

Importance of Graphene in the Electro-Fenton Process

Govindaraj Divyapriya and Puthiya Veetil Nidheesh*



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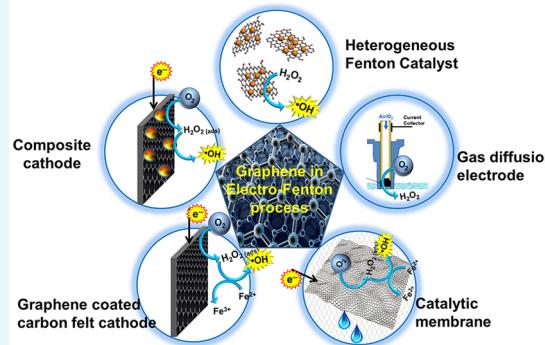
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ABSTRACT: Graphene-based nanomaterials have attracted researchers from various fields due to their extraordinary physical, chemical, and electrochemical properties. An emerging class of graphene-based nanostructures and nanocomposites is considered to be a promising solution to various types of environmental pollution. The electro-Fenton process is one of the easy and effective approaches to treating a wide range of organic pollutants in a liquid medium. The usage of graphene-based electrodes in the electro-Fenton process is considered to be a promising and cleaner way to produce reactive oxygen species to mineralize organic contaminants rapidly. Graphene derivatives are used to immobilize various heterogeneous Fenton catalysts for improved catalytic activity, stability, and reusability. In this review, the importance of graphene-based materials in improving the performance efficiency in the electro-Fenton process is presented along with an enhancement mechanism through the following discussions: (i) the significance of oxygen functional groups and nitrogen doping on graphene layers to enhance the two-electron oxygen reduction reactions; (ii) the advantages of iron-loaded graphene-based materials as catalysts and composite electrodes for the enhanced production of reactive oxygen species; (iii) a summary of various forms of graphene-based materials, modifications in their chemical structure, properties, and applications in the electro-Fenton process to remove organic contaminants.



INTRODUCTION

The electro-Fenton process has received much attention in water and wastewater treatment, after its first documentation by the research groups of Prof. M. A. Oturan¹ and Prof. Enric Brillas² in the early stages of 2000 and is mainly due to the higher mineralization efficiency of the process even for the persistent organic pollutants, lesser cost, and simplicity of operation. The electro-Fenton process utilizes in-situ-generated hydrogen peroxide and externally added ferrous ion for the generation of hydroxyl radicals, which have the highest standard redox potential ($E^\circ(\bullet\text{OH}/\text{H}_2\text{O}) = 2.8 \text{ V/SHE}$) next to fluorine ($E^\circ(\text{F}_2/\text{HF}) = 3.05 \text{ V/SHE}$) and are able to attack organic pollutants present in the aqueous medium non-selectively, until its complete mineralization.^{3–5}

A cathode is the working electrode of the electro-Fenton process as the rate of pollutant degradation mainly depends on hydrogen peroxide production at the cathode by the two-electron reduction of oxygen under acidic conditions and the regeneration of the ferrous ion via the cathodic reduction of ferric ions.^{6,7} Carbonaceous materials were found to be effective electrodes for the generation of hydrogen peroxide, and materials such as graphite, carbon felt, graphite felt, carbon-polytetrafluoroethylene, graphite-polytetrafluoroethylene, carbon nanotubes, carbon sponges, activated carbon fibers, and reticulated vitreous carbon were used as effective cathodes in the electro-Fenton process.⁸ Two-dimensional

carbon, i.e., graphene and its allied forms such as graphene oxide and reduced graphene oxides, received much attention after the isolation of graphene by Novoselov and co-workers in 2004.⁹ In addition to water and wastewater treatment, these carbon materials were found to be effective in various applications including sensors, fuel cells, nanoantenna, touch screens, batteries, light-emitting diodes, sound transducers, and liquid crystal displays.¹⁰

The present study reviews the application of two-dimensional carbon materials in the electro-Fenton process. Graphene-based materials are used as effective cathodes as well as a catalyst support in the electro-Fenton process. The process efficiency enhancement mechanism and the importance of graphene in the improved performance of the electro-Fenton process are analyzed in detail.

