup> catalyst, pH 3.0, $j = 50$ mA cm <sup>-2</sup> , 300 min.	proposed. Total degradation in 30 min. $k_1 = 3.12 \times 10^{-3} \text{ s}^{-1}$ . 43% TOC removal, 2% MCE, and EC <sub>TOC</sub> = 8.67 kWh (g TOC) <sup>-1</sup> in 300 min. Good reusability. 18 by-products identified by LC-ESI-MS and HPLC.	Droguett et al. (2020)
Meropenem	Fig. 3d Goethite (3D Ti  IrO <sub>2</sub> -Ta <sub>2</sub> O <sub>5</sub>  CB <sup>b</sup> -PTFE)	Pressurized synthetic urine solution up to 3.0 bar with 50 mg L <sup>-1</sup> antibiotic and 10.8 g catalyst, pH 3.0, FR = 140 L h <sup>-1</sup> , $j = 5$ mA cm <sup>-2</sup> , $Q = 0.83$ Ah L <sup>-1</sup> .	Reaction sequence proposed. At 1 bar, 90% degradation and 3% TOC abatement. $k_1$ (min <sup>-1</sup> ) = $3.3 \times 10^{-3}$ (0 bar), $4.5 \times 10^{-3}$ (1.0 bar), $5.0 \times 10^{-3}$ (2.0 bar), and $5.7 \times 10^{-3}$ (3.0 bar), 11 by-products detected by LC-MS and HPLC.	Moratalla et al. (2021)
Fluoroquinolones Ciprofloxacin	Like of Fig. 3a CeO <sub>2</sub>  N,P-carbon (Pt/CF)	200 mL of air-saturated solution with 30 mg L <sup>-1</sup> antibiotic in pure water, 0.050 M Na <sub>2</sub> SO <sub>4</sub> , 1.5 g L <sup>-1</sup> catalyst, pH 2–7, $E_{cell} = 4$ V, 180 min.	Maximum degradation of 95% at pH 3, 90% at pH 4–6. 57% TOC decay, 6.2% MCE, and $EC_{TOC} = 0.43$ kWh (g TOC) <sup>-1</sup> at pH 3.0. Good reusability. 'OH and $O_2^{-}$ as main oxidants. 11 by-products detected by LC-MS. Reaction sequence proposed.	Han et al. (2022)
Tetracyclines Tetracycline	Fig. 3a Chalcopyrite (BDD, Pt/CF)	230 mL of air-saturated solution with 20 mg L <sup>-1</sup> antibiotic in pure water, 0.050 M Na <sub>2</sub> SO <sub>4</sub> , 0.5–2.0 g L <sup>-1</sup> catalyst or 0.2 mM Fe <sup>2+</sup> , pH 3.0, $I = 100$ –500 mA, 480 min.	For hetero-EF with BDD at 300 mA, total degradation in 12 min ( $k_1 = 0.383 \text{ min}^{-1}$ ), 9 min ( $k_1 = 0.561 \text{ min}^{-1}$ ), and 5 min ( $k_1 = 0.719 \text{ min}^{-1}$ ) for 0.5, 1.0, and 2.0 g L <sup>-1</sup> chalcopyrite, respectively. With 1.0 g L <sup>-1</sup> catalyst, total mineralization after 240 min with 6% MCE at 500 mA. The same results for homo-EF. For hetero-EF with Pt at 300 mA, total degradation in 15 min ( $k_1 = 0.183 \text{ min}^{-1}$ ), 12 min ( $k_1 = 0.230 \text{ min}^{-1}$ ), and 10 min ( $k_1 = 0.350 \text{ min}^{-1}$ ) for 0.5, 1.0, and 2.0 g L <sup>-1</sup> chalcopyrite, respectively. Detection of 10 by-products by LC-MS and HPLC, NO <sub>3</sub> <sup>-</sup> , and NH <sup>+</sup> Beaction sequence proposed	Barhoumi et al. (2017a)
	Fig. 3a Pyrite (BDD, Pt/CF)	230 mL of air-saturated solution with 20 mg L <sup><math>-1</math></sup> antibiotic in pure water, 0.050 M Na <sub>2</sub> SO <sub>4</sub> , 2.0 g L <sup><math>-1</math></sup> catalyst or 0.2 mM Fe <sup>2+</sup> , pH 3.0, $I = 300$ mA, 480 min.	and $M_4$ . (Action section protoc). Using BDD, total degradation: 40 min (AO-H <sub>2</sub> O <sub>2</sub> ), 25 min (homo-EF), and 15 min (hetero-EF). TOC removal and MCE at 480 min: 77% and 4.7% (AO-H <sub>2</sub> O <sub>2</sub> ), 92% and 5.5% (homo-EF), and 96% and 5.7% (hetero-EF). Using Pt, 87% TOC removal and 5.2% MCE at 480 min. Detection of 6 carboxylic acids by HPLC and NH <sub>4</sub> <sup>+</sup> .	Barhoumi et al. (2017b)
Real wastewaters Sulfonamides Sulfamethazine	Like of Fig. 3a Fe, MoS <sub>2</sub> /Fe (Ti RuO <sub>2</sub> -IrO <sub>2</sub> /GF)	200 mL of air-saturated solution with 10 mg L <sup>-1</sup> antibiotic in pure water or a real wastewater, 0.050 M Na <sub>2</sub> SO <sub>4</sub> , 0.224 g L <sup>-1</sup> Fe, 0.02 g L <sup>-1</sup> MoS <sub>2</sub> , pH 4.0, $I = 50$ mA, 30 min.	In pure water, total degradation and $k_1$ : 10 min and 0.54 min <sup>-1</sup> for MoS <sub>21</sub> Fe, 20 min and 0.25 min <sup>-1</sup> for Fe. Low reusability in 5 consecutive cycles. In real wastewater, total degradation and $k_1$ : 15 min and 0.13 min <sup>-1</sup> for MoS <sub>21</sub> Fe, 30 min and 0.06 min <sup>-1</sup> for Fe. EC <sub>TOC</sub> (kWh (g TOC) <sup>-1</sup> ) and operating cost (\$US (kg TOC) <sup>-1</sup> ): 0.012 and 1.22 for MoS <sub>21</sub> Fe, 0.020 and 2.02 for Fe. 8 by-products detected by GC–MS. Reaction sequence proposed.	Tian et al. (2021)
Various antibiotics Chloramphenicol Metronidazole	Like of Fig. 3a GO <sup>c</sup>  Fe <sub>3</sub> O <sub>4</sub> (Pt/CF)	100 mL of O <sub>2</sub> -saturated solution with 80 mg L <sup>-1</sup> of each antibiotic in pure water, 0.050 M Na <sub>2</sub> SO <sub>4</sub> , 0.2 mM Fe <sup>2+</sup> or 0.10–0.50 g L <sup>-1</sup> catalyst, pH 3.0–7.0, $I = 100$ –500 mA, 300 min.	In homo-EF at pH 3.0 and 300 mA: Degradation of 70% chloramphenicol and 57% metronidazole in 300 min. In hetero-EF at pH 3.0, 0.50 g $L^{-1}$ catalyst, and 300 mA: Total degradation in 45 min for chloramphenicol and 15 min for metronidazole. 85% and 70% mineralization in 300 min, respectively. Good reusability in 4 consecutive cycles. Detection of 8 by-products for chloramphenicol and 11 by-products for metronidazole by LC-MS and HPLC. Reaction sequences proposed	Görmez et al. (2019)

#### Table 4 (continued)

Antibiotic	System, solid catalyst (anode/cathode)	Experimental remarks	Best results	Ref.
Levofloxacin c,d) Trimethoprim	Fig. 3a Pd-Fe <sub>3</sub> O <sub>4</sub> (Ti  RuO <sub>2</sub> -IrO <sub>2</sub> /GF)	500 mL of air-saturated solution with 50 mg L <sup>-1</sup> of separated antibiotic in pure water, 0.050 M Na <sub>2</sub> SO <sub>4</sub> , 0.2 mM Fe <sup>2+</sup> , 50 mg L <sup>-1</sup> Fe <sub>3</sub> O <sub>4</sub> or Pd-Fe <sub>3</sub> O <sub>4</sub> , pH 3.0, $I = 100$ –400 mA, 480 min.	For levofloxacin, total degradation at 200 mA in >30 min for Fe <sup>2+</sup> ( $k_1 = 0.157 \text{ min}^{-1}$ ) and Fe <sub>3</sub> O <sub>4</sub> ( $k_1 = 0.158 \text{ min}^{-1}$ ), 15 min for Pd- Fe <sub>3</sub> O <sub>4</sub> ( $k_1 = 0.238 \text{ min}^{-1}$ ), For trimethoprim, overall degradation at 200 mA in >120 min for all methods ( $k_1 = 0.042-0.045 \text{ min}^{-1}$ ). For both antibiotics, after 480 min at 400 mA, 96% mineralization and 6% MCE. 'OH and 'H as main oxidants	Zhou et al. (2018)

<sup>a</sup> NLDH: Nano-layered double hydroxide.

<sup>b</sup> CB: Carbon black.

<sup>c</sup> GO: Graphene oxide.



**Fig. 13.** Tetracycline concentration vs. electrolysis time for the hetero-EF degradation of 230 mL of an air-saturated solution with 0.20 mM antibiotic in 0.050 M Na<sub>2</sub>SO<sub>4</sub> with different contents of chalcopyrite as solid catalyst at pH 3.0 using a: (a) BDD/carbon felt or (b) Pt/carbon felt call at I = 300 mA. Effect of I on the percentage of TOC removal for: (c) the above hetero-EF assay with 1.0 g L<sup>-1</sup> chalcopyrite using a BDD/carbon cell, and (d) the homologous homo-EF process with 0.20 mM Fe<sup>2+</sup> as catalyst. Time course of generated carboxylic acids during: (d) the hetero-EF assay of (c) and (e) the homo-EF assay of (d) at I = 300 mA. Adapted from Barhoumi et al. (2017a).



Fig. 14. Suggested reaction sequence for tetracycline mineralization in aqueous sulfate matrix by hetero-EF with chalcopyrite as solid catalyst. Adapted from Barhoumi et al. (2017a).

from Fenton's reaction (4) by the solubilized  $Fe^{2+}$  and the corresponding heterogeneous Fenton-like and Fenton reactions of these ions at the catalyst surface. Note that the relative proportion of both mixed mechanisms is described by not well-established and for this reason, the authors classified the treatments with pyrite and chalcopyrite simply as hetero-EF with iron solid catalysts (see Table 4).

The removal of sulfonamides such as sulfadiazine with Pd|CeO2 catalyst in simulated livestock and poultry breeding wastewater (Zhang et al., 2020b) and sulfamethazine with Fe and  $MoS_2$  |Fe catalysts in sulfate medium and real wastewater (Tian et al., 2021) has been considered as well. The latter authors tested the oxidation of 200 mL of air-saturated solutions with 10 mg  $L^{-1}$  antibiotic in 0.050 M Na<sub>2</sub>SO<sub>4</sub> with 0.224 g  $L^{-1}$  Fe and/or  $0.02 \text{ g L}^{-1} \text{ MoS}_2$  at pH 4.0 using a stirred Ti|RuO<sub>2</sub>-IrO<sub>2</sub>/GF tank reactor like of Fig. 3a at I = 50 mA for 30 min. As expected, the system with the real wastewater lost performance with respect to the sulfate solution because of the parallel destruction of their other organic pollutants, and the combined use of MoS<sub>2</sub> and Fe as co-catalysts became more effective than Fe alone (see Table 4). Nevertheless, good results were obtained for the real wastewater since the process degraded completely the antibiotic in 15 min for  $MoS_2$  |Fe and 30 min for Fe, with  $k_1$ -values of 0.13 and 0.06 min<sup>-1</sup>, respectively. The lower  $EC_{TOC} = 0.012$  kWh (g TOC)<sup>-1</sup> was determined for the combined MoS<sub>2</sub>|Fe catalyst, related to an operating cost of 1.22 \$US (kg TOC)<sup>-1</sup>. A reaction degradation scheme was suggested from the 8 by-products detected by GC-MS. The main drawback of this process was the low reusability of the catalyst due to Fe corrosion.

Several papers have described the hetero-EF process for various separated antibiotics that can serve to compare their reactivity vs. the generated oxidizing agents. Görmez et al. (2019) studied the remediation of 100 mL of O<sub>2</sub>-saturated solutions with 80 mg L<sup>-1</sup> of chloramphenicol or metronidazole with 0.050 M Na<sub>2</sub>SO<sub>4</sub> and 0.10–0.50 g  $L^{-1}$  of graphene oxide Fe<sub>3</sub>O<sub>4</sub> catalyst, at pH 3.0–7.0 using a stirred Pt/CF cell like of Fig. 3a at I =100-500 mA. Contradictory results were reported for the relative degradation and mineralization of both antibiotics. So, at pH 3.0 and 0.5 g  $L^{-1}$  catalyst, metronidazole was totally degraded in 15 min with  $k_1$  = 0.304 min<sup>-1</sup>, whereas chloramphenicol required a longer time of 45 min with  $k_1 = 0.145 \text{ min}^{-1}$ . In contrast, quicker mineralization was achieved for chloramphenicol (85%) in front of metronidazole (70%) after 300 min of electrolysis (see Table 4), indicating the higher recalcitrance of the byproducts formed from the latter compound. A total of 8 and 11 byproducts for chloramphenicol and metronidazole were identified by LC-MS and HPLC., with proposal of the corresponding reaction sequences.

