



Research Article

PbO₂/graphite and graphene/carbon fiber as an electrochemical cell for oxidation of organic contaminants in refinery wastewater by electro-fenton process; electrodes preparation, characterization and performance

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ABSTRACT

The electro-Fenton oxidation process was used to treat organic pollutants in industrial wastewater as it is one of the most efficient advanced oxidation processes. The novel cell in this process consists of a prepared PbO₂ electrode by electrodeposition on graphite substrate and carbon fiber modified with graphene as a cathode. X-ray diffraction, fluorescence, analysis system, atomic force microscopy, and scan electron microscopy were used to characterize the prepared anode and cathode. XRD patterns clearly show the characteristic reflection of the mixture of α - and β phases of PbO₂ on graphite and carbon fiber, and AFM results for cathode and anode present that PbO₂ on graphite substrate and graphene on carbon fiber surface are on a nanoscale. Contact angle measurement was determined for the carbon fiber cathode before and after modification. The anodic polarization curve showed a higher anodic current when utilizing the PbO₂ anode than the graphite anode. Phenol in simulated wastewater was removed by electro-Fenton oxidation at 8 mA/cm² current density, 0.4 mM of ferrous ion concentration at 35 °C up to 6 h of electrolysis. Chemical oxygen demand for the treated solution was removed by 94.02% using the cell consisting of modified anode and cathode compared with 81.23% using modified anode and unmodified cathode and 79.87% when using unmodified anode and modified cathode.

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INTRODUCTION

Organic pollutants such as benzoic acid, oxalic acid, phenols, and phenolic derivatives have been used in a variety of industries, such as formaldehyde resins, pharmaceuticals, pesticides, textiles, dyes, petroleum refineries, paint removal, varnish printing, and dyeing fabrics [1, 2]. After these industrial processes, this compound is discharged into the water effluents. The extensive pollution of these compounds

in aqueous streams has been considered the most harmful and persistent organic contaminants in wastewater produced by various industries [3, 4]. Degradation of aqueous effluent containing phenol and phenolic derivatives is of primary concern due to its toxicity to human and aquatic life, even at low concentrations. Phenolic wastewater is listed among the most severe environmental pollutants [5–7]. Complete oxidation of these organic pollutants is significant at the end of wastewater treatment [8].

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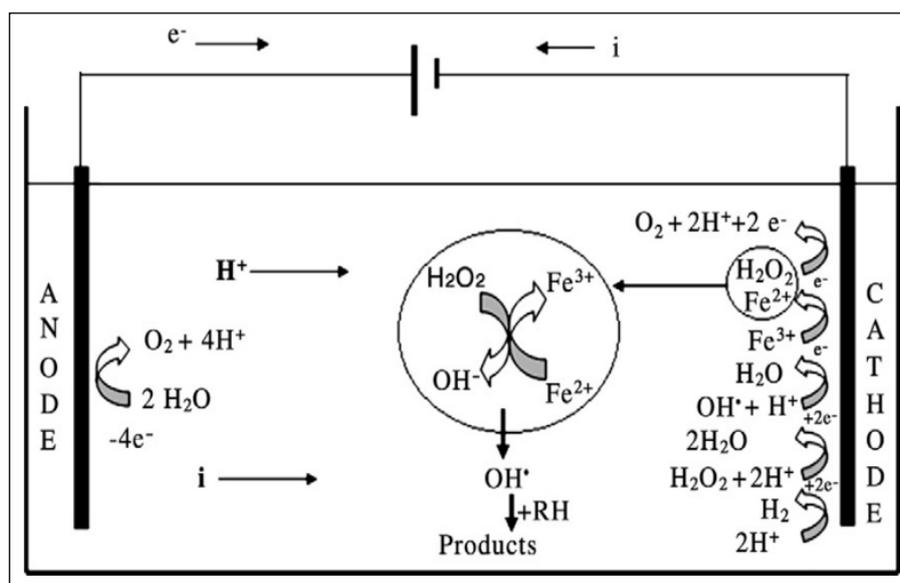


Figure 1. Electro-Fenton process.

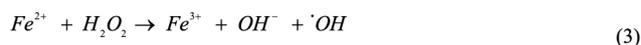
The traditional treatment technique, such as biological and chemical oxidation, no longer satisfies modern industry requirements for processes, so they need alternative methods [6]. Biodegradation is a very economical method for wastewater treatment for organic compounds, but this technique cannot treat phenolic wastes because of their resistance to microorganisms [9]. Phenol adsorption by some adsorbents like activated carbon adsorbs phenolic and phenolic compounds by firm contact between phenols and the positive charge of activated carbon. Adsorption is considered an economical and efficient method to remove pollutants, but the adsorption capacity of the adsorbent limits it and cannot be renewable easily [10]. Phenol removed by activated carbon is not degraded but removed from the aqueous stream and passed into another phase. Adsorption of a phenolic compound may cause the formation of hazardous by-products (secondary pollution) [11].