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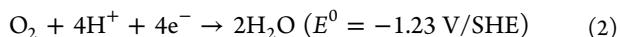
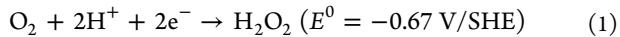
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■ APPLICATION OF GRAPHENE IN THE ELECTRO-FENTON PROCESS

Graphene as a Working Electrode. Though the electro-Fenton process is considered to be one of the promising processes in oxidizing organic contaminants, the reaction kinetics is mainly controlled by the rate of production of hydrogen peroxide. The production of hydrogen peroxide is mainly influenced by the electronic structure of carbon atoms and the physicochemical properties of carbon-based electrodes. Utilizing graphene-based electrodes in the electro-Fenton process as cathode materials is considered to be a more promising and cleaner way of producing hydrogen peroxide during the treatment process. Oxygen-based functional groups present in the carbon cathode act as the active sites to adsorb the dissolved oxygen molecules and subsequently convert them to hydrogen peroxide through a two-electron-based oxygen reduction reaction (ORR). Pristine graphene consist of sp^2 -hybridized carbon and oxygen defects introduced onto the graphene layers acting as the active site for producing hydrogen peroxide through two-electron ORR with enhanced selectivity.¹¹ Typically, graphene is produced through the Hummer's method, which primarily produces exfoliated graphene oxide (GO). GO is characterized to have highly reactive oxygen functional groups resulting from the over-oxidation of the graphite carbon framework during the synthesis processes.¹² These abundant oxygen functional groups present in GO exhibit high charge-transfer resistance. Hence, the electron-transfer ability of the GO is restored through the reduction of excess oxygen content present in GO sheets. The reduction of oxygen is done through a chemical, thermal, or electrochemical pathway.^{13,14} During the reduction of GO, major oxygen functionalities which introduced the charge-transfer resistance are reduced. Only the stable oxygen functionalities (O—H, C—O, and C=O) that are contributed by phenol, quinone, ether, and carbonyl groups remain.

The defects introduced by the stable oxygen functionalities acts as the catalytic active site to selectively enhance the two-electron ORR to produce hydrogen peroxide, whereas the metal-based catalysts/electrodes electrocatalytically convert the oxygen into water molecules through four-electron oxygen reduction reactions especially for fuel cell applications. Moreover, the overpotential required for two-electron ORR ($E^0 = -0.67$ V/SHE) in converting oxygen into hydrogen peroxide is less than the four-electron ORR ($E^0 = -1.23$ V/SHE) (eqs 1 and 2) because the production of hydrogen peroxide through the two-electron pathway involves breaking only the π bond of the oxygen while the σ bond is preserved (O—O).¹⁵ The four-electron pathway in producing the H₂O molecule requires the rupture of the strong O=O bonds of the oxygen molecule.¹²



As an efficient catalyst for the electrogeneration of hydrogen peroxide through the electroreduction of oxygen, graphene exhibits high selectivity and catalytic activity toward the two-electron pathway and suppresses the four-electron pathway for a wider potential window.¹¹

Graphene-modified carbon electrodes are proven to exhibit enhanced performance in producing hydrogen peroxide. The electrochemically reduced GO-modified carbon felt was used

as the cathode for the electro-Fenton process by Let et al.^{14,16} The reduced graphene oxide (rGO)-modified electrode exhibited a high electron-transfer ability with the increase in redox current and decrease in charge-transfer resistance compared to those of the raw carbon felt electrode. Typically, cyclic voltammetry, linear sweep voltammetry, and electrochemical impedance spectroscopy analysis were used as the electroanalytical techniques to prove the enhanced electrochemical property of the graphene-based electrode toward hydrogen peroxide production.^{12,14,16} The rGO-modified cathode decolorized model dye acid orange 7 within 5 min and completely mineralized after 8 h of treatment. The electrode was reported to be stable even after 10 cycles of reuse.¹⁴ Mousset et al.¹⁷ studied a graphene monolayer, multilayer, and foam as cathodes for the electro-Fenton process. They were proven to be feasible for electro-generating hydrogen peroxide effectively compared to unmodified graphite and carbon felt electrodes at the optimum applied potential of -0.6 V vs Ag/AgCl. When the hydrophilicity of the cathode surface is improved, the oxygen diffusion is also increased, thus resulting in enhanced H₂O₂ electrogeneration. All three forms of the graphene electrode efficiently produced ·OH radicals with a sustained Fe²⁺ regeneration rate and H₂O₂ electro-generation rate. Graphene foam was found to be superior to monolayer and multilayer graphene electrodes due to its high electroactive surface area, low charge-transfer resistance, high purity, and 3D porous nature. For the graphene foam cathode, the H₂O₂ electrogeneration yield was found to be 4.25 mg of H₂O₂ L⁻¹ cm⁻³. As a model contaminant, the phenol degradation rate was estimated to be 0.0081 min⁻¹ and the mineralization rate was about 0.0818 h⁻¹. An ultrahigh yield of H₂O₂ was reported for the graphite felt cathode modified with electrochemically exfoliated graphene.¹⁸ The electrochemically exfoliated graphene consists of three to four layers with a small number of oxygen defects. The H₂O₂ generation rate was 7.7 mg h⁻¹ cm⁻² with an energy consumption of 9.7 kW h kg⁻¹. Furthermore, electrochemically exfoliated graphene was characterized to exhibit a high electron-transfer rate and improved the surface hydrophilicity which enhanced the oxygen diffusion, thus resulting in the enhancement of H₂O₂ generation. A schematic representation of the ORR process in a modified graphite felt cathode with electrochemically exfoliated graphene is given in Figure 1.