Zhou et al. (2018) compared the removal of 50 mg  $L^{-1}$  of levofloxacin or thiamphenicol in 500 mL of air-saturated solutions with 0.050 M Na<sub>2</sub>SO<sub>4</sub> and 50 mg  $L^{-1}$  of Fe<sub>3</sub>O<sub>4</sub> or Pd-Fe<sub>3</sub>O<sub>4</sub>, at pH 3.0 with a stirred Ti|RuO<sub>2</sub>-IrO<sub>2</sub>/ GF tank reactor like of Fig. 3a at I = 100-400 mA lasting 480 min. Fig. 15a shows that at 200 mA, levofloxacin was more rapidly abated with Pd-Fe<sub>3</sub>O<sub>4</sub>  $(k_1 = 0.238 \text{ min}^{-1})$  than with Fe<sub>3</sub>O<sub>4</sub> or 0.2 mM Fe<sup>2+</sup> (homo-EF)  $(k_1 \sim 0.158 \text{ min}^{-1})$ . In contrast, thiamphenicol was much more slowly removed and at similar degradation rate for all the above catalysts with  $k_1 =$ 0.042–0.045 min<sup>-1</sup>, as shows Fig. 15c. Regarding the corresponding TOC decays with Pd- Fe<sub>3</sub>O<sub>4</sub> presented in Fig. 15b and 15d, one can infer that levofloxacin was more quickly mineralized, with total TOC reduction after 360 min at 400 mA. These figures highlight the expected increase in TOC removal with increasing I due to the concomitant generation of more oxidizing agents and the consequent decrease in MCE by the acceleration of their parasitic reactions. 'OH and 'H were proposed as the generated oxidants by the Pd- Fe<sub>3</sub>O<sub>4</sub> catalyst, as pointed out above from Fig. 5. Fig. 15e shows the EPR spectra that confirms the production of the above two radicals using t-butanol as scavenger of 'OH.

Tian et al. (2020) used a pre-magnetized Fe catalyst to mineralize 200 mL of 10 mg L<sup>-1</sup> of various antibiotics in 0.050 M Na<sub>2</sub>SO<sub>4</sub>with 0.5 mM of catalyst at pH 7 using a stirred cell like of Fig. 3a with a Ti/RuO<sub>2</sub>-IrO<sub>2</sub> anode and a carbon black modified CF cathode by providing a I = 25 mA. After 180 min of electrolysis, the TOC removal of antibiotics increased according to the sequence: oxytetracycline (8%) < sulfadiazine (23%) < sulfamethazine (25%) < tetracycline (37%).

The above findings confirm that the Fe<sup>2+</sup> catalyst in homo-EF can be replaced by iron solid catalysts in hetero-EF with similar or even better performance. The oxidation ability of solid catalysts is higher at pH 3.0, with the advantage of avoiding iron sludge when the solution is neutralized before disposal. Comparison of the reactivity between various antibiotics seems rather related to the recalcitrance of by-products formed than their families with analogous chemical groups.

#### 4.2.2. Iron functionalized cathodes

This section covers another approach to enhance the homo-EF treatment of antibiotics via application of hetero-EF with iron functionalized cathodes that allows the enlargement of the pH of the treated solution because  $H_2O_2$  electrogeneration and the oxidation processes directly occur at the cathode surface. Selected results reported for this procedure are collected in Table 5.

The hetero-EF treatment of the amphenicols chloramphenicol with a Fe N-graphene cathode (Song et al., 2021) and thiamphenicol with a seaurchin-shaped carbon-anchored single-atom iron. Cathode (Zhang et al., 2022) have been reported. The work of Song et al. (2021) electrolyzed 15 mL of an O<sub>2</sub>-saturated solution with 25 mg L<sup>-1-</sup>of chloramphenicol in 0.050 M Na<sub>2</sub>SO<sub>4</sub> at pH 1–13 using the stirred cell of Fig. 3a with a Pt anode at  $i = 2 \text{ mA cm}^{-2}$  for 180 min. At his time, the degradation decayed following the sequence: pH 1 (98%) > pH 4 (92%) > pH 7 (89%) = pH 10 (90) > pH 13 (82%). This means that the heterogeneous Fenton's reaction (22) produces high quantities of heterogeneous 'OH in all the pH interval tested, even being well-efficient in alkaline media where the homo-EF process is completely inhibited by the precipitation of the iron catalyst as iron hydroxide. The cathode showed a good reusability after 5 consecutive cycles. Better performance has been described by Zhang et al. (2022) who used a stirred tank reactor with a graphite anode of lower oxidation ability to degrade 50 mL of an  $O_2$ -saturated solution with 20 mg  $L^{-1}$ thiamphenicol and 0.1 M K<sub>2</sub>SO<sub>4</sub> at pH = 3-11, and j = 20 mA cm<sup>-2</sup> during 60 min. At this time, overall degradation was found in all the pH range, but TOC abatement decreased progressively with increasing pH from 68% at pH 3 to 44% at pH 11 (see Table 5), indicating that less heterogenous 'OH was generated at the cathode surface with raising pH to oxidize the by-products formed, which was detected as the main oxidant. However, the cathode rapidly lost performance in consecutive cycles and showed a relatively good reusability. LC-QQQ-MS analysis of treated solutions disclosed the production of 12 by-products and a feasible reaction degradation sequence for thiamphenicol was suggested.

The hetero-EF destruction of the  $\beta$ -lactams amoxicillin with an ionicliquid-derived N-doped carbon cathode (Ko et al., 2018) and cefazolin with a Cu,Fe nano layered double hydroxide multiwalled CNTs|CF cathode (Ghasemi et al., 2020) has been reported. In the latter case, 80 mL of airsaturated solutions with 20 mg L<sup>-1</sup> antibiotic and 0.050 M Na<sub>2</sub>SO<sub>4</sub> were treated at pH 3.0–12.0 with a stirred cell like of Fig. 3a by applying a I = 400 mA during 100 min. Again, it was found a drop of the antibiotic abatement at higher pH: 95% for pH 3.0, 88% for pH 6.0, 64% for pH 9.0, and 50% for pH 12.0. The authors remarked the potential use of the system at pH near neutral pH 6.0, determining a higher degradation of 91% with 0.075 M Na<sub>2</sub>SO<sub>4</sub>. The generation of the main oxidizing agents like 'OH and O<sub>2</sub>' was corroborated. Additionally, 11 by-products were MSidentified by GC–MS.

The same behavior with the pH change has been found for the hetero-EF process of the fluoroquinolone ciprofloxacin in sulfate medium with cathodes of Ce<sub>3</sub>ZrFe<sub>4</sub>O<sub>14-x</sub>|CF (Li et al., 2019), non-iron NiMn<sub>2</sub>O<sub>4</sub>|CF (Sun et al., 2019), ferrocene-graphene oxide|GF (Divyapriya et al., 2018a, 2018b), FeMn binary oxide|GF (Huang et al., 2021b), FeOCl@MoS<sub>2</sub>|GF Liu et al., 2021), and FeIIFeIII layered double hydroxide|CF (Yao et al., 2021). For instance, Divyapriya et al. (2018a) used a three-electrode undivided tank reactor with a Pt anode and an Ag|AgCl electrode reference for the degradation of 150 mL of air-saturated solutions with 10 mg L<sup>-1</sup> antibiotic with 0.050 M Na<sub>2</sub>SO<sub>4</sub> within a pH range of pH 3–9 and at  $E_{cat} = -0.75$  to -1.50 V. While complete degradation was achieved after 30 min at pH 3.0 and  $E_{cat} = -1.50$  V with  $k_1 = 0.222$  min<sup>-1</sup>, a longer



**Fig. 15.** (a,c) Time course for normalized antibiotic concentration and pseudo-first-order kinetic analysis (inset) obtained for the homo-EF and hetero-EF treatments of 500 mL of an air-saturated solution with 50 mg L<sup>-1</sup> of (a,b) levofloxacin or (c,d) trimethoprim in 0.050 M Na<sub>2</sub>SO<sub>4</sub> with 0.2 mM Fe<sup>2+</sup>, 50 mg L<sup>-1</sup> Fe<sub>3</sub>O<sub>4</sub>, or 50 mg L<sup>-1</sup> Pd-Fe<sub>3</sub>O<sub>4</sub> as catalyst at pH 3.0 using a stirred tank reactor with a Ti|RuO<sub>2</sub>-IrO<sub>2</sub> anode and a carbon felt cathode at I = 200 mA. (b,d) Effect of I over the percentages of TOC removal and mineralization current efficiency for the mineralization of the above antibiotic solutions with 50 mg L<sup>-1</sup> Pd-Fe<sub>3</sub>O<sub>4</sub> or Pd-Fe<sub>3</sub>O<sub>4</sub> at pH 3.0. *t*-butanol (DMPO)-'OH and DMPO-'H determined after 30 min of electrolysis of solutions with 0.050 M Na<sub>2</sub>SO<sub>4</sub> and 50 mg L<sup>-1</sup> of Fe<sub>3</sub>O<sub>4</sub> or Pd-Fe<sub>3</sub>O<sub>4</sub> at pH 3.0. *t*-butanol (TBA) was used as scavenger of 'OH. Adapted from Zhou et al. (2018).

time of 160 min with a smaller  $k_1 = 0.030 \text{ min}^{-1}$  was required for pH 6, and even greater of >180 min with  $k_1 = 0.014 \text{ min}^{-1}$  for pH 9 (see Table 5). A good reusability of the cathode was found over 5 consecutive cycles, the amount of 'OH generated was quantified, and 6 by-products were identified by LC-MS. Similarly, Huang et al. (2021b) reported a quick degradation up to 95% in 30 min and 94% TOC removal with a high MCE of 20% for the remediation of 350 mL of an O<sub>2</sub>-saturated solution with 25 mg L<sup>-1</sup> antibiotic with 0.050 M Na<sub>2</sub>SO<sub>4</sub> and 300 mg of the FeMn binary oxide at pH 7.0. The trials were performed with a stirred tank reactor like of Fig. 2a with a Ti|RuO<sub>2</sub>-IrO<sub>2</sub> anode at  $j = 2 \text{ mA cm}^{-2}$  (see Table 5). The

excellent performance of this simple iron functionalized cathode allowed to obtain the same degradation rate at pH 3.0 and 7.0, only dropping to 81% antibiotic removal at the alkaline pH 10.

It is noticeable the article of Yang et al. (2020) comparing the hetero-EF with a Fe<sup>II</sup>Fe<sup>III</sup> layered double hydroxide |CF cathode and the homo-EF with a CF cathode and 0.20 mM Fe<sup>2+</sup> as catalyst of 145 mL of air-saturated solutions with 0.20 mM of the fluoroquinolone of loxacin 0.050 M Na<sub>2</sub>SO<sub>4</sub> at pH 3.0–9.0- in pure water, The cell was a stirred tank reactor like of Fig. 3a containing a powerful BDD anode and a j = 12.5 mA cm<sup>-2</sup> was provided for 480 min. For the hetero-EF process, an extraordinary rapid total

#### Table 5

Selected results reported for the heterogeneous electro-Fenton treatment with iron functionalized cathodes of several antibiotics in synthetic and real wastewaters.

