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Highly active and stable ferrocene functionalized graphene encapsulated carbon felt array - A novel rotating disc electrode for electro-Fenton oxidation of pharmaceutical compounds

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ABSTRACT

In this study, ferrocene functionalized electrochemically reduced graphene oxide (Fc-ErGO) was used as electro-Fenton catalyst in rotating disc electrode system for the continuous generation of reactive oxygen species without external aeration. The nature of Fc-ErGO was evaluated using X-ray photoelectron spectroscopy, Raman spectroscopy, scanning electron microscopy and energy-dispersive X-ray spectroscopy analysis. Degradation of ciprofloxacin and carbamazepine were carried out to evaluate the performance of reactor. Enhanced removal rate was achieved at a wider range of pH as compared to the unmodified and ErGO modified graphite felt electrode systems. An increase in rotational speed of the disc electrodes resulted in enhanced removal rate due to improved mass transfer activity. At neutral condition, the removal rate was found to be 0.199 min^{-1} and 0.082 min^{-1} for ciprofloxacin and carbamazepine, respectively. Quantification of reactive oxygen species was also done. The Fc-ErGO modified cathode showed 644 μM, 264 μM, and 163 μM of •OH radicals at pH 3.0, 7.0 and 9.0 respectively; it confirms that ferrocene efficiently catalyses the conversion of H_2O_2 to •OH radicals and facilitates the degradation of contaminants. Stable catalytic activity was achieved even upto 10 cycles of repeatable experimental runs. A highly efficient, cleaner electro-Fenton system without external aeration and chemical addition was successfully demonstrated.

1. Introduction

Traditional wastewater treatment processes are often inadequate in removing these emerging contaminants and hence an efficient and appropriate technology is the need of the hour [1–4]. Among the various technologies, advanced oxidation processes (AOPs) have proven to be very successful in mineralizing toxic organic pollutants. One of the prominent AOPs is Fenton's process and has been a promising treatment option for complete removal of a variety of emerging contaminants such as pharmaceutical and personal care products. The conventional Fenton process produces highly reactive •OH radicals ($E^{\circ} = 2.8$ V/SHE) based on the reactions between hydrogen peroxide (H_2O_2) and ferrous iron catalyst as shown in Eqs (1) and (2). However, Fenton process has major drawbacks including ferric hydroxide sludge formation, a narrow working pH range (acidic condition: pH 2.0–3.0) and necessity for a periodic addition of Fenton reagents [5,6]. Moreover, production, storage and transportation of H_2O_2 involve high risks.

$$Fe_{2+}+H^2O^2 \rightarrow Fe^{3+}+HO^- + HO \quad (1)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\bullet} + H^+ \quad (2)$$

Electro-Fenton is one of the promising electrochemical AOPs which gets around with periodic addition of H_2O_2 as it is electrogenerated in the system through the two electron oxygen reduction reaction (Eq. (3)) [7]. Various carbon based electrodes such as graphite felt, activated carbon fiber, gas diffusion electrode, and graphite-polytetrafluoroethylene (PTFE) have been used for H_2O_2 generation in the case of homogeneous electro-Fenton studies [5,8]. In such cases, the Fe^{2+} ions are regenerated through the direct one electron reduction on the surface of electrode (Eq. (4)) or partially regenerated in reaction with H_2O_2.

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \quad (3)$$

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$$Fe^{3+} + e^- \rightarrow Fe^{2+} \quad (4)$$

Further, electrodes were modified to enhance the electrocatalytic generation of H_2O_2 by increasing the electroactive surface area and immobilizing quinone oxygen functionalities to catalyze the two-electron based oxygen reduction reaction (ORR) [9]. The electrode modifications involved acid/chemical/thermal treatment techniques, and were also coated with carbon black/carbon nanotubes/graphene in the presence of PTFE [10]. Recently, nanocarbon based electrodes have emerged as highly active cathode materials for electro-Fenton process due to their extraordinary electron transfer ability, catalytic stability and large specific surface area [11,12]. However, most studies are pertaining to homogenous electro-Fenton systems. Few recent studies have focused on the development of composite electrodes immobilized with a solid Fenton catalyst. Composite electrodes such as Fe@Fe_2O_3/activated carbon fiber [13], Fe_3O_4/Fe_2O_3/activated carbon aerogel [14], Fe_3O_4/graphite felt [15], Fe_3O_4/graphene [16] and Fe_3O_4/Fe/Fe_3C on porous carbon nanofiber [17] are known to work across a wide pH range and prevent iron sludge generation However, iron oxides are characterized with (i) poor electrical conductivity thus restricting the ion diffusion, (ii) decrease in stability of Fe_3O_4 or Fe^{2+} ion on the electrode surface with increasing number of reactions and (iii) immobilization of iron oxides results in increase in charge transfer resistance of the electrode [18]. Hence, it is essential to develop a stable nanocarbon supported iron based electrode for the simultaneous generation of H_2O_2 and •OH radials for the degradation of organic pollutants [19].

Ferrocene is a water insoluble organometallic compound consisting of a central ferrous ion bound with two cyclopentadienyl rings on the opposite sides [20]. It is highly stable, non-toxic with good reversible redox property owing to the electron donor–acceptor conjugated structure [21]. Ferrocene (Fc) is a non-toxic, highly active and stable heterogeneous Fenton catalyst [22,23]. Furthermore, Ferrocene modified graphene has been proven to enhance the electrochemical performance in the view of redox reversibility and regeneration at low potentials [21,24]. In this study, Fc functionalized graphene is explored as a novel catalyst for the electro-Fenton oxidation of pharmaceutical compounds.