Researchers also reported that the doping of nitrogen onto the graphene sheets can significantly enhance the H₂O₂ electrogeneration through increasing the selectivity for the two-electron ORR pathway. N-Doping on carbon-based materials creates favorable synergy among the electronic structure, chemical compositions, and physicochemical properties, resulting in a higher faradaic efficiency (95–98% at acidic pH) toward the production of hydrogen peroxide.¹⁹ N-Doping onto the graphene sheet can introduce highly efficient active sites to electrocatalytically reduce the oxygen molecules and also change the oxygen adsorption mode. The incorporation of nitrogen atoms into the carbon lattice creates relatively positive charge density adjacent to the carbon atoms along with the electron-accepting property.¹² Though the conventional N-doped carbon-based catalysts are reported to be efficient at catalyzing the four-electron ORR, recent studies report the excellent catalytic ability of N-doped graphene toward the improved selectivity of two-electron ORR.²⁰ It explicitly shows the importance of the chemical structure of electrocatalyst material to introduce selectivity into oxygen reduction

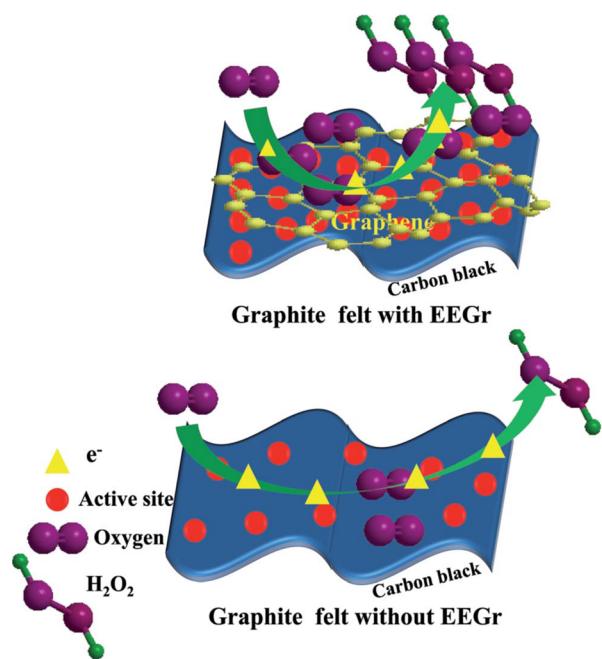


Figure 1. Schematic representation of the oxygen reduction reaction process on a cathode with and without electrochemically exfoliated graphene (EEGr). Reprinted with permission from ref 18. Copyright (2017) The Royal Society of Chemistry.

reactions to obtain the desired products. Graphite felt modified with N-doped graphene was used as a cathode for the electro-Fenton process.²⁰ The selectivity of the two-electron pathway was improved due to the increased mass transfer and oxygen diffusion, which prevent the further conversion of H₂O₂ to water. Also, the presence of a high percentage of pyridinic nitrogen in the N-doped graphene enhances the selectivity and catalytic activity toward the two-electron pathway by impairing the ability to weaken the O–O bond. A schematic illustration of ORR on N-doped graphene is given in Figure 2. Yang et al.²¹ reported the in situ metal-free electrochemical advanced oxidation process using an N-doped graphene-modified graphite felt cathode. The graphene-modified cathode increased the electron-transfer rate and also enhanced the oxygen diffusion by increasing the surface hydrophilicity, resulting in improved H₂O₂ production. Using the cathode, the

