

Research note

Fe₃O₄ Magnetic Nanoparticles/ Graphene Oxide Nanosheets/Carbon Cloth as an Electrochemical Sensing Platform

A. Jafarizad^{1*}, H. Hazrati^{1,2}, A. M. Jabbari Esgandani³

¹ Faculty of Chemical Engineering, Sahand University of Technology, Tabriz, Iran

² Environmental Engineering Research Center, Sahand University of Technology, Tabriz, Iran

³ Faculty of Chemical Engineering, Paris-Sud University, Paris, France

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ABSTRACT

To eliminate the (RR1346), which is considered as a waste in wastewater from dye industries, the electrochemical advanced oxidation process is used in this study. Graphene oxide coated carbon cloth (GO/CC) and Fe₃O₄/GO coated carbon cloth (Fe₃O₄/GO/CC) electrodes are fabricated by synthesis of GO and Fe₃O₄ nanoparticles. Characteristic properties such as surface morphology as the main reason for utilizing Fe₃O₄/GO/CC as electrodes have been investigated and determined by various instrumental analyses including Atomic Force Microscopy (AFM), Field Emission Scanning Electron Microscopy (FESEM), Cyclic Voltammetry (CV), and Cathodic polarization. In addition, for investigating the process yield by the mentioned electrodes, UV-vis spectrophotometric analysis has been conducted to determine dye concentration in the sample wastewater. After comparing the removal efficiency of fabricated electrodes at the same time intervals and determining the concentration of RR1346 dye in samples after oxidation process at different time intervals, results indicated better removal efficiency of Fe₃O₄/GO/CC fabricated electrode than the other two electrodes, in which this conclusion was proved by AFM, FESEM, and UV-vis results.

1. Introduction

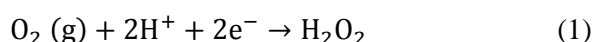
Nowadays, the water problem is completely clear to people, scientists, and governments and cannot be denied; besides, global warming, melting glaciers, evaporation of surface waters, and increased water consumption by human add fuel to this problem [1]. The industry is a huge source of wastewater production, hazardous wastewater creating health risks for human, and a

pollution issue for the environment [2]. One of the mentioned industries is the dye industry, in which water plays a certain role and, as a result, wastewater containing various chemical dyes is produced and is considered as hazardous waste. Due to the lack of required technology or high expenses of wastewater treatments, unfortunately, these wastewaters are released in the environment, e.g., free water [3]. Hence, research and study

*Corresponding author: jafarizad.abbas@gmail.com

on new low-cost methods for treating wastewaters is considered a crucial need. The current methods for wastewater treatments or handling include precipitation, evaporation, solvent extraction, ion exchange, reverse osmosis, and membrane separation [4]. One of the promising methods of dye removal is advanced electrochemical oxidation process.

Related literature covers the utilization of various types of electrodes of different materials [5]. More potent indirect electro-oxidation methods with hydrogen peroxide electro generation have also been developed for wastewater remediation. In these techniques, H_2O_2 is continuously supplied to the contaminated solution from the two-electron reduction of O_2 usually at carbon-felt [6-11] and carbon-polytetrafluoroethylene (PTFE) O_2 -diffusion [12, 13] cathodes:



The oxidizing power of the hydrogen peroxide is highly enhanced by the addition of Fe^{2+} that generates the Fenton reaction [14]:



Contaminants are then removed by their homogeneous degradation with generated OH^\bullet .

In this study, synthesized Fe_3O_4 NPs and GO nanosheets have been coated on carbon cloth and fabricated as an electrode to be used in the electrochemical process.

Due to its spectacular magnetite properties, Fe_3O_4 NPs have been applied to various fields such as medicine, drug delivery systems (DDS), magnetic resonance imaging (MRI), cancer therapy and microwave devices, magneto-optics devices, sensors, high-frequency applications, catalysis, and magnetic sensing [15, 16].

Easy functionalization of graphene oxide, considered as an electrical insulator, large specific surface area, and easy dispersability in water and other organic solvents and in different matrices due to the presence of the oxygen functionalities are some particular properties of graphene oxide [17].

From many favored properties of $Fe_3O_4@GO$ nanocomposite, considerably high saturation magnetization, interesting electronic transport properties, low toxicity and high bio-compatibility, excellent platform for the generation of a new type of composites, availability of hydroxyl, epoxy, and carbocyclic acid groups can be noted [18].