Antibiotic	System (anode/cathode)	Experimental remarks	Best results	Ref.
Synthetic solutions Amphenicols				
Chloramphenicol	Like of Fig. 3a (Pt/Fe  N-graphene)	15 mL of O <sub>2</sub> -saturated solution with 25 mg L <sup>-1</sup> antibiotic in pure water, 0.050 M Na <sub>2</sub> SO <sub>4</sub> , pH 1-13, i = 2 mA cm <sup>-2</sup> 180 min	Degradation: 98% (pH 1), 92% (pH 4), 89% (pH 7), 90% (pH 10), and 82% (pH 13). Good reproducibility in 5 successive cycles	Song et al. (2021)
Thiamphenicol	Like of Fig. 3a (Graphite/SAFe@HSC <sup>a</sup> )	50 mL of O <sub>2</sub> -saturated solution with 20 mg L <sup>-1</sup> antibiotic in pure water, 0.1 M K <sub>2</sub> SO <sub>4</sub> , pH = 3–11, j = 20 mA cm <sup>-2</sup> , 60 min.	Similar total degradation at pH 3-11. TOC decay: 68% (pH 3), 61% (pH 5), 53% (pH 7), 50% (pH 9), and 44% (pH 11). Detection of OH as main oxidant. Relatively good reusability. Identification of 12 by-products by LC-QQQ-MS. Reaction sequence proposed.	Zhang et al. (2022)
β-lactams Cefazolin	Like of Fig. 3a (Pt/Cu,Fe-NLDH-CNTs  CF)	80 mL of air-saturated solution with 20 mg L <sup>-1</sup> antibiotic in pure water, 0.050 M Na <sub>2</sub> SO <sub>4</sub> , pH 3.0-12.0, 25 °C, $I = 400$ mA, 100 min.	Degradation: 95% (pH 3.0), 88% (pH 6.0), 64% (pH 9.0), and 50% (pH 12.0). At pH 6.0, higher degradation of 91% using 0.075 M Na <sub>2</sub> SO <sub>4</sub> . Detection of 'OH and O <sub>2</sub> ' as main oxidants. 11 by-products identified by GC-MS.	Ghasemi et al. (2020)
Fluoroquinolones Ciprofloxacin	Three-electrode tank reactor (Pt/Ferrocene-GO GF) and Ag AgCl reference Like of Fig. 3a (Tti RuO <sub>2</sub> -IrO <sub>2</sub> /FeMn binary oxide GF)	150 mL of air-saturated solution with 10 mg L <sup>-1</sup> antibiotic in pure water, 0.050 M Na <sub>2</sub> SO <sub>4</sub> , pH 3- 9, $E_{cat} = -0.75$ to $-1.50$ V, 180 min. 350 mL of O <sub>2</sub> -saturated solution with 25 mg L <sup>-1</sup> antibiotic in pure water, 0.050 M Na <sub>2</sub> SO <sub>4</sub> , 150-600 mg of binary oxide,	Total degradation and $k_1$ at $E_{cat} = -1.50$ V: 30 min and 0.222 min <sup>-1</sup> (pH 3), 160 min and 0.030 min <sup>-1</sup> (pH 6), and > 180 min and 0.014 min <sup>-1</sup> (pH 9). Good reusability over 5 consecutive cycles. Quantification of 'OH generated. 6 intermediates detected by LC-MS. 95% degradation in 30 min and 94% TOC removal with 20% MCE in 120 min for the optimum conditions of 300 mg binary oxide, pH 7, and $i = 2$ mA cm <sup>-2</sup> . Similar	Divyapriya et al. (2018a) Huang et al. (2021b)
Ofloxacin	Like of Fig. 3a (BDD/Fe <sup>ll</sup> Fe <sup>lT</sup> LDH <sup>b</sup> , CF)	pH 3–10, $j = 1-4$ mA cm <sup>-2</sup> , 120 min. 230 mL of air-saturated solution with 0.1 mM antibiotic in pure water, 0.050 M Na <sub>2</sub> SO <sub>4</sub> , 0.20 mM Fe <sup>2+</sup> for homo-EF with a CF cathode, pH 3.0 or 7.0, $j = 3.1-12.5$ mA cm <sup>-2</sup> , 480 min.	degradation at pH 3, dropping to 81% at pH 10. For hetero-EF at pH 7.0 and 12.5 mA cm <sup>-2</sup> , 20 min for total degradation, $k_1 = 0.19 \text{ min}^{-1}$ , and 100% mineralization with 1.3% MCE and EC <sub>TOC</sub> = 3.3 kWh (g TOC) <sup>-1</sup> . Low reusability over 6 cycles. Quantification of 'OH produced. For homo-EF at pH 3.0 and 12.5 mA cm <sup>-2</sup> , 50 min for total degradation, $k_1 = 0.09 \text{ min}^{-1}$ , and 83% mineralization with 1.1% MCE and EC <sub>TOC</sub> = 3.9 kWh (g TOC) <sup>-1</sup> . Identification of 9 by-products by GG-MS and HPLC, F <sup>-</sup> , NO <sub>3</sub> , and NH <sub>4</sub> <sup>+</sup> . Reaction sequence proposed.	Yang et al. (2020)
Sulfonamides Sulfamethoxazole	Like of Fig. 3a (Ti4O7/Fe <sup>II</sup> Fe <sup>III</sup> LDH CF)	145 mL of air-saturated solution with 0.20 mM antibiotic in pure water, 0.050 M Na <sub>2</sub> SO <sub>4</sub> , 0.20 mM Fe <sup>2+</sup> for homo-EF with a CF cathode, pH 3.0-9.0, j = 7.5 mA cm <sup>-2</sup> , 480 min.	Degradation at 120 min by AO- H <sub>2</sub> O <sub>2</sub> at pH 3.0, 6.0, and 9.0: 96%, 86%, and 84%. Total degradation for homo- and hetero-EF: 60 min (pH 3.0), 120 min (pH 6.0), and 240 min (pH 9.0). Greater TOC abatement for hetero- EF at 480 min: 95% (pH 3.0), 90% (pH 6.0), and 88% (pH 9.0). Inhibition of the luminescence of <i>Vibrio fischeri</i> . Detection of 18 by-products by GC–MS and HPLC. Reaction sequence proposed.	Ganiyu et al. (2018a)
Tetracyclines	Like of Fig. 3a (Pt/Cu <sub>2</sub> O@ CNTs CF)	200 mL of air-saturated solution with 20 mg L <sup><math>-1</math></sup> antibiotic in pure water, 0.050 M Na <sub>2</sub> SO <sub>4</sub> , pH 3- 11, <i>j</i> = 6–15 mA cm <sup><math>-2</math></sup> , 75 min.	Total and similar degradation rate within the pH 3–9, decreasing to 87% at pH 11 for 12 mA cm <sup>-2</sup> . Detection of 'OH as main oxidant. Identification of 12 by-products by LC-QQQ-MS, $SO_4^{2-}$ , $NO_3^{-}$ , and $NH_4^+$ . Reaction sequence proposed.	Mao et al. (2021)
Tetracycline	Flow-through filter-press cell (Ti/Fe <sub>2</sub> O <sub>3</sub> -CNTs)	50 mL of O <sub>2</sub> -saturated solution with 0.04 mM antibiotic in pure water, 10 mM Na <sub>2</sub> SiO <sub>3</sub> , pH 3.6- 9.4, FR = 1.5 mL min <sup>-1</sup> , $E_{cell} = 2.5 V, I = 2 mA$ , 180 min.	Total and similar rate degradation at pH 3.6 and 6.8, decreasing to 87% at pH 9.4. Identification of 10 by-products by LC-MS. Reaction sequence proposed.	Guo et al. (2021)
Real wastewaters Sulfonamides				
Sulfadimethoxine Sulfathiazole	Like of Fig. 3a (BDD/Fe,N,S-SS)	200 mL of air-saturated pharmaceutical WWTP effluent, 0.050 M Na $_2$ SO $_4$ , pH 3–9,	Sulfathiazole degradation and wastewater TOC removal at 10 mA cm $^{-2}$ : 92% and 67% (pH 3.0), 80% and 57%	Zhu et al. (2022)

(continued on next page)

#### Table 5 (continued)

Antibiotic	System (anode/cathode)	Experimental remarks	Best results	Ref.	
Sulfodiazine		$j = 2-15 \text{ mA cm}^{-2}$ , 180 min.	(pH 5.0), 65% and 50% (pH 7.0), and 57% and 46% (pH 9.0) Identification of OH, $^{1}O_{2}$ , and $O_{2}^{2}$ as main oxidants. Detection of 6 aromatic derivatives by LC-QQQ-MS		

<sup>a</sup> SAFe@HSC: Sea-urchin-shaped carbon-anchored single-atom iron.

 $^{\rm b}~{\rm Fe}^{\rm II}{\rm Fe}^{\rm II}$  LDH |CF:  ${\rm Fe}^{\rm II}{\rm Fe}^{\rm II}$  layered double hydroxide multiwall |CF.

degradation with  $k_1 = 0.19 \text{ min}^{-1}$  was achieved in only 20 min, and at the end of the assay, 100% mineralization with 1.3% MCE and EC<sub>TOC</sub> = 3.3 kWh (g TOC)<sup>-1</sup> was determined (see Table 5). This points to consider that the surface Fe<sup>3+</sup>/Fe<sup>2+</sup> pair originates very rapidly high amounts of heterogeneous 'OH from the heterogeneous Fenton's reaction (22), which were quantified. However, the cathode was quickly coated by the byproducts formed and lost reusability in 6 cycles. This 'OH generation clearly upgraded that produced in the homo-EF process at the optimum pH 3.0, which required a much longer time of 50 min with  $k_1 = 0.09 \text{ min}^{-1}$  for complete degradation, finally yielding 83% mineralization with 1.1% MCE and EC<sub>TOC</sub> = 3.9 kWh (g TOC)<sup>-1</sup>. For this compound, 9 byproducts were identified by GC–MS and HPLC, alongside the loss of F<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, and NH<sub>4</sub><sup>+</sup> ion, and a reaction sequence was proposed.

Sulfamethoxazole has been the sulfonamide molecule selected as model to study the hetero-EF treatment with cathodes of Fe<sup>II</sup>Fe<sup>III</sup> layered double hydroxide|CF (Ganiyu et al., 2018a), Cu<sub>2</sub>O@CNTs|CF (Mao et al., 2021), and Cu-doped Fe<sub>2</sub>O<sub>3</sub> nanoparticles (Qi et al., 2022). The work of Ganiyu et al. (2018a) was centered on a comparative study by AO-H<sub>2</sub>O<sub>2</sub> with a CF cathode without catalyst, homo-EF with the same cathode and 0.20 mM Fe<sup>2+</sup>, and the hetero-EF with the prepared cathode. The experiments were carried out with 145 mL of air-saturated solutions with 50 mg  $L^{-1}$  antibiotic in 0.050 M Na<sub>2</sub>SO<sub>4</sub> at pH 3.0–9.0 using a stirred tank reactor like of Fig. 3a with a powerful non-active Ti<sub>4</sub>O<sub>7</sub> anode at j = 7.5 mA cm<sup>-2</sup>. Fig. 16a-16c highlight the decay of the degradation rate when pH increased gradually from 3.0 to 9.0 in the order: AO- $H_2O_2$  < homo-EF ~ hetero-EF. For instance, at the better pH of 3.0, total degradation was obtained at 240, 60, and 60 min, respectively (see Table 5). In contrast, Fig. 16d discloses the superior mineralization reached by the hetero-EF process after 480 min of electrolysis, with a TOC removal of 95% at pH 3.0, which slightly decayed down to 90% at pH 6.0 and 88% at pH 9.0. This makes in evidence again, as in the above case of ofloxacin, the powerful behavior of the Fe<sup>II</sup>Fe<sup>III</sup> layered double hydroxide|CF cathode to produce heterogeneous 'OH at its surface, which became operative in acid and alkaline conditions. The faster mineralization rate at pH 3.0 was also reflected in the more rapid inhibition of the luminescence of the marine bacteria Vibrio fischeri, as can be seen in Fig. 16e. Fig. 16f depicts that the ultimate oxalic, glycoxylic, oxamic, maleic, and pyruvic were rapidly formed and slowly practically destroyed during 540 min of the hetero-EF process at pH 6.0. Moreover, 18 by-products were identified by GC-MS and HPLC, and a reaction sequence was suggested.

Mao et al. (2021) studied the hetero-EF process of 200 mL of airsaturated solutions with 20 mg L<sup>-1</sup> sulfamethoxazole and 0.050 M Na<sub>2</sub>SO<sub>4</sub> at a wide pH interval of pH 3–11 using a stirred tank reactor like of Fig. 3a with a Pt anode at j = 6-15 mA cm<sup>-2</sup> lasting 75 min. At the optimum j = 12 mA cm<sup>-2</sup>, the antibiotic was completely degraded at pH 3–9, decreasing its removal up to 84% at pH 11 (see Table 5). These authors detected the generation of 'OH as main oxidant and identified 12 by-products by LC-QQQ-MS, as well as the generation of SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, and NH<sub>4</sub><sup>+</sup> ions. Fig. 17 shows the reaction sequence for sulfamethoxazole (1) mineralization proposed from the by-products detected. The initial 'OH attack over 1 gives either the oxidation of its -NH<sub>2</sub> to a nitro group to form the compound 2 or the demethylation followed by hydroxylation of the isoazole ring to originate the compound 3. Subsequent cleavage of the sulfonamide bond of 2 yields the loss of the benzene ring to produce the compound 4 or the direct release of 3-amino-5-methylisoxazole (5). Compound 3 evolves via breaking of the isoazole group generating the compound 6, followed by the cleavage of the SN bond giving rise to the compound 7. Further oxidation of the above intermediates yields the sulfoxide compound 8, which is then transformed into the aliphatic S-compound 9, nitrosobenzene (10), and the sulfone derivative 11. The cleavage of these by-products finally leads to the ultimate acetic and formic acids that are mineralized to CO<sub>2</sub>. It is noticeable that the reaction sequences for amoxicillin in Fig. 8, ciprofloxacin in Fig. 10, tetracycline in Fig. 14, and sulfamethoxazole in Fig. 17 are proposed depending on the EF method used and the analytical techniques applied (GC-MS, HPLC, LC-MS, and/or ionic chromatography, and their varieties). So, the suggested sequence can substantially change if other intermediates are detected by varying the process and analysis performed. The generated by-products always follow as degradative sequence: antibiotic  $\rightarrow$  aromatic/heteroaromatic/cyclic derivatives  $\rightarrow$  short-linear aliphatic acids  $\rightarrow CO_2$  + released inorganic ions. As general rule, the 'OH formed from Fenton's reaction originates the conversion of the antibiotic up to the aliphatic acids, whereas the destruction of the latter, highly recalcitrant, is rather due to the action of the heterogeneous M('OH) formed at the anode surface where the BDD electrode is preferable because it is the most powerful anode known (Brillas and Garcia-Segura, 2020; Brillas, 2022).

The hetero-EF treatment of tetracycline has been investigated with cathodes of FeOCl-CNTs (Li et al., 2020), Fe<sub>2</sub>O<sub>3</sub>-CNTs (Guo et al., 2021), and FeOCl-carbon cloth (Tang et al., 2021). Guo et al. (2021) used a flowthrough cell with a Ti anode at FR = 1.5 mL min<sup>-1</sup> to degrade 50 mL of O<sub>2</sub>-saturated solutions with 0.04 mM antibiotic and 10 mM Na<sub>2</sub>SiO<sub>3</sub> as electrolyte at pH 3.6–9.4. An  $E_{cell}$  = 2.5 V, equivalent to a I = 2 mA, was provided during 180 min. The antibiotic was slowly removed with total and similar rate degradation at pH 3.6 and 6.8, dropping to 87% at pH 9.4 (see Table 5). LC-MS analysis of electrolyzed solution allowed the identification of 10 by-products, suggesting a possible reaction sequence.