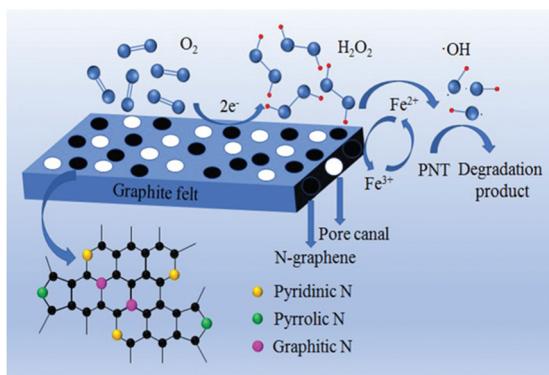


Figure 2. Schematic representation of the oxygen reduction reaction process on the N-doped graphene cathode in the EF process. Reprinted with permission from ref 20. Copyright (2019) The Royal Society of Chemistry.

electrogeneration of H₂O₂ was not found to be changed, but the existence of ·OH and ·O₂ radicals was found using electron-spin resonance spectra even without the addition of the ferrous ion catalyst. The degradation rate in the metal-free process was found to be 4 times higher than in the conventional electro-Fenton process. Enhanced selectivity toward two-electron ORR by graphitized N-doped single-walled carbon nanohorns is reported by Iglesias et al.²² The faradaic efficiency needed to produce hydrogen peroxide was found to be 98% in an acidic environment; excellent catalytic reactivity was also observed in an alkaline environment. Moreover, the onset potential was found to be more positive under all of the pH conditions, such as +0.40 V at pH 1.0, +0.53 V at 7.4, and +0.71 V at pH 13.0. Synergistic effects such as favorable electronic structure, the distribution of N atoms, and enhanced porosity resulted in the selectivity toward two-electron ORR.

Table 1 summarizes the H₂O₂ generation rate, electrical energy consumption for H₂O₂ production, and corresponding current efficiency obtained at various graphene-based electrons used in the electro-Fenton process.

Among the conventional electro-Fenton cathodes, the gas diffusion electrode (GDE) was reported to exhibit a higher removal rate due to the special porous membrane designed to create an efficient three-phase contact among solid, liquid, and gas.²³ GDE efficiently produces a large amount of hydrogen peroxide due to the improved oxygen mass transfer by its porous nature. Researchers also reported the graphene-based GDE for the enhanced electrogeneration of reactive oxygen species (ROS) in the electro-Fenton process. Graphene@graphite-based GDE was developed by Zhang et al.²³ and used as a cathode in the electro-Fenton process to oxidize rhodamine B dye. About 16% less energy consumption was achieved compared to that of conventional GDE. An electron-transfer number of about 2.1 to 2.2 was estimated for ORR in a particular potential range using a rotating disk electrode. A higher corrosive resistance and reuse ability were also reported. Garcia-Rodriguez et al.²⁴ used graphene-based GDE for the mineralization of the electronic wastewater. Carbon cloth-poly(tetrafluoroethylene) (PTFE) GDE was coated with electrochemically exfoliated graphene. An electrogenerated H₂O₂ concentration of as high as 495 mg L⁻¹ was reached in the liquid medium, and about 80% of the wastewater was mineralized in 180 min. Liu et al.²⁵ developed a nitrogen-doped graphene@carbon nanotube (CNT) composite-based GDE that was employed in the degradation of dimethyl phthalate. The kinetic rate constant was found to be 0.0322 min⁻¹, which was 14, 19, and 54 times higher than that for graphite GDE, graphene GDE, and CNT GDE, respectively. The lowest energy consumption was found for the novel electrode rather than for the other GDE electrodes. The lowest onset potential was achieved due to the connection established between graphene and CNT and the nitrogen doping.