Characteristic properties such as summits density and surface morphology as the main reason of utilizing Fe_3O_4 , GO, and carbon cloth as electrodes have been investigated and determined by several instrumental analyses such as AFM, FESEM, Cyclic Voltammetry (CV), and cathodic polarization. In addition, for investigating the removal yield, UV-vis spectrophotometric analysis has been conducted to determine the concentration of the mentioned dye component in the sample after the treatment process and investigate removal efficiency.

2. Materials and methods

2.1. Materials

Reactive Red (RR1346), a commercial dye (Boyakhsaz Co., Iran), was chosen as the model compound and was used without further purification. Analytical grade n-butanol, graphite Na_2SO_4 , and $FeCl_3$ were obtained from Merck. Polytetrafluoroethylene (PTFE) and carbon cloth were purchased from Electro Chem and Pars Hydro Pasargad, Iran, respectively.

2.2. Synthesis of graphene oxide

Appropriate amount of Graphite along with designated amount of sodium nitrate was added to 50 mL of sulfuric acid in a 250 mL Erlenmeyer at room temperature and agitated for 10 min. Then, it was placed in an ice-water bath at 4 °C. KMnO₄ (6 g) was slowly added to the solution, which was agitated for 30 min. Then, the mixture was placed in an oil bath at 35 °C and agitated for 3 h till the solution color turned into brown color. Once again, the Erlenmeyer was placed in an ice-water bath at 4 °C and the appropriate amount of water was added. Then, solution temperature was raised to 80 °C, and reaction continued for 15 min and temperature was controlled till it reached 40 °C. After half of an hour, certain amount of water was added to the mixture, and hydrogen peroxide was added to the resulted solution in a drop-wise fashion until solution turned to a yellowish color. In the final step, the mixture was filtered and washed by distilled water and dried in an oven at 80 °C.

2.3. Synthesis of Fe₃O₄ nanoparticles

Iron (III) acetylacetonate (Fe(acac)₃, 1.06 g) was dissolved in a mixture of 15 mL of oleylamine (OAm) and 15 mL of benzyl ether (BE) in a four-necked round bottom glass reactor under continuous stirring. The mixture was heated to 120 °C and kept at this temperature for 1 h to remove humidity under a flow of nitrogen gas. The stirring process was kept on during all steps. Then, the temperature of the mixture rapidly increased to 300 °C, and the reaction continued for 1 h at this temperature. Finally, the mixture was separated into two centrifuge tubes and 40 mL of ethanol was added and centrifuged at 8500 rpm for 12 min. After the purification of Fe₃O₄ nanoparticles, the nanoparticles were

dispersed in hexane and saved for further use.

2.4. Synthesis of Fe₃O₄@GO nanocomposites

Desired amount of Fe₃O₄ nanoparticles was dispersed in chloroform and added into a round bottom flask containing GO suspension in DMF. The GO-Fe₃O₄ solution was sonicated at room temperature for 3 h. Next, using a magnet, the GO@Fe₃O₄ nanocomposites were separated. Finally, GO@Fe₃O₄ nanocomposites were dispersed in 40 mL of n-hexane and mixture was centrifuged at 7500 rpm for 10 min and dried under vacuum.

2.5. Fabrication of GO/CC and Fe₃O₄@GO/CC electrodes

Appropriate amounts of GO (0.1 g) or Fe₃O₄/GO (0.1 g), PTFE (0.42 g), distilled water (60 ml), and n-butanol (3 %) were mixed in an ultrasonic bath (Grant, England) for 10 min to create a highly dispersed mixture. The resulting mixture was heated at 80 °C until it resembled an ointment in appearance. The ointment was bound to carbon cloth and sintered at 350 °C for 30 min under inert conditions (N₂).

2.6. Instrumentation

The experiments were conducted in an open, undivided cell with a DC power supply. The solution pH was measured with a Metrohm 654 pH-meter, Switzerland. The removal of color was followed by a UV 1700 Shimadzu UV-Vis spectrophotometer, Japan. Current-potential curve was plotted by cyclic voltammetry using a conventional three-electrode cell in conjunction with a computer-controlled multichannel potentiostat (PG-Stat 30, Netherland) with a scan rate equal to 10mVs⁻¹. The surface morphology of

fabricated electrodes was analyzed by atomic force microscope (AFM) of Nanosurf mobile S, Switzerland. Scanning electron microscopy (SEM) was carried out on a Tescan Mira3 field emission device, Czech after gold-plating of the samples.