Few authors have considered the comparative study of various antibiotics by hetero-EF with functionalized cathodes. The behavior of sulfadiazine and ofloxacin in sulfate medium with a non-iron N,S-exfoliated graphene CF cathode was investigated by Yang et al. (2021), whereas that of sulfadiazine, sulfathiazole, and sulfadimethoxine in sulfate matrix and in a pharmaceutical WWTP effluent with a Fe,N,S-SS cathode has been reported by Zhu et al. (2021) and Zhu et al. (2022), respectively. The article of Zhu et al. (2021) electrolyzed 100 mL of an air-saturated solution with 10 mg  $L^{-1}$  of each antibiotic in 0.050 M Na<sub>2</sub>SO<sub>4</sub> at pH 3.0 with a stirred tank reactor with a BDD anode at I = 50 mA. Overall degradation was obtained for increasing times of 25 min for sulfadiazine, 40 min for sulfathiazole, and 55 min for sulfadimethoxine, with a TOC abatement at 60 min of 53%, 43%, and 41%, respectively. The same trend was further described by Zhu et al. (2022) for the same system and treating 200 mL of a pharmaceutical WWTP effluent after adding 0.050 M Na<sub>2</sub>SO<sub>4</sub> at pH 3.0–9.0, by applying a i = 2-15 mA cm<sup>-2</sup> for 180 min. Fig. 18a and b depict the abatement of the more easily degradable sulfadiazine and the wastewater TOC at the different pH values tested for  $i = 10 \text{ mA cm}^{-2}$ . As expected, these parameters slowed down with raising.

pH, showing a degradation of 92%, 80%, 65%, and 57% at pH 3.0, 5.0, 7.0, and 9.0, respectively, with corresponding TOC reduction of 67%, 57%, 50%, and 46% (see Table 5). These results confirm again an acceptable performance of the system at near neutral pH. It is noticeable the effort made to identify the main oxidants using *t*-butanol for 'OH, furfuryl alcohol for  ${}^{1}O_{2}$ ,



**Fig. 16.** Variation of sulfamethoxazole concentration with electrolysis time for the destruction of 145 mL of air-saturated solutions with 50 mg L<sup>-1</sup> (0.20 mM) antibiotic in 0.050 M Na<sub>2</sub>SO<sub>4</sub> at different pH values using a stirred tank reactor with a Ti<sub>4</sub>O<sub>7</sub> anode by means of (a) AO-H<sub>2</sub>O<sub>2</sub> with a carbon-felt cathode, (b) homo-EF with 0.20 mM Fe<sup>2+</sup> and a carbon-felt cathode, and (c) hetero-EF with a Fe<sup>II</sup>Fe<sup>III</sup> LDH|CF cathode at *j* = 7.5 mA cm<sup>-2</sup>. (d) Percent of TOC removal after 480 min of the above trials. (e) Percentage of inhibition after 15 min of exposure to the luminescence of *Vibrio fischeri* by hetero-EF. (f) Evolution of generated carboxylic acids during the hetero-EF process at pH 6.0. Adapted from Ganiyu et al. (2018a).

and *p*-benzoquinone for  $O_2^-$  as scavengers (see Fig. 18c). Fig. 18d-18e highlight the clear DMPO-'OH and TEMP-<sup>1</sup>O<sub>2</sub> spectra recorded by EPR for the two former radicals, whereas Fig. 18f show a non-clear DMPO-O<sub>2</sub> spectrum. A total of 6 aromatic derivatives were identified by LC-QQQ-MS.

The research of hetero-EF with iron functionalized cathodes corroborates, in most cases, its good effectiveness to destroy antibiotics at neutral pH, although it offers better performance at pH 3.0, which can be even superior to that of homo-EF. Sophisticated cathodes have been tested for this purpose, which are doubtful fpr their application in practice. Simpler materials like FeMn binary oxide or Fe<sub>2</sub>O<sub>3</sub>-CNTs should be better checked in the next future to corroborate their oxidation ability over a large variety of antibiotics, preferentially in real wastewaters using pilot plants to open the way to industrial scale.

#### 4.3. Combined electro-Fenton processes

This section examines the hybrid and sequential processes of EF developed to destroy antibiotics. Coupling with absorption and membranes, and the use of microbial EF, are described as hybrid methods, whereas the sequential ones consider the post-treatment with adsorption or biological processes. Table 6 lists selected results obtained for these combined EF treatments.

#### 4.3.1. Hybrid processes

Chen et al. (2019b) proposed a hybrid EF/absorbent method to remove sulfathiazole, schematized in Fig. 19a. The cell was a stirred tank reactor with a Ni anode and a graphite cathode, and an absorbent membrane



Fig. 17. Proposed reaction sequence for sulfamethoxazole mineralization in sulfate medium by hetero-EF with a functionalized Cu<sub>2</sub>O nanoparticles anchored on 3D bifunctional CNTs|CF foam cathode. Adapted from Mao et al. (2021).

with zero-valent iron (ZVI) nanoparticles or spongy ZVI between them. Fig. 19a highlights that the antibiotic crossed the absorbent membrane to be destroyed at the cathode surface where  $H_2O_2$  is generated and the oxidants 'OH and HO<sub>2</sub> are formed with the Fe<sup>2+</sup> produced from ZVI in the membrane.

Air-saturated solutions of 400 mL containing 1.50 mg L<sup>-1</sup> antibiotic, 0.050 M Na<sub>2</sub>SO<sub>4</sub>, and 1 g L<sup>-1</sup> of each separated catalyst, at pH 5 and 15 °C, were treated at j = 7.5 mA cm<sup>-2</sup>. A synergistic effect was found due to the iron converted into Fe<sup>2+</sup> in the membrane, much superior for

spongy ZVI giving a total TOC decay in 160 min (see Fig. 19b and Table 6). Fig. 19c shows that greater amount of OH was produced from spongy ZVI. LC-MS/MS revealed the generation of 9 cyclic derivatives and a reaction sequence was suggested.

Jiang et al. (2018, 2021) used a hybrid EF with membrane method operating in continuous mode, depicted in Fig. 20a, for the degradation of florfenicol and a mixture of antibiotics, respectively. The dead-end membrane cell was equipped with a Pt anode, a carboxylated carbon nanotubes intercalated reduced graphene oxide doped with iron oxide



**Fig. 18.** Influence of pH over (a) the normalized sulfathiazole concentration and (b) normalized TOC of 200 mL of an air-saturated real pharmaceutical wastewater containing this antibiotic with 0.050 M Na<sub>2</sub>SO<sub>4</sub> using a stirring tank reactor with a BDD anode and a Fe,N,S co-doped cathode onto SS by applying  $a j = 10 \text{ mA cm}^{-2}$ . (c) Effect of 50 mM of scavenger (BTA for 'OH, furfuryl alcohol for <sup>1</sup>O<sub>2</sub>, and *p*-benzoquinone for O<sup>5</sup><sub>2</sub>) over the antibiotic degradation after 60 min of the assay at pH 3.0. EPR spectra recorded under the latter conditions for: (d) 'OH, (e) <sup>1</sup>O<sub>2</sub>, and (f) O<sup>5</sup><sub>2</sub> using 100 mM DMPO or 50 mM 2,2,6,6-tetramethylpiperidine (TEMP). Adapted from Zhu et al. (2022).

membrane, and an Ag|AgCl reference electrode. Jiang et al. (2021) degraded a mixture of 1.0 mg L<sup>-1</sup> of each antibiotic with 0.050 M Na<sub>2</sub>SO<sub>4</sub> at pH 7.0, upon a pressure of 2.5 bar and 25 °C, by providing an  $E_{cat} = -0.6$  V. Fig. 20b shows the percentage of excellent antibiotic degradations determined in this hybrid treatment. From this figure and data of Table 6, one can infer a relative larger reactivity for the degradation of several antibiotic families with 'OH following the sequence: sulfonamides (78% for sulfadiazine and 83% for sulfamethoxazole) ~ fluoroquinolones (80% for ofloxacin) < amphenicols (94% for florfenicol) <  $\beta$ -lactams (100% for amoxicillin, ampicillin, and cefalexin). Note that all these antibiotics are negatively charged in the medium, and the effectiveness of the procedure should then be confirmed for positively charged antibiotics like chloramphenicol and thiamphenicol.

Several hybrid microbial EF processes have been proposed for the destruction of the macrolide erythromycin (Li et al., 2020c), sulfamethoxazole and norfloxacin (Wang et al., 2019), sulfamethoxazole (Li et al., 2020b), tetracycline (Soltani et al., 2021), and tetracycline and sulfaquinoxaline (Hassan et al., 2020). Fig. 21a and b illustrate the setup of two successful divided two-electrode cells with electricity generation proposed by Li et al. (2020c) and Hassan et al. (2020) for hybrid microbial EF, respectively. In Fig. 21a, the antibiotic was oxidized in both compartments (anolyte and catholyte) separated by a cation exchange membrane. The anolyte contained 76.3 mL of 50  $\mu$ g L<sup>-1</sup> antibiotic in 1 g L<sup>-1</sup> acetate and 50 mM Table 6

Selected results determined for the removal of several antibiotics by hybrid and sequential electro-Fenton processes.

Antibiotic	System (anode/cathode)	Experimental remarks	Best results	Ref.		
Hybrid electro-Fenton/absorbent Sulfonamides						
Sulfathiazole	Fig. 19a ZVI NPs, spongy ZVI catalysts (Ni/graphite)	400 mL of air-saturated solution with 1.50 mg L <sup>-1</sup> antibiotic in pure water, 0.050 M Na <sub>2</sub> SO <sub>4</sub> , 1 g L <sup>-1</sup> catalyst, pH 5, 15 °C, $j = 7.5$ mA cm <sup>-2</sup> , 330 min.	Total TOC removal: 160 min (spongy ZVI), 240 min (ZVI NPs), 330 min (no catalyst). Quantification of OH. 9 cyclic derivatives detected by LC-MS/MS. Reaction sequence proposed.	Chen et al. (2019b)		
Amoxicillin Ampicillin Cefalexin Ofloxacin Sulfadiazine Sulfamethoxazole Florfenicol	Fig. 20a (Pt/RGO-CNTs-Fe) and Ag AgCl reference	Continuous O <sub>2</sub> -saturated solution with a mixture of 1.0 mg L <sup><math>-1</math></sup> of each antibiotic in pure water, 0.050 M Na <sub>2</sub> SO <sub>4</sub> , pH 7.0, pressure 2.5 bar, 25 °C, $E_{cat} = -0.6$ V.	Degradation: 100% for amoxicillin, ampicillin, and cefalexin, 80% for ofloxacin, 78% for sulfadiazine, 83% for sulfamethoxazole, and 94% for florfenicol.	Jiang et al. (2021)		
Hybrid microbial elect Macrolides	ro-Fenton					
Erythromycin	Fig. 21b (carbon cloth/CNT γ-FeOOH SS) and a cation exchange membrane	76.3 mL of anolyte and catholyte. Anolyte: 50 $\mu$ g L <sup>-1</sup> antibiotic in 1 g L <sup>-1</sup> acetate and 50 mM phosphate buffer. Catholyte: O <sub>2</sub> -saturated solution with 50 $\mu$ g L <sup>-1</sup> antibiotic in 50 mM phosphate buffer, pH 7, 30 °C, 48 h.	89% degradation and 87% COD removal. Maximum power output and current density: 0.193 W m <sup>-2</sup> and 0.583 A m <sup>-2</sup> ( $R = 1000 \Omega$ ),	Li et al. (2020c)		
Tetracycline Sulfaquinoxaline	Fig. 21b (CF/CF with SrFe <sub>12</sub> O <sub>19</sub> catalyst) and a cation exchange membrane	250 mL of anolyte and catholyte. Anolyte: 1 g L <sup><math>-1</math></sup> acetate and growth medium. Catholyte: Air-saturated solution with a mixture of 10 mg L <sup><math>-1</math></sup> of each antibiotic in pure water with phosphate, 0.3 g L <sup><math>-1</math></sup> of catalyst or FeSO <sub>4</sub> ·7H <sub>2</sub> O, pH 3–7, 24 °C, 24 h.	With the catalyst at pH 3 and $R = 1000 \Omega$ , 86–88% degradation of all antibiotics in 17 h, 100% in 24 h. Coulombic efficiency of 33-43% and maximum power output of 136.4 mW m <sup>-2</sup> . Lower degradation of 71–75% at pH 5, and 58–63% at pH 7. Using FeSO <sub>4</sub> /7H <sub>2</sub> O at pH 3, 80% degradation in 24 h.	Hassan et al. (2020)		
Tetracycline	Fig. 21b (CF/CF) and a cation exchange membrane	450 mL of anolyte and catholyte. Anolyte: anaerobic sludge + synthetic feeding wastewater + salts + phosphate buffer, pH 7 (1000–10,000 mg L <sup><math>-1</math></sup> COD). Catholyte: Air-saturated solution with 10 mg L <sup><math>-1</math></sup> antibiotic in pure water, 0.10 M K <sub>2</sub> SO <sub>4</sub> , 2–10 mg L <sup><math>-1</math></sup> FeSO <sub>4</sub> , pH 3–7, 30 °C, 24 h.	Degradation with 2000 mg L <sup>-1</sup> COD at pH 3: 99% for short-circuit ( $R = 0 \Omega$ ), 90% for open circuit ( $R = 1000 \Omega$ ). 97–99% degradation between 1000 and 10,000 mg L <sup>-1</sup> of anodic COD in short-circuit at pH 3, 91% at pH 5, and 88% at pH 7. Maximum voltage, current density, and power density at pH 3 and 10,000 mg L <sup>-1</sup> of anodic COD: 322 mV, 1195 mA m <sup>-2</sup> , and 141.60 mW m <sup>-2</sup> .	Soltani et al. (2021)		
Sequential adsorption- Sulfonamides	electro-Fenton					
Sulfamethiazole	Adsorption: stirred vessel with pellet carbonaceous material. EF: Like of Fig. 3a Iron-perlite catalyst (BDD/CF)	Adsorption: 25 mL of 0.1: 25 g of adsorbent per mol of 25 mg L <sup>-1</sup> antibiotic in pure water, 25 °C, 240 min. Desorption with 15 mL of acetonitrile, 25 °C, 240 min. EF: 150 mL of air-saturated solution with 25 mg L <sup>-1</sup> of antibiotic in pure water, 0.10 M Na <sub>2</sub> SO <sub>4</sub> , pH 3.0, 25 °C, <i>I</i> = 100 mA, 240 min.	Adsorption: 95% antibiotic removed. Overall desorption in 3 consecutive cycles. Total degradation and $k_1$ : 240 min and 0.019 min <sup>-1</sup> (AO-H <sub>2</sub> O <sub>2</sub> ), 20 min and 0.300 min <sup>-1</sup> (homo-EF with Fe <sup>2+</sup> ), 10 min and 0.403 min <sup>-1</sup> (hetero-EF with iron-perlite). Detection of 4 carboxylic acids by HPLC, NO <sub>3</sub> <sup>-</sup> , NO <sub>2</sub> <sup>-</sup> , and NH <sub>4</sub> <sup>+</sup> .	Puga et al. (2020a)		
Sulfamethoxazole	Adsorption: stirred vessel EF: Stirred cubic cell (BDD/CF)	Adsorption; 50 mL of 50 mg L <sup>-1</sup> antibiotic and 0.1 g biochar, stirring at 150 rpm, pH 5.6, 25 °C, 180 min. EF: 150 mL of air-saturated solution with 0.1 g biochar in 0.01 M Na <sub>2</sub> SO <sub>4</sub> , 0.29 mM Fe <sup>2+</sup> , pH 3.0, $I = 300$ mA, 360 min.	Adsorption: 100% antibiotic removed. Low reusability of the adsorbent. EF: 88% of antibiotic decay for adsorbent regeneration. Reusability during 6 consecutive cycles.	Acevedo-García et al. (2020)		
Nitroimidazoles Metronidazole	EF: Like of Fig. 3a (Pt/GF) Biological: Stirred tank reactor	250 mL of air-saturated solution with 100 mg L <sup>-1</sup> antibiotic in pure water, 0.050 M Na <sub>2</sub> SO <sub>4</sub> , 0.1 mM Fe <sup>2+</sup> , pH 3.0, 20 °C, j = 0.07 mA cm <sup>-2</sup> , 120 min. Biological: 200 mL of pre-treated solution, 0.5 g L <sup>-1</sup> of activated sludge, pH 7, stirring at 150 rpm, 28 °C, 504 h.	EF; total degradation in 20 min. 16% and 32% mineralization after 60 and 120 min, respectively. Increase of BDO <sub>5</sub> /COD from 0 to 0.44 in 60 min or 0.60 in 120 min. Biological: 89% total mineralization using pre-treated EF solutions at 60 or 120 min. 5 heterocyclic derivatives identified by LC-MS/MS, NO <sub>3</sub> <sup>-</sup> , and NH <sup>4</sup> <sub>4</sub> <sup>+</sup> .	Aboudalle et al. (2018)		