Graphene as a Supporting Material. Graphene and its derivatives are promising materials to be potentially used for the immobilization of various nanoparticles in multiple applications. GO is very attractive for use as a support material because of its edge reactivity due to the presence of abundant oxygen functional groups, a large surface area, surface accessibility, and unique 2D lamellar structure. Due to the existence of strong π–π interactions among the graphene sheets, they are prone to restack on each other, which results in the reduced accessible surface sites and stability.²⁶ When

Table 1. Graphene-Based Cathode Materials for the Electro-Fenton Process

electrode	experimental conditions	H ₂ O ₂ generation rate (mg h ⁻¹ cm ⁻²)	electrical energy consumption for H ₂ O ₂ production, EEC (kWh kg ⁻¹)	current efficiency, CE (%)	reference
electrochemically exfoliated graphene/Fe ₃ O ₄ composite coated on carbon cloth	pH 3, -1.5 V	0.375			13
electrochemically reduced GO coated on carbon felt through electrodeposition of GO	pH 3, 2.5–30 mA cm ⁻²				14, 16
graphene monolayer, graphene multilayer	pH 3, -0.58 V	0.0032 0.0048			17
graphene foam		4.25 (mg cm ⁻²)			
electrochemically exfoliated graphene coated on graphite felt	pH 5, -0.5 V pH 5, -0.7 V pH 7, -0.9 V	1.3 2.2 7.7	6.42 4.9 9.7	67–87 62–92 42–92	18
N-graphene–graphite felt (GF) cathode	pH 3, 7 mA cm ⁻²	0.502			20
N-doped electrochemically exfoliated graphene coated on graphite felt	pH 7, -0.9 V	6.2	10.3		21
graphene@graphite-based gas diffusion electrode	pH 3, 20 mA cm ⁻²	1			23
electrochemically exfoliated graphene@carbon cloth-based gas diffusion electrode	pH 3, 29 mA cm ⁻²	9.33		43.5	24
N-doped graphene@carbon nanotube-based gas diffusion electrode	pH 3, -0.2 V	0.26			25
graphene–FeO dispersed onto Ni foam	FeO				26
graphene/carbon nanotube-based carbon aerogel/Fe ₃ O ₄	pH 3, 15 mA	0.125			27
anthraquinone@graphene nanohybrid cathode	pH 3, -0.5 V			90	28
ferrocene functionalized graphene-coated graphite felt	pH 3, -0.6 V	0.055			29
graphene/polypyrrole-modified membrane cathode	pH 2.5 to 8.5, -0.5 to 1 V				30
graphene–iron oxide-modified PTFE membrane	pH 3, -0.6 V	0.26 mg L ⁻¹ cm ⁻²			31

graphene-based derivatives are used as supporting materials, it prevents the aggregation of both graphene sheets as well as the nanoparticles that need to be immobilized. This enhances the overall catalytic activity as well as the stability of both components due to the synergistic interaction existing among them.³² Graphene sheets lack the essential oxygen functional groups for the likely immobilization of the nanoparticles. The presence of oxygen functional groups on GO/mildly reduced GO favors potential utilization as a supporting matrix to synthesize nanocomposites. The presence of abundant oxygen functional groups on the basal plane (hydroxyl and epoxides) as well as on edges (carboxyl and carbonyl) acts as the nucleation site for metal ions to produce GO-based nanocomposites.³² The major problem associated with the conventional Fenton process is the utilization of a homogeneous iron catalyst which produces a large amount of iron sludge and prevents the reuse of the iron catalyst. A heterogeneous iron catalyst was developed for the reuse of iron catalysts such as Fe₃O₄, Fe₂O₃, and Fe@Fe₂O₃. Recently, graphene-supported iron oxide catalysts were examined as potential heterogeneous Fenton, photo-Fenton, and electro-Fenton catalysts, and those catalysts exhibited enhanced performance over a wide range of pH with higher catalytic stability, activity, and reusability.^{23,32}

Iron-Loaded Graphene as Both a Catalyst and a Working Electrode. The important aspect of cathode material selection in the electro-Fenton process depends on the high production of H₂O₂ and the faster regeneration of the iron catalyst, whereas the iron-loaded graphene electrodes could produce ·OH and ·O₂ radicals as major products at the interface due to the simultaneous decomposition of electro-