3. Results and discussion

3.1. AFM results

Fig. 1 shows AFM images of CC, GO/CC,

and GO@Fe₂O₃/CC, respectively. Figs. 1 (a) and (d) show AFM image (2μm×2μm) of the CC electrode surface. Figs.1 (b) and (e) show AFM image (2.51μm×2.51μm) of the GO/CC electrode surface. Figs.1 (c) and (f) show AFM image (3.91μm×3.91μm) of the GO@Fe₂O₃/CC electrode surface. It is clear that the roughness of the GO@Fe₂O₃/CC electrode surface was more than that of two other electrode surfaces.

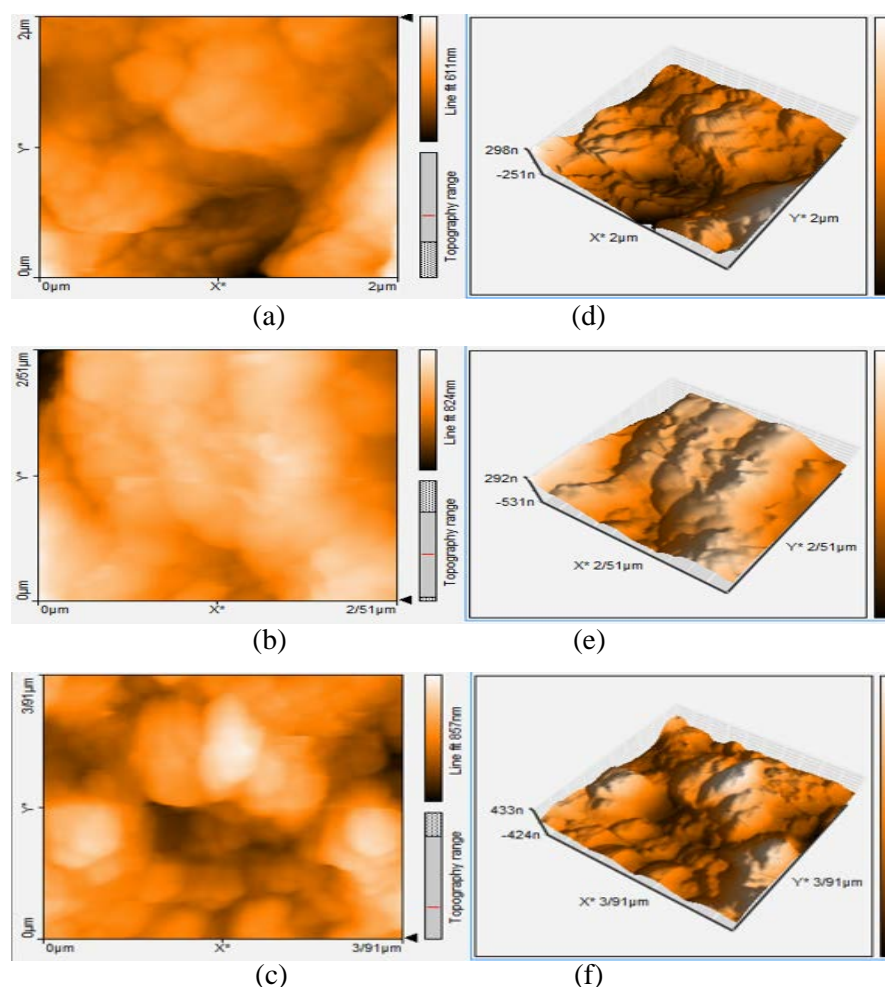


Figure 1. Three-dimensional (3D) AFM images of (a) CC, (b) GO/CC, (c) Fe₃O₄@GO/CC. Two-dimensional (2D) top views of (d) CC, (e) GO/CC, (f) Fe₃O₄@GO/CC.

3.2. FESEM results

Figs.2 (a) and (b) show FESEM images of the carbon cloth and GO@CC fabricated electrodes, respectively. Fig.2 (c) illustrates the GO@Fe₂O₃/CC fabricated electrode. It is clear that the Fe₂O₃ nanoparticles are confined in the GO/CC, implying a strong

interaction of GOs can prevent the aggregation of Fe₂O₃ particles in the GO@Fe₂O₃/CC fabricated electrode. Other works also demonstrated that we must use a material to prevent the aggregation of nano particle in the electrode [19].