phosphate buffer (pH 7) with a carbon cloth anode, whereas the catholyte was an O<sub>2</sub>-saturated solution with 50  $\mu g$  L $^{-1}$  antibiotic in 50 mM phosphate buffer (pH 7) and a CNT| $\gamma$ -FeOOH|SS cathode. The system worked at 30 °C

during 48 h, attaining 89% degradation and 87% COD removal. The electrons circulating through the external circuit with a resistance of 1000  $\Omega$  generated a maximum power output of 0.193 W m<sup>-2</sup> and current density



**Fig. 19.** (a) Sketch of the experimental setup and proposed mechanism for the hybrid EF/absorbent process of sulfathiazole using a stirred tank reactor with a Ni anode, a graphite cathode, and a spongy zero-valent iron (ZVI) between them as particle catalytic electrodes. (b) Normalized concentration vs. electrolysis time for the no catalyst treatment and the processes with ZVI NPs and spongy ZVI of 400 mL of air-saturated solution with 50 mg L<sup>-1</sup> antibiotic and 0.050 M Na<sub>2</sub>SO<sub>4</sub> at pH 5 and 15 °C, by applying j = 7.5 mA cm<sup>-2</sup>. (c) Relative accumulated 'OH content in the above trials. Adapted from Chen et al. (2019b).



**Fig. 20.** (a) Sketch of the setup used for the hybrid EF with membrane treatment in continuous mode of a mixture of antibiotics with a dead-end membrane setup equipped with a Pt anode, a carboxylated carbon nanotubes (CCNTs) intercalated reduced graphene oxide (RGO) composite EF (doped with iron oxide) membrane, and an Ag|AgCl reference electrode. (b) Removal efficiency for an O<sub>2</sub>-saturated solution with 1.0 mg L<sup>-1</sup> of each antibiotic with 0.050 M Na<sub>2</sub>SO<sub>4</sub> at pH 7.0 and 25 °C, pressure of 2.5 bar, and  $E_{cat} = -0.6 \text{ V/Ag}|AgCl$ . Adapted from Jiang et al. (2021).

of 0.583 A m  $^{-2}$  (see Table 6). In contrast, Fig. 21b shows that the antibiotic was only destroyed in the catholyte by 'OH produced by hetero-EF with a functionalized M-type strontium hexaferrite nanoparticles cathode. The anolyte with a CF anode coated with a biofilm contained 250 mL of 1 g L<sup>-1</sup> acetate in a growth medium. Oxidation of acetate to CO<sub>2</sub> provided the electrons that passed through a resistance of 1000  $\Omega$  to the cathode in the catholyte, composed of 250 mL of an air-saturated solution with a mixture of 10 mg  $L^{-1}$  of tetracycline and sulfaquinoxaline in phosphate medium with 0.3 g  $L^{-1}$  of catalyst at the cathode or 0.3 g  $L^{-1}$  of FeSO<sub>4</sub>·7H<sub>2</sub>O (homo-EF with a CF cathode) at pH 3-7. The trials were made at 24 °C for 24 h. As expected, the cells showed better performance at pH 3 where the heterogeneous Fenton's reaction (22) or the Fenton's reaction (4) are optimal. Under these conditions, the antibiotics underwent 86-88% degradation in 17 h, which rose to 100% in 24 h, with a coulombic efficiency of 33-43% and maximum power output of 136.4 mW m<sup>-2</sup>. Lower degradations of 71-75% at pH 5 and 58-63% at pH 7 were determined (see Table 6). Poorer results were found by homo-EF with FeSO<sub>4</sub>·7H<sub>2</sub>O at pH 3 since only 80% degradation was reached for both antibiotics in 24 h.

Other interesting microbial EF system like of Fig. 21b with two CF electrodes has been reported by Soltani et al. (2021) for tetracycline removal. The anolyte contained 450 mL of an organic load with

1000–10,000 mg L<sup>-1</sup> COD composed of anaerobic sludge, synthetic feeding wastewater, salts, and a phosphate buffer of pH 7. The catholyte of 450 mL contained an air-saturated solution with 10 mg L<sup>-1</sup> antibiotic, 0.10 M K<sub>2</sub>SO<sub>4</sub>, and 2–10 mg L<sup>-1</sup> FeSO<sub>4</sub> operating at pH between 3 and 7 and at 30 °C. Results of Table 6 make in evidence that for all anodic COD loads and in 24 h, 97–99%, 91%, and 88% degradation was obtained in short-circuit (resistance 0  $\Omega$ ), with maximum voltage of 322 mV, current density of 1195 mA m<sup>-2</sup>, and power density of 141.60 mW m<sup>-2</sup> for 10,000 mg L<sup>-1</sup> of anodic COD at pH 3.

#### 4.3.2. Sequential processes

The Spanish Sanromán group proposed a sequential adsorption-EF method for the remediation of sulfanoamides like sulfamethiazole (Puga et al., 2020a) and sulfamethoxazole (Acevedo-García et al., 2020; Puga et al., 2020b). The aim of the method was the adsorption of the antibiotic from diluted solutions, followed by desorption from the adsorbent to a solution to be effectively degraded by EF. Puga et al. (2020a) checked that 95% of sulfamethiazole was adsorbed in 0.1:25 g of pellet carbonaceous as adsorbent per mol in 25 mL of 25 mg L<sup>-1</sup> antibiotic in pure water with a stirred vessel at 25 °C for 240 min. The adsorbent desorbed completely the antibiotic in 15 mL of acetonitrile after 3 cycles at 25 °C during 240 min. Once confirmed that the antibiotic could be desorbed from the



Fig. 21. Examples of hybrid microbial EF processes for the treatment of (a) erythromycin in phosphate buffer (pH 7) with a carbon cloth anode and a CNT $|\gamma$ -FeOOH|stainless steel (SS) cathode (adapted from Li et al., 2020c), and (b) tetracycline and sulfaquinoxaline in phosphate buffer (pH 7) with a carbon-felt anode and a carbon-felt cathode with M-type strontium hexaferrite nanoparticles (adapted from Hassan et al., 2020). In both cases, a divided H-cell with a cation exchange membrane as separator was used.

adsorbent to be potentially treated by EF, a parallel hetero-EF treatment with an iron-perlite catalyst and other AOPs was undertaken to treat 150 mL of an air-saturated solution with 25 mg L<sup>-1</sup> of antibiotic in 0.10 M Na<sub>2</sub>SO<sub>4</sub> at pH 3.0 and 25 °C using a stirred tank reactor like of Fig. 3a at *I* = 100 mA. Total degradation was attained in 240 min ( $k_1$  = 0.019 min<sup>-1</sup>) by AO-H<sub>2</sub>O<sub>2</sub> (without catalyst), decreasing to 20 min ( $k_1$  = 0.300 min<sup>-1</sup>) by homo-EF with Fe<sup>2+</sup> and to only 10 min ( $k_1$  = 0.403 min<sup>-1</sup>) by hetero-EF with iron-perlite solid catalyst (see Table 6). The authors detected 4 carboxylic acids by HPLC, as well the loss of NO<sub>3</sub><sup>-</sup>, NO<sub>2</sub><sup>-</sup>, and NH<sub>4</sub><sup>+</sup> ions. This research pointed the feasible application of a sequential adsorption-EF process, which was applied to the destruction of sulfamethoxazole by Acevedo-García et al. (2020). To do this, they spiked 50 mg L<sup>-1</sup> of antibiotic in 50 mL of pure water in a stirred vessel with 0.1 g of biochar as adsorbent at pH 5.6 and 25 °C during 180 min. Under these conditions, the biochar adsorbed all the antibiotic and then, 0.1 g of the contaminated biochar was introduced in a stirred BDD/CF cubic cell containing 150 mL of an air-saturated 0.01 M Na<sub>2</sub>SO<sub>4</sub> solution with 0.29 mM Fe<sup>2+</sup> at pH 3.0 and a *I* = 300 mA was applied. The antibiotic was slowly desorbed from the biochar to the aqueous matrix and oxidized by .OH, and after 360 min of the homo-EF process, a maximal of 88% of it was removed with adsorbent regeneration (see Table 6). A good reusability was found during 6 consecutive cycles.

Several authors have investigated the behavior of sequential EFbiological processes related to the destruction of the fluoroquinolones gatifloxacin and gentamicin (Arhoutane et al., 2019a), and the nitroimidazole metronidazole (Aboudalle et al., 2018, 2021). The EF process was applied as pre-treatment of the antibiotic wastewater strongly reducing its toxicity and allowing an efficient biological post-treatment. This arrangement seems more useful in practice because it is easily scalable to industrial level since the biological processes can be performed with large volumes of liquid and are very cost-effective. For instance, Table 6 shows the results obtained for metronidazole removal by this sequential process (Aboudalle et al., 2018). The EF pre-treatment was performed with a stirred Pt/GF cell like of Fig. 3a containing 250 mL of an airsaturated solution with 100 mg  $L^{-1}$  antibiotic in 0.050 M Na<sub>2</sub>SO<sub>4</sub> with 0.1 mM Fe<sup>2+</sup> at pH 3.0 and 20 °C upon a very low j = 0.07 mA cm<sup>-2</sup>. Total degradation was obtained after 20 min of electrolysis, attaining a low mineralization of 32% in 120 min. Fortunately, the BDO<sub>5</sub>/COD ratio of the electrolyzed solution rose to 0.60, making it biodegradable. A volume of 200 mL of the pre-treated solution was then subsequently transferred into a stirred tank reactor with 0.5 g L<sup>-1</sup> of activated sludge at pH 7 and 28 °C for 504 h, giving rise to a high mineralization of 88%. Additionally, 5 heterocyclic derivatives were identified by LC-MS/MS, as well as  $NO_3^$ and NH<sub>4</sub><sup>+</sup> as released ions.

#### 5. Conclusions and prospects

The homo- and hetero-EF processes show an excellent oxidation ability to destroy a large variety of antibiotics in synthetic and real wastewaters. These methods have the common feature of generating the strong oxidant 'OH from Fenton's reaction (4), heterogeneous Fenton's reaction (22), and heterogeneous M('OH) from reaction (24) at optimum pH 3.0, which can effectively remove aromatic/heteroaromatic/cyclic by-products and aliphatic pollutants. At present, the studies published for these EF treatments have been made at bench-scale level and do not support any mature method for its direct application to industrial scale. To solve this situation, it is necessary in the next future to extend the research to pilot plants, preeminently with real wastewaters, to obtain operating and energetic parameters industrially affordable. It is also required deep techno-economic analyses showing their advantages to benchmark these EF technologies in front of other available AOPs. The knowledge of by-products and their relative toxicity and biodegradability are also key parameters to infer the duration of the treatment and their possible combination with subsequent cheaper post-treatments such as post-biological processes, which are very interesting to be developed at industrial level to offer more clear advantages over other possible competitive AOPs. Homo-EF is the most studied process for antibiotic remediation in sulfate medium. It is much more powerful than AO-H2O2 and the amount of H2O2 electrogenerated determines its oxidation power because it controls the 'OH production to destroy organics. Carbonaceous cathodes like carbon sponge, carbon felt, and GDE seem the better materials for this purpose, although some modified cathodes favor the electrogeneration of  $H_2O_2$ , which depend on the applied I or j in twoelectrode systems and  $E_{cat}$  in three-electrode ones The parallel ability of the anode to form heterogeneous M('OH) also plays an important role in the process. The non-active BDD is the best anode for homo-EF, with a much greater oxidation power than active anodes like Pt and DSA. The process is optimal at pH 3.0 and regulated by Fenton's reaction (4). From the by-products detected after electrolysis, one can infer that the antibiotic is rapidly transformed into more recalcitrant aromatic and cyclic derivatives, which slowly evolve to ultimate carboxylic acids that are difficultly converted into CO2. This explains the enlargement of the antibiotic mineralization respect to its degradation, as well as the low TOC abatement found in many treatments depending on the recalcitrance of intermediates, although the wastewater toxicity usually diminishes. Other co-catalysts as Cu<sup>2+</sup> and Mn<sup>2+</sup> also producing 'OH from Fenton-like reactions are beneficial for the oxidative process. The increase in j or  $E_{cat}$  leads to a faster mineralization, but with lower MCE and higher  $EC_{TOC}$ , because of the acceleration of the parasitic reactions of 'OH and M('OH). More comparative studies with different antibiotics are needed to clarify their reactivity respect to 'OH.