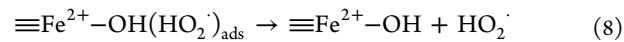
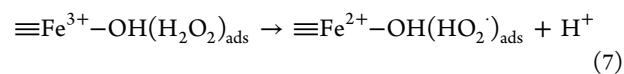
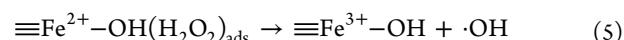
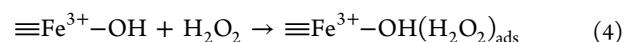
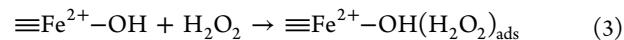
generated H₂O₂. In this case, H₂O₂ could be electrogenerated by graphene; meanwhile, the immobilized iron catalyst catalyzes the decomposition of electrogenerated H₂O₂ into ·OH radicals. This can complete the electro-Fenton reaction without any need of external chemical addition. The iron catalyst to be immobilized on the graphene-based cathode should possess an excellent reversible redox property along with high catalytic stability. Hence, the electrocatalytic decomposition can efficiently occur through the reversible electron-transfer reactions. Magnetite is one the heterogeneous Fenton catalysts, has a permanent magnetic property, and contains both Fe²⁺ and Fe³⁺, hence transferring the electrons effectively without changing its octahedral structure.¹³ Moreover, pure Fe₃O₄ is not suitable as the electro-Fenton cathode since it has low electrical conductivity, a difficult H₂O₂ electrogeneration capacity, and will be easily dissolved at low pH.²⁶ The graphene/Fe₃O₄ oxide composite is reported to have excellent electrochemical properties.^{13,26}

In the clean electro-Fenton process (involving the heterogeneous iron catalyst impregnated on the conductive carbon matrix with no production of iron sludge), the graphene/Fe₃O₄ composite cathode was reported to produce ROS effectively. Shen et al.²⁶ used the aerosol synthesis methodology to produce graphene-Fe₃O₄ hollow hybrid microspheres for use as a catalyst for the heterogeneous Fenton and electro-Fenton reaction. A uniform microsphere with hollow structure, high magnetization, and high Fenton catalytic ability was achieved with 30 wt % graphene catalyst (30G-FeO). Electrochemical analysis showed that an enhancement of the electrocatalytic ability of the electrode material was achieved as a result of the two-electron-dominated process.



Figure 3. Mechanisms involving the production of reactive oxygen species on the graphene/Fe₃O₄ composite electrode during the electro-Fenton oxidation process. Reprinted with permission from ref 13. Copyright (2017) Elsevier.

Iron oxide containing a graphene/carbon nanotube-based carbon aerogel was used as the cathode for the electro-Fenton process by Chen et al.²⁷ The electrode was synthesized by the sol–gel method, followed by a carbonization step. The coexistence of graphene and carbon nanotubes increased the surface area and strength of the electrode. An enhancement in the production of reactive oxygen species was observed due to the abundant porosity and large surface area along with the excellent adsorption capacity. About 5% iron loading on graphene/carbon nanotubes was found to be optimum. About 99% removal of MB was obtained in 60 min at pH 3 with an applied current of 15 mA. Moreover, the ·OH radical generation rate mainly depends on the H₂O₂ generation rate and the iron regeneration rate. The H₂O₂ generation rate depends on the active sites for the two-electron oxygen reduction reaction. Quinone-based functional groups can act as the active site. Zhang et al.²⁸ fabricated the anthraquinone-functionalized reduced graphene oxide electrode and used it as a cathode in the electro-Fenton process. Synthesized α -goethite and γ -lepidocrocite mixed-phase FeOOH catalysts was used as the heterogeneous Fenton catalyst. It was reported that the decomposition of electrogenerated H₂O₂ was mainly catalyzed by surface iron species (\equiv indicates surface-bound iron species in heterogeneous catalyst). Initially, the electrogenerated H₂O₂ formed a complex with surface-bound iron oxide as $\equiv\text{Fe}^{\text{III}}-\text{OH}\cdot\text{H}_2\text{O}_2$ and decomposed into HO₂[·], ·OH, and ferryl iron species ($\equiv\text{Fe}^{\text{IV}}=\text{O}$). Divyapriya et al.¹³ reported the innate quinone-functionalized electrochemically exfoliated graphene (QEEG)/Fe₃O₄ composite electrode for the electro-Fenton application. The mechanism of formation of reactive oxygen species on the graphene/Fe₃O₄ composite electrode was given in detail (Figure 3). The presence of the innate quinone functional group on the electrochemically exfoliated graphene mainly acts as the active site for the electrogeneration of H₂O₂ through the two-electron pathway. The electrogenerated H₂O₂ prefers to bind with the $\equiv\text{Fe}^{\text{3+}}-\text{OH}/\equiv\text{Fe}^{\text{2+}}-\text{OH}$ active sites of the Fe₃O₄ (eqs 3 and 4). Furthermore, $\equiv\text{Fe}^{\text{2+}}$ in immobilized Fe₃O₄ catalyzes the decomposition of adsorbed H₂O₂ (H₂O₂_(ads)) into ·OH radicals and converted them to $\equiv\text{Fe}^{\text{3+}}$ during the reaction (eq 5).