Moreover, in most electro-Fenton systems, air or oxygen is continuously purged for the electrogeneration of H_2O_2. However, the solubility of oxygen in water and the mass transfer of oxygen from bulk to electrode-electrolyte interface are key limiting factors which govern H_2O_2 generation. In majority of the EF systems, only less than 0.1% of the oxygen purged is efficiently utilized for H_2O_2 generation [25]. Further, major energy requirement for an electro-Fenton process is during the continuous purging of air/oxygen and stirring process [26,27]. In rotating disc electrode based electro-Fenton systems, the portion of the disc which is brought upwards carries a thin layer of liquid film on its surface enabling contact between the liquid film and oxygen. Further, as the disc rotates, this portion of the disc gets immersed and the film is taken up by the liquid. This results in the establishment of continuous contact between phases and thus minimizes mass transfer resistance from gas phase to liquid phase [10,25]. Table 1 summarizes the recent electro-Fenton studies that eliminated external aeration during the treatment process.

In this study, ferrocene functionalized electrochemically reduced graphene oxide (Fc-ErGO) coated graphite felt has been used as the rotating disc cathode in a heterogeneous electro-Fenton system for the direct generation of the reactive oxygen species (H_2O_2 and •OH radicals). The performance of the system was evaluated by studying the degradation of ciprofloxacin and carbamazepine, and quantifying the reactive oxygen species in the Fc–ErGO electro-Fenton system. The influence of operational parameters such as pH of the reaction liquid, rotational speed of the disc electrode, applied electric potential and initial contaminant concentration on the efficiency of electro-Fenton oxidation was studied. Reusability studies were carried out to evaluate the stability and feasibility of using the electrode material over a long run. Finally, the mechanism of oxidation in this Fc-ErGO electro-Fenton system has been discussed in detail.

2. Materials and methods

2.1. Materials

Ciprofloxacin, carbamazepine, titanium (IV) oxysulfate-sulphuric acid solution, ferrocene carboxylic acid and PTFE 60 wt % was purchased from sigma aldrich. Graphite felt was procured from Sainergy Fuel Cell India Pvt. Ltd, Chennai India. Dimethyl sulfoxide (DMSO) and 2, 4-Dinitrophenylhydrazine (DNPH) were supplied by Avra Chemicals, India. Other chemicals were purchased from Merck, India.

2.2. Synthesis of ferrocene functionalized graphene oxide

Ferrocene functionalized graphene oxide (Fc-GO) was prepared based on the modified methodology mentioned by Fan et al. [21]. Initially, 2.5 mg L^{-1} of GO (volume of 100 mL) was dispersed well using an ultrasonicator. 100 mg of N,N′-Dicyclohexyl-carbodiimide was intermittently dispersed with GO and 100 mL of ethylenediamine, followed by ultrasonication for 2 h. Then, the mixture was heated at 70 °C for 24 h under continuous stirring. The resulting aminated graphene oxide was centrifuged, washed well to remove the unreacted reagents. Subsequently, it was resuspended in 100 mL deionized water. Thereafter, 10 mL of Ferrocene carboxylic acid (Fc-COOH) (10 mg mL^{-1}) was added to the aminated graphene oxide solution under stirring condition at room temperature for 3 h.

Table 1
Summarization of the electro-Fenton studies carried out without external aeration.

Reactor type	Anode	Cathode	Catalyst	Contaminant	Reference
Rotating disk reactor (100 mL)	Platinum sheet (30 mm × 20 mm)	Graphite felt (Ø 50 mm, thickness of 5 mm)	Homogenous 0.2 mM Fe^{2+}	Methyl orange (50 mg L^{-1})	[25]
Rotating disk reactor (250 mL)	Graphite column (Ø 20 mm)	Graphite disk cathode (Ø 80 mm, thickness of 8 mm)	Homogenous 1 mM Fe^{2+}	Tetracycline (50 mg L^{-1})	[26]
Rotating disk reactor (100 mL)	Pt sheet (1.0 × 1.0 cm)	Rotating Fe_3O_4/gas diffusion cathode	Immobilized Fe_3O_4	Tetracycline (50 mg L^{-1})	[27]
A modified divided electrolytic system (250 mL)	Platinum flakes (Compartment 1) (1 × 1 cm)	Platinum flakes (Compartment 1& 2) (1 × 1 cm)	Pd/C catalysts (2.5 mg mL^{-1} and 1 mM Fe^{2+})	Rhodamine B (10 mg L^{-1})	[28]
Undivided electrolytic cell (400 mL)	Mixed metalOxide/Ti (IrO_2/Ta_2O_5) (85 × 15 × 1.8 mm)	Mixed metalOxide/Ti (IrO_2/Ta_2O_5) (85 × 15 × 1.8 mm)	Pd/Al_2O_3 (1 g $L^{-1}$and Fe^{2+}(13.6 mg L^{-1})	Trichloroethylene (26.1 mg L^{-1})	[29]
Three-electrode column	Mixed metalOxide/Ti (IrO_2/Ta_2O_5)	Mixed metalOxide/Ti (IrO_2/Ta_2O_5)	Pd/Al_2O_3(2 g), Fe^{2+}	Trichloroethylene (5.3 mg L^{-1})	[30]