Much less attention has received the homo-EF treatment of real wastewaters, where additional oxidants and toxic species like active chlorine,  $ClO_3^-$ ,  $ClO_4^-$ , and chloramines are formed from the oxidation of  $Cl^-$  present in the aqueous matrix. Active chlorine also attacks the antibiotic yielding toxic and recalcitrant chloroderivatives. The oxidation of the antibiotic is slower than in synthetic sulfate solutions as result of the consumption of oxidizing agents in the parallel destruction of the other pollutants present in the medium. Studies with flow plants demonstrate that better performance is found operating with flow-through than flow-by regimes, a behavior that needs a deeper investigation in future work to clarify the best efficient technique for the homo-EF process. TPP as ligand of  $Fe^{2+}$  also produces 'OH from a Fenton-like reaction and can efficiently destroy the antibiotic at near neutral pH 6, very far from the optimum pH 3 of Fenton's reaction (4). The main drawback of using TPP is that it must be extracted from the medium to obtain a clean water before disposal.

The Fe<sup>2+</sup> catalyst in homo-EF can be replaced by iron solid catalysts in hetero-EF with similar or even better performance. The oxidation ability of iron solid catalysts is again higher at pH 3.0, with the advantage of avoiding iron sludge when the solution is neutralized. Iron oxides and sulfides, sometimes with copper, have been explored as catalysts, showing an acceptable reusability. The heterogeneous Fenton's reaction (22) is promoted at the catalyst surface to form heterogeneous 'OH as the main oxidant, although O<sub>2</sub> generation has been claimed as well. 'OH and 'H are proposed as the generated oxidants by Pd- Fe<sub>3</sub>O<sub>4</sub> catalyst. Addition of more catalyst causes higher antibiotic removal due to the presence of more electrocatalytic surface, which is enhanced with raising I. The BDD anode is again the better electrode for the mineralization process. The antibiotic removal is relied on the iron solid catalyst and its reactivity seems rather related to the recalcitrance of by-products formed. An increasing mineralization sequence involving oxytetracycline < sulfadiazine < sulfamethazine < tetracycline, has been reported.

Hetero-EF with iron functionalized cathodes can operate at near neutral pH where it shows a good effectiveness to destroy antibiotics, although it offers better performance at pH 3.0, which can be even superior to that of homo-EF. This is feasible because  $H_2O_2$  electrogeneration and heterogeneous Fenton's reaction (22) occur simultaneously at the cathode surface favoring the oxidant generation and antibiotic destruction at pH > 3.0. 'OH,  $O_2^-$ , and  ${}^1O_2$  have been proposed as main oxidizing agents. Sophisticated cathodes that are not useful in practice have been tested. This suggests that in the next future, the treatments should be centered on simple materials like FeMn binary oxide or Fe<sub>2</sub>O<sub>3</sub>-CNTs to confirm their oxidation ability over a large variety of antibiotics, preferentially in real wastewaters using pilot plants to open the way to industrial scale.

Several hybrid and sequential EF methods have been proposed for an effective destruction of antibiotics. More research is needed to develop mature technologies for their practical application. It has been found that the relative reactivity of negatively charged antibiotics follows the order: sulfonamides ~ fluoroquinolones < amphenicols <  $\beta$ -lactams. The hybrid microbial EF systems proposed show a large mineralization of antibiotics, along with the generation of an excellent electric power density. The sequential EF-biological process should be extensively explored since the EF pre-treatment reduces the toxicity enough to ensure an efficient and cost-effective subsequent biological treatment.

#### CRediT authorship contribution statement

I am the only author of this article.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### References

Aboudalle, A., Djelal, H., Fourcade, F., Domergue, L., Assadi, A.A., Lendormi, T., Taha, S., Amrane, A., 2018. Metronidazole removal by means of a combined system coupling an electro-Fenton process and a conventional biological treatment: by-products monitoring and performance enhancement. J. Hazard. Mater. 359, 85–95. https://doi.org/10. 1016/j.jhazmat.2018.07.006.

#### Science of the Total Environment 819 (2022) 153102

- Aboudalle, A., Djelal, H., Domergue, L., Fourcade, F., Amrane, A., 2021. A novel system coupling an electro-Fenton process and an advanced biological process to remove a pharmacentical compound, metronidazole. J. Hazard. Mater. 415, 125705. https://doi.org/10. 1016/j.jhazmat.2021.125705.
- Acevedo-García, V., Rosales, E., Puga, A., Pazos, M., Sanromán, M.A., 2020. Synthesis and use of efficient adsorbents under the principles of circular economy: waste valorisation and electroadvanced oxidation process regeneration. Sep. Purif. Technol. 242, 116796. https://doi.org/10.1016/j.seppur.2020.116796.
- Arhoutane, M.R., Kaichouh, G., Yahya, M.S., El Karbane, M.E., Chakchak, H., El Kacemi, K., 2019a. Elimination of gatifloxacin from water: treatment by electro-Fenton process and highlighting of a biological post-treatment. Mediterr. J. Chem. 8, 308–319. https://doi. org/10.13171/mjc841906066mra.
- Arhoutane, M.R., Yahya, M.S., El Karbane, M., Guessous, A., Chakchak, H., El Kacemi, K., 2019b. Removal of pyrazinamide and its by-products from water: treatment by electro-Fenton process and feasibility of a biological post-treatment. Mediterr. J. Chem. 8, 53–65. https://doi.org/10.13171/mjc811903420mra.
- Arhoutane, M.R., Yahya, M.S., Karbane, M.E., Kacemi, K.E., 2019c. Oxidative degradation of gentamicin present in water by an electro-Fenton process and biodegradability improvement. Open Chem. 17, 1017–1025. https://doi.org/10.1515/chem-2019-0110.
- Barhoumi, N., Olvera-Vargas, H., Oturan, N., Huguenot, D., Gadri, A., Ammar, S., Brillas, E., Oturan, M.A., 2017a. Kinetics of oxidative degradation/mineralization pathways of the antibiotic tetracycline by the novel heterogeneous electro-Fenton process with solid catalyst chalcopyrite. Appl. Catal. B Environ. 209, 637–647. https://doi.org/10.1016/j. apcatb.2017.03.034.
- Barhoumi, N., Oturan, N., Ammar, S., Gadri, A., Oturan, M.A., Brillas, E., 2017b. Enhanced degradation of the antibiotic tetracycline by heterogeneous electro-Fenton with pyrite catalysis. Environ. Chem. Lett. 15, 689–693. https://doi.org/10.1007/s10311-017-0638-y.
- Boye, B., Michaud, P.A., Marselli, B., Dieng, M.M., Brillas, E., Comninellis, C., 2002. Anodic oxidation of 4-chlorophenoxyacetic acid on synthetic boron-doped diamond electrodes. New Diamond Front. Carbon Technol. 12, 63–72.
- Brillas, E., 2021. Recent development of electrochemical advanced oxidation of herbicides. A review on its application to wastewater treatment and soil remediation. J. Clean. Prod. 290, 125841. https://doi.org/10.1016/j.jclepro.2021.125841.
- Brillas, E., 2022. Fenton, photo-Fenton, electro-Fenton, and their combined treatments for the removal of insecticides from waters and soils. A review. Sep. Purif. Technol. 284, 120290. https://doi.org/10.1016/j.seppur.2021.120290.
- Brillas, E., Garcia-Segura, S., 2020. Benchmarking recent advances and innovative technology approaches of Fenton, photo-Fenton, electro-Fenton, and related processes: a review on the relevance of phenol as model molecule. Sep. Purif. Technol. 237, 11633. https:// doi.org/10.1016/j.seppur.2019.116337.
- Campos, S., Salazar, R., Arancibia-Miranda, N., Rubio, M.A., Aranda, M., García, A., Sepúveda, P., Espinoza, L.C., 2020. Nafcillin degradation by heterogeneous electro-Fenton process using Fe, Cu and Fe/Cu nanoparticles. Chemosphere 247, 125813. https://doi.org/10. 1016/j.chemosphere.2020.125813.
- Chen, Y., Wang, A., Zhang, Y., Bao, R., Tian, X., Li, J., 2017. Electro-Fenton degradation of antibiotic ciprofloxacin (CIP): formation of Fe3 + -CIP chelate and its effect on catalytic behavior of Fe2 + /Fe3 + and CIP mineralization. Electrochim. Acta 256, 185–195. https:// doi.org/10.1016/j.electacta.2017.09.173.
- Chen, S., Tang, L., Feng, H., Zhou, Y., Zeng, G., Lu, Y., Yu, J., Ren, X., Peng, B., Liu, X., 2019a. Carbon felt cathodes for electro-Fenton process to remove tetracycline via synergistic adsorption and degradation. Sci. Total Environ. 670, 921–931. https://doi.org/10.1016/j. scitotenv.2019.03.086.
- Chen, Y.-P., Yang, L.-M., Paul Chen, J., Zheng, Y.-M., 2019b. Electrospun spongy zero-valent iron as excellent electro-Fenton catalyst for enhanced sulfathiazole removal by a combination of adsorption and electro-catalytic oxidation. J. Hazard. Mater. 371, 576–585. https://doi.org/10.1016/j.jhazmat.2019.03.043.
- Divyapriya, G., Nambi, I., Senthilnathan, J., 2018a. Ferrocene functionalized graphene based electrode for the electró-Fenton oxidation of ciprofloxacin. Chemosphere 209, 113–123. https://doi.org/10.1016/j.chemosphere.2018.05.148.
- Divyapriya, G., Srinivasan, R., Nambi, I.M., Senthilnathan, J., 2018b. Highly active and stable ferrocene functionalized graphene encapsulated carbon felt array - a novel rotating disc electrode for electro-Fenton oxidation of pharmaceutical compounds. Electrochim. Acta 283, 858–870. https://doi.org/10.1016/j.electacta.2018.06.186.
- Divyapriya, G., Thangadurai, P., Nambi, I., 2018c. Green approach to produce a graphene thin film on a conductive LCD matrix for the oxidative transformation of ciprofloxacin. ACS Sustain. Chem. Eng. 6, 3453–3462. https://doi.org/10.1021/acssuschemeng.7b03687.
- dos Santos, A.J., Kronka, M.S., Fortunato, G.V., Lanza, M.R.V., 2021. Recent advances in electrochemical water technologies for the treatment of antibiotics: a short review. Curr. Opin. Electrochem. 26, 100674. https://doi.org/10.1016/j.coelec.2020.100674.
- Droguett, C., Salazar, R., Brillas, E., Sirés, I., Carlesi, C., Marco, J.F., Thiam, A., 2020. Treatment of antibiotic cephalexin by heterogeneous electrochemical Fenton-based processes using chalcopyrite as sustainable catalyst. Sci. Total Environ. 740, 140154. https://doi. org/10.1016/j.scitotenv.2020.140154.
- Ganiyu, S.O., Huong Le, T.X., Bechelany, M., Oturan, N., Papirio, S., Esposito, G., van Hullebusch, E., Cretin, M., Oturan, M.A., 2018a. Electrochemical mineralization of sulfamethoxazole over wide pH range using FeIIFeIII LDH modified carbon felt cathode: degradation pathway, toxicity and reusability of the modified cathode. Chem. Eng. J. 350, 844–855. https://doi.org/10.1016/j.cej.2018.04.141.
- Ganiyu, S.O., Zhou, M., Martínez-Huitle, C.A., 2018b. Heterogeneous electro-Fenton and photoelectro-Fenton processes: a critical review of fundamental principles and application for water/wastewater treatment. Appl. Catal. B Environ. 235, 103–129. https:// doi.org/10.1016/j.apcatb.2018.04.044.
- Ganzenko, O., Trellu, C., Oturan, N., Huguenot, D., Péchaud, Y., van Hullebusch, E.D., Oturan, M.A., 2020. Electro-Fenton treatment of a complex pharmaceutical mixture: mineralization efficiency and biodegradability enhancement. Chemosphere 253, 126659. https:// doi.org/10.1016/j.chemosphere.2020.126659.