The regeneration of $\equiv\text{Fe}^{\text{3+}}$ to $\equiv\text{Fe}^{\text{3+}}$ happens through the single electron transfer from the cathode carbon skeleton (eq 6). The conversion of $\equiv\text{Fe}^{\text{3+}}$ to $\equiv\text{Fe}^{\text{2+}}$ can also happen during the conversion of H₂O₂_{ads} to (HO₂[·])_{ads} (eq 7). Furthermore, the desorbed HO₂[·] radicals (eq 8) involve the successive oxidation of organic contaminants.

This reaction more likely occurs in an alkaline environment. This cycle continues to convert electrogenerated H₂O₂ to ·OH radicals. The electrode showed the stable catalytic property even after 10 cycles of electrode reuse.

Ferrocene is an iron-based organometallic compound that exhibits a highly reversible redox property and catalytic stability due to its electron donor–acceptor conjugate structure. Divyapriya et al.²⁹ reported the application of the ferrocene-functionalized graphene-based electrode for the oxidation of ciprofloxacin. During the catalytic conversion of electrogenerated H₂O₂ on graphene, H₂O₂ reacts with Fe²⁺-centered ferrocene (Fc) and further decomposes to ·OH radicals. After the reaction, Fe²⁺-centered ferrocene is transformed to the Fe³⁺-centered ferricinium ion (Fc⁺). The regeneration of Fc further occurred by single electron transfer directly from the graphene cathode or can also occur along with the conversion of adsorbed H₂O₂ to HO₂[·] radicals. Greater than 99% removal of ciprofloxacin was achieved within 15 min at the target pH, with a removal rate of 0.222 min⁻¹.

Membrane-based treatment processes are fast and efficient and have a small footprint. However, biofouling and concentrate generation are the major issues that affect the

performance and economics of the process. On the other hand, the electro-Fenton process needs more energy to treat the low-concentration wastewater. A hybrid membrane and the electro-Fenton process can complement each other and reduce the limitations. Zhao et al.³⁰ produced the conductive membrane to be used as the cathode material for the electro-Fenton reaction. This novel conductive cathode membrane was synthesized through the modification of a commercial polyester filter cloth membrane by coating with graphene and polypyrrole via the vapor-phase polymerization process. The synthesized membrane was reported to be highly conductive and showed low charge-transfer resistance. Methylene blue was removed in filtration mode. A conductive membrane was connected to the cathode, and stainless steel was used as the anode. The treatment efficiency was significantly affected by the pH, aeration, applied current, and membrane flux. Degradation was significantly achieved by the electrogenerated H_2O_2 along with the membrane function. At the end of 120 min of treatment, removal efficiencies of about 59.2, 64.0, and 74.6% were obtained for the PPy, Gr/PPy, and Fe-Gr/PPy membranes, respectively. Jiang et al.³¹ reported the graphene-modified catalytic membrane for the oxidation of antibiotic florfenicol at a low concentration. The removal rate of florfenicol during the electro-Fenton catalytic membrane process ($10.2 \pm 0.1 \text{ mg m}^{-2} \text{ h}^{-1}$) was much higher than during the single filtration process ($2.5 \pm 0.1 \text{ mg m}^{-2} \text{ h}^{-1}$) and electro-Fenton process ($4.3 \pm 0.05 \text{ mg m}^{-2} \text{ h}^{-1}$). The process utilized the membrane process as a way to concentrate the florfenicol and to increase the mass transfer for the effective oxidation through the electrogenerated reactive oxygen species.