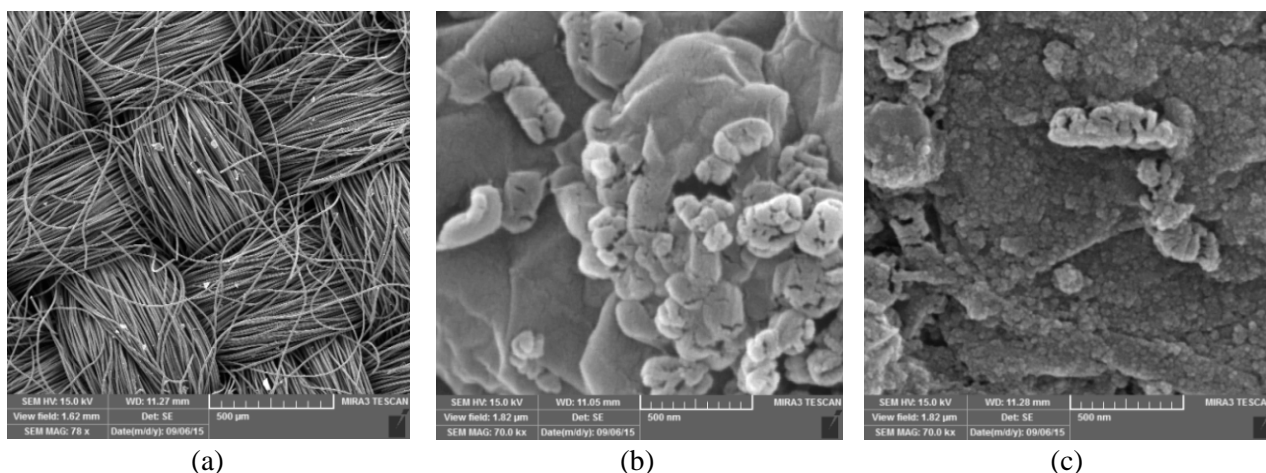


Figure 2. FESEM images of (a) carbon cloth, (b) GO@CC, and (c) GO@Fe₃O₄/CC fabricated electrodes.

3.3. Cyclic voltammetry (CV) and cathodic polarization results

Fig.3 illustrates the cyclic voltammetry curve of GO@Fe₃O₄/CC in aqueous solution at pH

3.0 with O₂ atmosphere at 25 °C. The cyclic voltammetry pattern of GO@Fe₃O₄/CC electrode matches the standard CV curve.

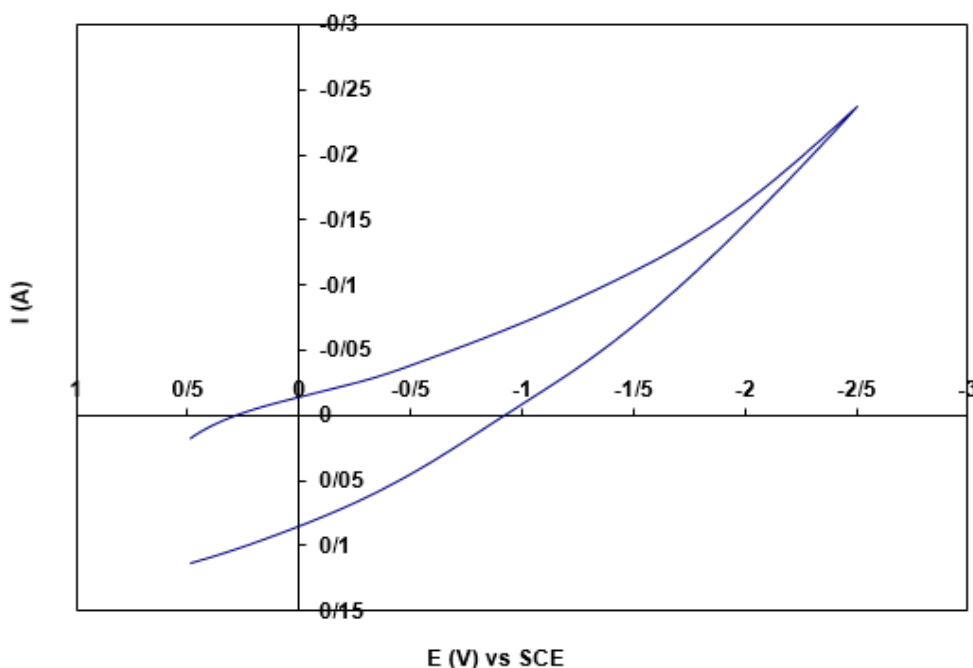


Figure 3. Cyclic Voltammetry (CV) curve of GO@Fe₃O₄/CC in aqueous solution at pH 3.0 with O₂ atmosphere. Sweep rate = 10 mVs⁻¹, [Na₂SO₄] = 0.05 M, room temperature (25 °C).