- Garcia-Segura, S., Nienhauser, A.B., Fajardo, A.S., Bansal, R., Coonrod, C.L., Fortner, J.D., Marcos-Hernández, M., Rogers, T., Villagran, D., Wong, M.S., Westerhoff, P., 2020. Disparities between experimental and environmental conditions: research steps toward making electrochemical water treatment a reality. Curr. Opin. Electrochem. 22, 9–16. https:// www.elsevier.com/open-access/userlicense/1.0/.
- Ghasemi, M., Khataee, A., Gholami, P., Cheshmeh Soltani, R.D., 2019. Template-free microspheres decorated with cu-fe-NLDH for catalytic removal of gentamicin in heterogeneous electro-Fenton process. J. Environ. Manag. 248, 109236. https://doi.org/10.1016/j. jenvman.2019.07.007.
- Ghasemi, M., Khataee, A., Gholami, P., Soltani, R.D.C., Hassani, A., Orooji, Y., 2020. In-situ electro-generation and activation of hydrogen peroxide using a CuFeNLDH-CNTs modified graphite cathode for degradation of cefazolin. J. Environ. Manag. 26, 110629. https://doi.org/10.1016/j.jenvman.2020.110629.
- Gonzaga, I.M.D., Moratalla, A., Eguiluz, K.I.B., Salazar-Banda, G.R., Cañizares, P., Rodrigo, M.A., Saez, C., 2021. Novel Ti/RuO2IrO2 anode to reduce the dangerousness of antibiotic polluted urines by Fenton-based processes. Chemosphere 270, 129344. https://doi.org/ 10.1016/j.chemosphere.2020.129344.
- Görmez, F., Görmez, Ö., Gözmen, B., Kalderis, D., 2019. Degradation of chloramphenicol and metronidazole by electro-Fenton process using graphene oxide-Fe3O4 as heterogeneous catalyst. J. Environ. Chem. Eng. 7, 102990. https://doi.org/10.1016/j.jece. 2019.102990.
- Guo, D., Liu, Y., Ji, H., Wang, C.-C., Chen, B., Shen, C., Li, F., Wang, Y., Lu, P., Liu, W., 2021. Silicate-enhanced heterogeneous flow-through electro-Fenton system using iron oxides under nanoconfinement. Environ. Sci. Technol. 55, 4045–4053. https://doi.org/10. 1021/acs.est.1c00349.
- Han, Z., Li, Z., Li, Y., Shang, D., Xie, L., Lv, Y., Zhan, S., Hu, W., 2022. Enhanced electron transfer and hydrogen peroxide activation capacity with N, P-codoped carbon encapsulated CeO2 in heterogeneous electro-Fenton process. Chemosphere 287, 132154. https://doi. org/10.1016/j.chemosphere.2021.132154.
- Hasani, K., Hosseini, S., Gholizadeh, H., Dargahi, A., Vosoughi, M., 2021. Enhancing the efficiency of electrochemical, Fenton, and electro-Fenton processes using SS316 and SS316/ β-PbO2 anodes to remove oxytetracycline antibiotic from aquatic environments. Biomass Convers. Biorefin. https://doi.org/10.1007/s13399-021-01967-z.
- Hassan, M., Ashraf, G.A., Zhang, B., He, Y., Shen, G., Hu, S., 2020. Energy-efficient degradation of antibiotics in microbial electro-Fenton system catalysed by M-type strontium hexaferrite nanoparticles. Chem. Eng. J. 380, 122483. https://doi.org/10.1016/j.cej. 2019.122483.
- He, H., Zhou, Z., 2017. Electro-Fenton process for water and wastewater treatment. Crit. Rev. Environ. Sci. Technol. 47, 2100–2131. https://doi.org/10.1080/10643389.2017. 1405673.
- Heidari, Z., Pelalak, R., Alizadeh, R., Oturan, N., Shirazian, S., Oturan, M.A., 2021. Application of mineral iron-based natural catalysts in electro-Fenton process: a comparative study. Catalysts 11, 1–18. https://doi.org/10.3390/catal11010057.
- Hu, X., Deng, Y., Zhou, J., Liu, B., Yang, A., Jin, T., Fai Tsang, Y., 2020. N- and O self-doped biomass porous carbon cathode in an electro-Fenton system for chloramphenicol degradation. Sep. Purif. Technol. 251, 117376. https://doi.org/10.1016/j.seppur.2020. 117376.
- Huang, A., Zhi, D., Tang, H., Jiang, L., Luo, S., Zhou, Y., 2021a. Effect of Fe2+, Mn2+ catalysts on the performance of electro-Fenton degradation of antibiotic ciprofloxacin, and expanding the utilizing of acid mine drainage. Sci. Total Environ. 720, 137560. https://doi.org/10.1016/j.scitotenv.2020.137560.
- Huang, A., Zhi, D., Zhou, Y., 2021b. A novel modified fe-mn binary oxide graphite felt (FMBO-GF) cathode in a neutral electro-Fenton system for ciprofloxacin degradation. Environ. Pollut. 286, 117310. https://doi.org/10.1016/j.envpol.2021.117310.
- Jiang, W.-L., Xia, X., Han, J.-L., Ding, Y.-C., Haider, M.R., Wang, A.-J., 2018. Graphene modified electro-Fenton catalytic membrane for in situ degradation of antibiotic florfenicol. Environ. Sci. Technol. 52, 9972–9982. https://doi.org/10.1021/acs.est.8b01894.
- Jiang, W.-L., Haider, M.R., Han, J.-L., Ding, Y.-C., Li, X.-Q., Wang, H.-C., Adeel Sharif, H.M., Wang, A.-J., Ren, N.-Q., 2021. Carbon nanotubes intercalated RGO electro-Fenton membrane for coenhanced permeability, rejection and catalytic oxidation of organic micropollutants. J. Membr. Sci. 623, 119069. https://doi.org/10.1016/j.memsci.2021. 119069.
- Kalantary, R.R., Farzadkia, M., Kermani, M., Rahmatinia, M., 2018. Heterogeneous electro-Fenton process by nano-Fe3O4 for catalytic degradation of amoxicillin: process optimization using response surface methodology. J. Environ. Chem. Eng. 6, 4644–4652. https:// doi.org/10.1016/j.jece.2018.06.043.
- Ko, Y.-J., Kim, H.-G., Seid, M.G., Cho, K., Choi, J.-W., Lee, W.-S., Hong, S.W., 2018. Ionic-liquid-derived nitrogen-doped carbon electrocatalyst for peroxide generation and divalent iron regeneration: its application for removal of aqueous organic compounds. ACS Sustain. Chem. Eng. 6, 14857–14865. https://doi.org/10.1021/ acssuschemeng.8b03383.
- Lai, W., Xie, G., Dai, R., Kuang, C., Xu, Y., Pan, Z., Zheng, L., Yu, L., Ye, S., Chen, Z., Li, H., 2020. Kinetics and mechanisms of oxytetracycline degradation in an electro-Fenton system with a modified graphite felt cathode. J. Environ. Manag. 257, 109968. https:// doi.org/10.1016/j.jenvman.2019.109968.
- Lei, J., Duan, P., Liu, W., Sun, Z., Hu, X., 2020. Degradation of aqueous cefotaxime in electrooxidation-electro-Fenton-persulfate system with Ti/CNT/SnO2-sb-er anode and Ni@ NCNT cathode. Chemosphere 250, 126163. https://doi.org/10.1016/j.chemosphere. 2020.126163.
- Li, Y., Han, J., Mi, X., Mi, X., Li, Y., Zhang, S., Zhan, S., 2017a. Modified carbon felt made using CexA1-xO2 composites as a cathode in electro-Fenton system to degrade ciprofloxacin. RSC Adv. 7, 27065–27078. https://doi.org/10.1039/c7ra03302h.
- Li, Y., Han, J., Xie, B., Li, Y., Zhan, S., Tian, Y., 2017b. Synergistic degradation of antimicrobial agent ciprofloxacin in water by using 3D CeO2/RGO composite as cathode in electro-Fenton system. J. Electroanal. Chem. 784, 6–12. https://doi.org/10.1016/j.jelechem. 2016.11.057.

- Li, Y., Zhang, S., Han, Y., Cheng, S., Hu, W., Han, J., Li, Y., 2019. Heterogeneous electrocatalytic degradation of ciprofloxacin by ternary Ce3ZrFe4O14-x/CF composite cathode. Catal. Today 327, 116–125. https://doi.org/10.1016/j.cattod.2018.05.043.
- Li, S., Hua, T., Li, F., Zhou, Q., 2020a. Bio-electro-Fenton systems for sustainable wastewater treatment: mechanisms, novel configurations, recent advances, LCA and challenges. An updated review. J. Chem. Technol. Biotechnol. 95, 2083–2097. https://doi.org/10. 1002/jctb.6332.
- Li, S., Hua, T., Yuan, C.-S., Li, B., Zhu, X., Li, F., 2020b. Degradation pathways, microbial community and electricity properties analysis of antibiotic sulfamethoxazole by bio-electro-Fenton system. Bioresour. Technol. 298, 122501. https://doi.org/10.1016/j.biortech. 2019.122501.
- Li, S., Liu, Y., Ge, R., Yang, S., Zhai, Y., Hua, T., Ondon, B.S., Zhou, Q., Li, F., 2020c. Microbial electro-Fenton: a promising system for antibiotics resistance genes degradation and energy generation. Sci. Total Environ. 699, 134160. https://doi.org/10.1016/j.scitotenv. 2019.134160.
- Li, Z., Shen, C., Liu, Y., Ma, C., Li, F., Yang, B., Huang, M., Wang, Z., Dong, L., Wolfgang, S., 2020d. Carbon nanotube filter functionalized with iron oxychloride for flow-through electro-Fenton. Appl. Catal. B Environ. 260, 118204. https://doi.org/10.1016/j.apcatb. 2019.118204.
- Liu, X., Yang, D., Zhou, Y., Zhang, J., Luo, L., Meng, S., Chen, S., Tan, M., Li, Z., Tang, L., 2017. Electrocatalytic properties of N-doped graphite felt in electro-Fenton process and degradation mechanism of levofloxacin. Chemosphere 182, 306–315. https://doi.org/10. 1016/j.chemosphere.2017.05.035.
- Liu, X., Zhou, Y., Zhang, J., Luo, L., Yang, Y., Huang, H., Peng, H., Tang, L., Mu, Y., 2018. Insight into electro-Fenton and photo-Fenton for the degradation of antibiotics: mechanism study and research gaps. Chem. Eng. J. 347, 379–397. https://doi.org/10.1016/j.cej. 2018.04.142.
- Liu, F., Liu, Y., Yao, Q., Wang, Y., Fang, X., Shen, C., Li, F., Huang, M., Wang, Z., Sand, W., Xie, J., 2020a. Supported atomically-precise gold nanoclusters for enhanced flow-through electro-Fenton. Environ. Sci. Technol. 54, 5913–5921. https://doi.org/10.1021/acs.est. 0c00427.
- Liu, X., Xie, L., Liu, Y., Zhao, P., Han, Y., Cheng, S., Bai, X., Li, Y., 2020b. Rapid preparation of highly stable ZnO-CeO2/CF cathode by one-step electro-deposition for efficient degradation of ciprofloxacin in electro-Fenton system. Catal. Today 355, 458–465. https://doi. org/10.1016/j.cattod.2019.07.005.
- Liu, Z., Wan, J., Ma, Y., Wang, Y., 2021. In situ synthesis of FeOCl@MoS2 on graphite felt as novel electro-Fenton cathode for efficient degradation of antibiotic ciprofloxacin at mild pH. Chemosphere 273, 129747. https://doi.org/10.1016/j.chemosphere.2021.129747.
- Mao, S., Sun, X., Qi, H., Sun, Z., 2021. Cu2O nanoparticles anchored on 3D bifunctional CNTs/copper foam cathode for electrocatalytic degradation of sulfamethoxazole over a broad pH range. Sci. Total Environ. 793, 148492. https://doi.org/10.1016/j.scitotenv. 2021.148492.
- Martínez-Huitle, C.A., Brillas, E., 2021. A critical review over the electrochemical disinfection of bacteria in synthetic and real wastewaters using a boron-doped diamond anode. Curr. Opin. Solid State Mater. Sci. 25, 100926. https://doi.org/10.1016/j.cossms.2021. 100926.
- Meijide, J., Dunlop, P.S.M., Pazos, M., Sanromán, M.A., 2021. Heterogeneous electro-Fenton as "Green" technology for pharmaceutical removal: a review. Catalysts 11, 1–22. https:// doi.org/10.3390/catal11010085.
- Mi, X., Li, Y., Ning, X., Jia, J., Wang, H., Xia, Y., Sun, Y., Zhan, S., 2019. Electro-Fenton degradation of ciprofloxacin with highly ordered mesoporous MnCo2O4-CF cathode: enhanced redox capacity and accelerated electron transfer. Chem. Eng. J. 358, 299–309. https://doi.org/10.1016/j.cej.2018.10.047.
- Mi, X., Yang, M., Xie, L., Li, Y., Sun, Y., Zhan, S., 2020. RGO/MoS2/Ce0.75Zr0.25O2 electro-Fenton cathode with higher matching and complementarity for efficient degradation of ciprofloxacin. Catal. Today 339, 371–378. https://doi.org/10.1016/j.cattod.2019.03. 013.
- Monteil, H., Péchaud, Y., Oturan, N., Oturan, M.A., 2019. A review on efficiency and cost effectiveness of electro- and bio-electro-Fenton processes: application to the treatment of pharmaceutical pollutants in water. Chem. Eng. J. 376, 119577. https://doi.org/10. 1016/j.cei.2018.07.179.
- Moratalla, A., Araújo, D.M., Moura, G.O.M.A., Lacasa, E., Cañizares, P., Rodrigo, M.A., Sáez, C., 2021. Pressurized electro-Fenton for the reduction of the environmental impact of antibiòtics. Sep. Purif. Technol. 276, 119398. https://doi.org/10.1016/j.seppur.2021. 119398.
- Murillo-Sierra, J.C., Sirés, I., Brillas, E., Ruiz-Ruiz, E.J., Hernández-Ramírez, A., 2018. Advanced oxidation of real sulfamethoxazole + trimethoprim formulations using different anodes and electrolytes. Chemosphere 192, 225–233. https://doi.org/10.1016/j. chemosphere.2017.10.136.
- Nair, K.M., Kumaravel, V., Pillai, S.C., 2021. Carbonaceous cathode materials for electro-Fenton technology: mechanism, kinetics, recent advances, opportunities and challenges. Chemosphere 269, 129325. https://doi.org/10.1016/j.chemosphere.2020.129325.
- Niaei, H.A., Rostamizadeh, M., 2020. Adsorption and electro-Fenton processes over FeZSM-5 nano-zeolite for tetracycline removal from wastewater. Adv. Nano Res. 9, 173–181. https://doi.org/10.12989/anr.2020.9.3.173.
- Olvera-Vargas, H., Wee, V.Y.H., Garcia-Rodriguez, O., Lefebvre, O., 2019. Near neutral electro-Fenton treatment of pharmaceutical pollutants: effect of using a triphosphate ligand and BDD electrode. ChemElectroChem 6, 937–946. https://doi.org/10.1002/celc. 201801732.
- Olvera-Vargas, H., Gore-Datar, N., Garcia-Rodriguez, O., Mutnuri, S., Lefebvre, O., 2021. Electro-Fenton treatment of real pharmaceutical wastewater paired with a BDD anode: reaction mechanisms and respective contribution of homogeneous and heterogenous •OH. Chem. Eng. J. 404, 126524. https://doi.org/10.1016/j.cej.2020.126524.
- Oturan, N., Sirés, I., Oturan, M.A., Brillas, E., 2009. Degradation of pesticides in aqueous medium by electro-Fenton and related methods. A review. J. Environ. Eng. Manage. 19, 235–255.