CONCLUSIONS AND FUTURE PERSPECTIVES

In this review, applications of various graphene-based working electrodes and a heterogeneous catalyst support used for the electro-Fenton process have been summarized, showing that graphene-based electrodes and catalysts are recognized to efficiently produce reactive oxygen species and mineralize the wide range of organic contaminants in synthetic/real wastewater effluents with reduced energy consumption. They are also proven to be highly active, catalytically stable, and reusable. The modification of the graphene chemical structure with oxygen functionalities and nitrogen doping significantly enhances the ORR selectivity. Stable oxygen functional groups present in the rGO act as the active site for the adsorption of dissolved oxygen and subsequently convert it to hydrogen peroxide. In N-doped graphene, synergistic effects such as a favorable electronic structure, the distribution of N atoms, and enhanced porosity resulted in the selectivity toward two-electron ORR. Graphene-iron oxide-based composite electrodes, graphene-based gas diffusion electrodes, and graphene-based membranes open the way for a cleaner and greener treatment of water and wastewater. Hydroxyl radical production and the mineralization efficiency of graphene-based electrodes and catalysts are largely influenced by various parameters such as the graphene-to-Fenton catalyst ratio, nature of the support material used to fabricate the cathode, process of reduction of GO, applied potential, nature of the electrolyte, and concentration of contaminants.

Though the graphene-based electrodes are proven to be highly efficient cathodes in the electro-Fenton process, the large-scale applications of these materials are still questionable. More research needs to be focused on producing cost-effective, mechanically stable electrodes on a larger scale along with the

firm attachment of the graphene/graphene-based composite on the support electrode. Many applications of graphene in the electro-Fenton process have been intensely examined on the laboratory scale; however, there have been no pilot-scale studies reported until now. For the practical application of these potential nanomaterials, upgrading the laboratory-scale studies to pilot-scale studies is necessary for a greater perspective. It is also important to explore various kinds of electrode and reactor configurations and support materials for the large-scale applications of these promising materials. Furthermore, for the real world applications of the graphene-based materials, detailed studies on the environmental implications need to be carried out along with the synthesis methodology and the economic feasibility. Excellent physical, chemical, electrochemical, optical, thermal, and mechanical properties are reported for graphene and for carbon nanotubes, fullerene, carbon quantum dots and will be reported for many more materials yet to come in the near future. This introduces numerous ways to explore these nanocarbons in the electro-Fenton process with a wider horizon.

AUTHOR INFORMATION

Corresponding Author

Puthiya Veetil Nidheesh — CSIR-National Environmental Engineering Research Institute, Nagpur, Maharashtra 440020, India; orcid.org/0000-0001-6112-1314; Phone: +918380095670; Email: nidheeshpv129@gmail.com, pv_nidheesh@neeri.res.in

Author

Govindaraj Divyapriya — Indian Institute of Technology Madras, Chennai, Tamil Nadu 600036, India; Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061, United States

Complete contact information is available at:

<https://pubs.acs.org/10.1021/acsomega.9b04201>

Notes

The authors declare no competing financial interest.

Biographies



Divyapriya Govindaraj is a Fulbright-Nehru postdoctoral scholar at Virginia Polytechnic Institute and State University (Blacksburg, VA, U.S.) (2019–2021). Divyapriya received her Ph.D. degree from Indian Institute of Technology Madras (Chennai, India) (2013–2018). She pursued her M. Tech. (2011–2013) from the Indian Institute of Technology (Bombay, India) in Environmental Engineering and her bachelor's degree is in biotechnology from Anna University (2007–2011). Her research interests include the develop-

ment of biodegradable bacterial cellulose-based membranes for water treatment, electrochemically based advanced removal of emerging contaminants, applications of advanced oxidation processes and nanotechnology for the treatment of water and wastewater, and resource recovery from waste.



Puthiya Veetil Nidheesh completed his B. Tech. in civil engineering from the Government College of Engineering (Kannur, India) and his M. Tech. in environmental engineering and Ph.D. from the National Institute of Technology (Trichy, Tamil Nadu, India). After the completion of his doctoral degree, he worked as an ad hoc faculty member at the National Institute of Technology Calicut (Kattangal, Kerala, India), and as an associate professor at Vimal Jyothi Engineering College (Chemperi, Kannur, Kerala, India). Currently, he is working as a senior scientist at CSIR-National Environmental Engineering Research Institute (Nagpur, India). His research interests include water and wastewater treatment, advanced oxidation processes, and solid waste management. He has published 82 international journal articles, 9 conference articles, 1 book, and 2 book chapters. He is an author of highly cited and highly downloaded articles. He is a reviewer of various journals published by Nature, Wiley, Springer, and Elsevier.

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