Fig.4 shows the cathodic polarization of cells with CC, GO/CC, and GO@Fe₃O₄/CC electrodes, measured in aqueous solution at pH 3.0 with O₂ atmosphere at 25 °C. The Cathodic polarization of the GO@Fe₃O₄/CC cathode was much higher than the GO/CC

and CC cathodes. These results are in agreement with those of other works [20]. In GO@Fe₃O₄/CC electrode, it is possible that Fe₃O₄ plays the role of an electrocatalyst for oxidation.

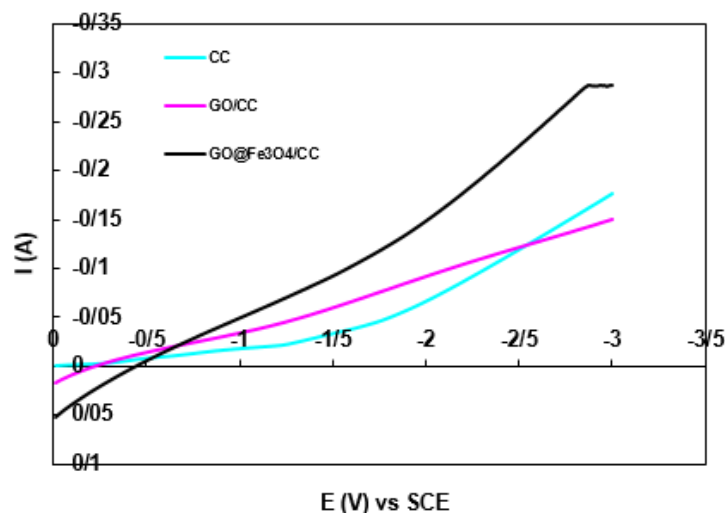


Figure 4. Cathodic polarization curve of CC, GO/CC, and GO@Fe₃O₄/CC in aqueous solution at pH 3.0 with O₂ atmosphere. Sweep rate = 10 mVs⁻¹, [Na₂SO₄] = 0.05 M, room temperature (25 °C).

4. UV-vis results

Fig.5 shows UV-vis results for CC, GO/CC, and GO@Fe₃O₄/CC electrodes. Clearly, UV-vis results indicate better removal efficiency for GO@Fe₃O₄/CC fabricated electrode rather than the other two electrodes in different concentrations of RR1346 dye. This is mainly due to the counterbalancing of proton

consumed during the Fenton reaction (eq.2) [21] by the protons produced via water oxidation at the anode [22]. This phenomenon can be observed even in GO@Fe₃O₄/CC electrode. Therefore, the removal efficiency of dye for this system is higher than that of another electrode.

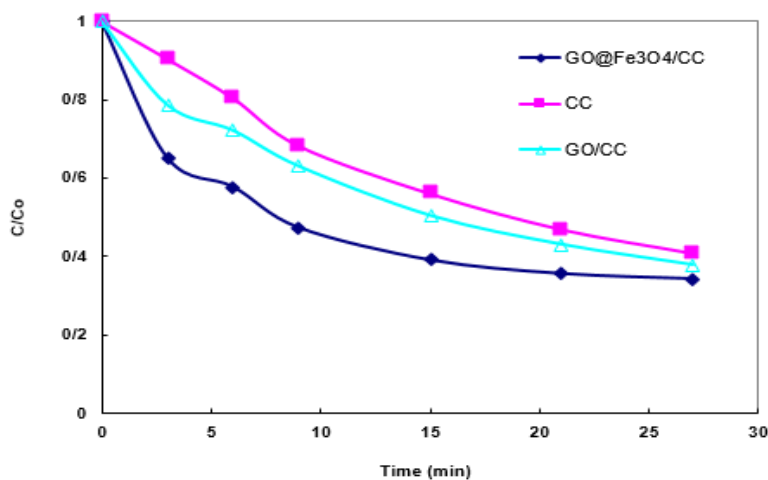


Figure 5. Removal efficiency for a 20 mg RR1346 solution at room temperature (25 °C), pH 3.0, I = 100 mA, and [Na₂SO₄] = 0.05M.

5. Conclusions

In this work, the advanced electrochemical oxidation process of dye, named red reactive 1346, was carried out by CC and fabricated GO/CC and Fe₃O₄@GO/CC electrodes. By

determining the concentration of RR1346 dye in samples after oxidation process at different time intervals, results indicated better removal efficiency for Fe₃O₄@GO/CC fabricated electrode rather than the other two electrodes,

which can be directly related to the results of AFM and FESEM analyses, producing higher summits density and active H₂O₂ generation sites for Fe₃O₄@GO/CC electrode.

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