- Oturan, N., Ganiyu, S.O., Raffy, S., Oturan, M.A., 2017. Sub-stoichiometric titanium oxide as a new anode material for electro-Fenton process: application to electrocatalytic destruction of antibiotic amoxicillin. Appl. Catal. B Environ. 217, 214–223. https://doi.org/10.1016/ i.apcatb.2017.05.062.
- Oturan, N., Aravindakumar, C.T., Olvera-Vargas, H., Sunil Paul, M.M., Oturan, M.A., 2018. Electro-Fenton oxidation of Para-aminosalicylic acid: degradation kinetics and mineralization pathway using Pt/carbon-felt and BDD/carbon-felt cells. Environ. Sci. Pollut. Res. 25, 20363–20373. https://doi.org/10.1007/s11356-017-9309-6.
- Oturan, N., Bo, J., Trellu, C., Oturan, M.A., 2021. Comparative performance of ten electrodes in electro-Fenton process for removal of organic pollutants from water. ChemElectroChem 8, 3294–3303. https://doi.org/10.1002/celc.202100588.
- Pan, G., Sun, X., Sun, Z., 2020. Fabrication of multi-walled carbon nanotubes and carbon black co-modified graphite felt cathode for amoxicillin removal by electrochemical advanced oxidation processes under mild pH condition. Environ. Sci. Pollut. Res. 27, 8231–8247 0.1007/s11356-019-07358-2.
- Pourzamani, H., Mengelizadeh, N., Mohammadi, H., Niknam, N., Neamati, B., Rahimi, R., 2018. Comparison of electrochemical advanced oxidation processes for removal of ciprofloxacin from aqueous solutions. Desalin. Water Treat. 113, 307–318. https://doi.org/10. 5004/dwt.2018.22275.
- Poza-Nogueiras, V., Rosales, E., Pazos, M., Sanromán, M., 2018. Current advances and trends in electro-Fenton process using heterogeneous catalysts - a review. Chemosphere 201, 399–416. https://doi.org/10.1016/j.chemosphere.2018.03.002.
- Puga, A., Rosales, E., Pazos, M., Sanromán, M.A., 2020a. Prompt removal of antibiotic by adsorption/electro-Fenton degradation using an iron-doped perlite as heterogeneous catalyst. Process Saf. Environ. Protect. 144, 100–110. https://doi.org/10.1016/j.psep.2020. 07.021.
- Puga, A., Rosales, E., Sanromán, M.A., Pazos, M., 2020b. Environmental application of monolithic carbonaceous aerogels for the removal of emerging pollutants. Chemosphere 248, 125995. https://doi.org/10.1016/j.chemosphere.2020.125995.
- Qi, H., Sun, X., Sun, Z., 2022. Cu-doped Fe2O3 nanoparticles/etched graphite felt as bifunctional cathode for efficient degradation of sulfamethoxazole in the heterogeneous electro-Fenton process. Chem. Eng. J. 427, 131695. https://doi.org/10.1016/j.cej.2021. 131695.
- Rani, V., Das, R.K., Golder, A.K., 2017. Fabrication of reduced graphene oxide-graphite paste electrode for H2O2 formation and its implication for ciprofloxacin degradation. Surf. Interfaces 7, 99–105. https://doi.org/10.1016/j.surfin.2017.03.003.
- Ren, G., Zhou, M., Su, P., Yang, W., Lu, X., Zhang, Y., 2019. Simultaneous sulfadiazines degradation and disinfection from municipal secondary effluent by a flow-through electro-Fenton process with graphene-modified cathode. J. Hazard. Mater. 368, 830–839. https://doi.org/10.1016/j.jhazmat.2019.01.109.
- Sathe, S.M., Chakraborty, I., Dubey, B.K., Ghangrekar, M.M., 2022. Microbial fuel cell coupled Fenton oxidation for the cathodic degradation of emerging contaminants from wastewater: applications and challenges. Environ. Res. 204, 112135. https://doi.org/10.1016/j. envres.2021.112135.
- Serra-Clusellas, A., Sbardella, L., Herrero, P., Delpino-Rius, A., Riu, M., Correa, M.L., Casadellà, A., Canela, N., Martínez-Lladó, X., 2021. Erythromycin abatement from water by electro-Fenton and peroxyelectrocoagulation treatments. Water 13, 1129. https://doi.org/10.3390/w13081129.
- Sirés, I., Brillas, E., 2021. Upgrading and expanding the electro-Fenton and related processes. Curr. Opin. Electrochem. 27, 100686. https://doi.org/10.1016/j.coelec.2020.100686.
- Soltani, F., Navidjouy, N., Khorsandi, H., Rahimnejad, M., Alizadeh, S., 2021. A novel bioelectro-Fenton system with dual application for the catalytic degradation of tetracycline antibiotic in wastewater and bioelectricity generation. RSC Adv. 11, 27160–27173. https://doi.org/10.1039/d1ra04584a.
- Song, X., Zhang, H., Bian, Z., Wang, H., 2021. In situ electrogeneration and activation of H2O2 by atomic fe catalysts for the efficient removal of chloramphenicol. J. Hazard. Mater. 412, 125162. https://doi.org/10.1016/j.jhazmat.2021.125162.
- Sopaj, F., Oturan, N., Pinson, J., Podvorica, F.I., Oturan, M.A., 2020. Effect of cathode material on electro-Fenton process efficiency for electrocatalytic mineralization of the antibiotic sulfamethazine. Chem. Eng. J. 384, 123249. https://doi.org/10.1016/j.cej.2019.123249.
- Sun, Y., Li, Y., Mi, X., Zhan, S., Hu, W., 2019. Evaluation of ciprofloxacin destruction between ordered mesoporous and bulk NiMn2O4/CF cathode: efficient mineralization in a heterogeneous electro-Fenton-like process. Environ. Sci.: Nano 6, 661–671. https://doi.org/10. 1039/c8en01279b.
- Tang, H., Zhu, Z., Shang, Q., Tang, Y., Zhang, D., Du, Y., Liu, M., Yin, K., Liu, C., 2021. Highly efficient continuous-flow electro-Fenton treatment of antibiotic wastewater using a double-cathode system. ACS Sustain. Chem. Eng. 9, 1414–1422. https://doi.org/10. 1021/acssuschemeng.0c08705.
- Tao, L., Yang, Y., Yu, F., 2020. Highly efficient electro-generation of H2O2 by a nitrogen porous carbon modified carbonaceous cathode during the oxygen reduction reaction. New J. Chem. 44, 15942–15950. https://doi.org/10.1039/d0nj02360d.
- Tian, Y., Zhou, M., Pan, Y., Cai, J., Ren, G., 2020. Pre-magnetized Fe0 as heterogeneous electro-Fenton catalyst for the degradation of p-nitrophenol at neutral pH. Chemosphere 240, 124962. https://doi.org/10.1016/j.chemosphere.2019.124962.
- Tian, Y., Zhou, M., Pan, Y., Du, X., Wang, Q., 2021. MoS2 as highly efficient co-catalyst enhancing the performance of Fe0 based electro-Fenton process in degradation of sulfamethazine: approach and mechanism. Chem. Eng. J. 403, 126361. https://doi.org/10. 1016/j.cej.2020.126361.
- Vidal, J., Huiliñir, C., Santander, R., Silva-Agredo, J., Torres-Palma, R.A., Salazar, R., 2019. Degradation of ampicillin antibiotic by electrochemical processes: evaluation of antimicrobial activity of treated water. Environ. Sci. Pollut. Res. 26, 4404–4414. https://doi. org/10.1007/s11356-018-2234-5.
- Villegas-Guzman, P., Hofer, F., Silva-Agredo, J., Torres-Palma, R.A., 2017. Role of sulfate, chloride, and nitrate anions on the degradation of fluoroquinolone antibiotics by photoelectro-Fenton. Environ. Sci. Pollut. Res. 24, 28175–28189. https://doi.org/10. 1007/s11356-017-0404-5.

- Wang, Y., Zhang, H., Feng, Y., Li, B., Yu, M., Xu, X., Cai, L., 2019. Bio-electro-Fenton (BEF) process driven by sediment microbial fuel cells (SMFCs) for antibiotics desorption and degradation. Biosens. Bioelectron. 136, 8–15. https://doi.org/10.1016/j.bios.2019.04.009.
- Wang, A., Zhang, Y., Han, S., Guo, C., Wen, Z., Tian, X., Li, J., 2021a. Electro-Fenton oxidation of a β-lactam antibiotic cefoperazone: mineralization, biodegradability and degradation mechanism. Chemosphere 270, 129486. https://doi.org/10.1016/j.chemosphere.2020. 129486.
- Wang, Y., Chen, J., Gao, J., Meng, H., Chai, S., Jian, Y., Shi, L., Wang, Y., He, C., 2021b. Selective electrochemical H2O2 generation on the graphene aerogel for efficient electro-Fenton degradation of ciprofloxacin. Sep. Purif. Technol. 272, 118884. https://doi.org/ 10.1016/j.seppur.2021.118884.
- Yahya, M.S., Kaichouh, G., Khachani, M., Karbane, M.E., Arshad, M.A., Zarrouk, A., Kacemi, K.E., 2020. Mineralization of ofloxcacin antibiotic in aqueous medium by electro-Fenton process using a carbon felt cathode: influencing factors. Anal. Bioanal. Electrochem. 12, 425–426.
- Yang, W., Zhou, M., Oturan, N., Bechelany, M., Cretin, M., Oturan, M.A., 2020. Highly efficient and stable FeIIFeIII LDH carbon felt cathode for removal of pharmaceutical ofloxacin at neutral pH. J. Hazard. Mater. 393, 122513. https://doi.org/10.1016/j. jhazmat.2020.122513.
- Yang, W., Zhou, M., Mai, L., Ou, H., Oturan, N., Oturan, M.A., Zeng, E.Y., 2021. Generation of hydroxyl radicals by metal-free bifunctional electrocatalysts for enhanced organics removal. Sci. Total Environ. 791, 148107. https://doi.org/10.1016/j.scitotenv.2021. 148107.
- Yao, B., Luo, Z., Yang, J., Zhi, D., Zhou, Y., 2021. FeIIFeIII layered double hydroxide modified carbon felt cathode for removal of ciprofloxacin in electro-Fenton process. Environ. Res. 197, 111144. https://doi.org/10.1016/j.envres.2021.111144.
- Yu, T., Breslin, C.B., 2020. Graphene-modified composites and electrodes and their potential applications in the electro-Fenton process. Materials 13, 2254. https://doi.org/10.3390/ ma13102254.
- Zarei, M., Beheshti Nahand, F., Khataee, A., Hasanzadeh, A., 2019. Removal of nalidixic acid from aqueous solutions using a cathode containing three-dimensional graphene. J. Water Process Eng. 32, 100978. https://doi.org/10.1016/j.jwpe.2019.100978.
- Zhang, Y., Wang, A., Ren, S., Wen, Z., Tian, X., Li, D., Li, J., 2019. Effect of surface properties of activated carbon fiber cathode on mineralization of antibiotic cefalexin by electro-

Fenton and photoelectro-Fenton treatments: mineralization, kinetics and oxidation products. Chemosphere 221, 423–432. https://doi.org/10.1016/j.chemosphere.2019.01.016.

- Zhang, D., Liu, T., Yin, K., Liu, C., Wei, Y., 2020a. Selective H2O2 production on N-doped porous carbon from direct carbonization of metal organic frameworks for electro-Fenton mineralization of antibiotics. Chem. Eng. J. 383, 123184. https://doi.org/10.1016/j. cej.2019.123184.
- Zhang, S., Pang, X., Yue, Z., Zhou, Y., Duan, H., Shen, W., Li, J., Liu, Y., Cheng, Q. 2020b. Sulfonamides removed from simulated livestock and poultry breeding wastewater using an in-situ electro-Fenton process powered by photovoltaic energy. Chem. Eng. J. 397, 125466. https://doi.org/10.1016/j.cej.2020.125466.
- Zhang, J., Zheng, C., Dai, Y., He, C., Liu, H., Chai, S., 2021. Efficient degradation of amoxicillin by scaled-up electro-Fenton process: attenuation of toxicity and decomposition mechanism. Electrochim. Acta 381, 138274. https://doi.org/10.1016/j.electacta.2021. 138274.
- Zhang, D., Yin, K., Tang, Y., Wei, Y., Tang, H., Du, Y., Liu, H., Chen, Y., Liu, C., 2022. Hollow Sea-urchin-shaped carbon-anchored single-atom iron as dual-functional electro-Fenton catalysts for degrading refractory thiamphenicol with fast reaction kinetics in a wide pH range. Chem. Eng. J. 427, 130996. https://doi.org/10.1016/j.cej.2021. 130996.
- Zhou, Y., Liu, X., Zhao, Y., Luo, S., Wang, L., Yang, Y., Oturan, M.A., Mu, Y., 2018. Structurebased synergistic mechanism for the degradation of typical antibiotics in electro-Fenton process using pd-Fe3O4 model catalyst: theoretical and experimental study. J. Catal. 365, 184–194. https://doi.org/10.1016/j.jcat.2018.07.006.
- Zhou, W., Meng, X., Gao, J., Sun, F., Zhao, G., 2021. Janus graphite felt cathode dramatically enhance the H2O2 yield from O2 electroreduction by the hydrophilicity-hydrophobicity regulation. Chemosphere 278, 130382. https://doi.org/10.1016/j.chemosphere.2021. 130382.
- Zhu, Y., Deng, F., Qiu, S., Ma, F., Zheng, Y., Lian, R., 2021. Enhanced electro-Fenton degradation of sulfonamides using the N, S co-doped cathode: mechanism for H2O2 formation and pollutants decay. J. Hazard. Mater. 403, 123950. https://doi.org/10.1016/j. ihazmat.2020.123950.
- Zhu, Y., Deng, F., Qiu, S., Ma, F., Zheng, Y., Gao, L., 2022. A self-sufficient electro-Fenton system with enhanced oxygen transfer for decontamination of pharmaceutical wastewater. Chem. Eng. J. 429, 132176. https://doi.org/10.1016/j.cej.2021.132176.