The chemical oxidation process utilizes strong oxidants that degrade phenolic pollutants with a fast oxidation rate and do not produce secondary pollutants. However, this process is costly and has some operational problems [12, 13]. Other treatment methods include Fenton oxidation, photocatalytic degradation, ozone treatment, and electrochemical [14].

Recently, a more efficient and non-selective process, advanced oxidation processes (AOPs), offer an effective and rapid alternative treatment for various pollutants. In AOPs, a strong oxidant, hydroxyl radical ($\cdot\text{OH}$), generated in situ, destroyed more organic pollutants until their complete mineralization into CO_2 , water, and inorganic ions [15–17]. One of these AOPs is Fenton oxidation. The Fenton process is an essential treatment method as it is simple, does not need special equipment, and gives high efficiency in removing organic pollutants [18].

The Fenton oxidation process has some disadvantages, such as the storage and transportation of hydrogen peroxide (H_2O_2); its activity is less than the modified one called the

electro-Fenton oxidation process. In the electro-Fenton oxidation process, ferrous ion (Fe^{2+}) is added, and H_2O_2 is generated electrochemically in situ at the cathode by two-electron oxygen reduction as shown in Figure 1 (RH represents an organic molecule) [15]. The cathode must have an appropriate potential to form H_2O_2 from the two-electron reduction of O_2 (Eq. 1), and the famous electrodes used for his purpose are the carbonous electrodes such as reticulated vitreous carbon, carbon felt, carbon sponge, and graphite [15, 19, 20]. Electro-decomposition of H_2O_2 produced ($\cdot\text{OH}$) also at the cathode (Eqs. 2 and 3) [21, 22].



Through (Eq. 3), Fe^{3+} is formed continuously, and through (Eq. 4), continuous regeneration of Fe^{2+} at the cathode, thus avoiding Fe^{3+} accumulation in the reaction medium and accordingly eliminating the production of iron sludge [23].



The anode material is one of the leading parameters in the electrochemical reaction processes because it intensely influences the mechanism of the decomposition reaction and, accordingly, the products of the anodic reaction [24]. The generally used anode materials for decomposing organic contaminants in wastewater are graphite, lead dioxide, nickel, and platinum. Some electrodes lose their activity rapidly or have high cost and mechanical resistance problems; also, it is difficult to find a suitable material that deposits on it [25]. Other electrodes have a short lifetime, and they have partially oxidized the organic pollutants in wastewater [26]. Active anodes, such as platinum (Pt), ruthenium oxide (RuO_2), and iridium oxide (IrO_2), have been used a lot recently because they have high electrocatalytic activity and high chemical stability [27, 28]. Active anodes partially

oxidize organic pollutants because of their low oxygen evolution potential, which reduces their current efficiency for degradation reactions [29]. On the other hand, the PbO_2 electrode has high electrochemical stability [30], good electrical conductivity, high chemical inertness, and high stability in corrosive solutions [31, 32], and oxidized organic compounds such as phenol effectively [33]. PbO_2 electrodes can be efficiently and economically prepared [30].

The cathode anode material is also crucial in electrochemical oxidation, especially in electro-Fenton oxidation. Carbonous material is used extensively as cathodes in electro-Fenton oxidation due to its surface area, porosity, chemical inertness, etc. In order to increase the efficiency of the electro-Fenton process, effective H_2O_2 must be produced. The cathode is the working electrode in the electro-Fenton process, and its modification can be achieved by different methods to improve H_2O_2 production. The H_2O_2 rate produced in situ through the reaction and the hydroxyl radical rate depends mainly on the cathode material's nature and properties. Some modification methods aim to increase the cathode's specific surface area and hydrophilicity. Others raise catalytic activity by increasing the active site on its surface and electrode conductivity. This modification will increase the production rate of H_2O_2 and thereby increase the degradation rate of organic pollutants [34, 35].

This work deals with preparing PbO_2 electrodeposited on graphite substrate as an anode and carbon fiber modified by graphene as a cathode. PbO_2 was used to promote the electrochemical activity of graphite electrodes, and graphene was utilized to improve the H_2O_2 production on the cathode electrode. The prepared anode electrode was characterized by X-ray diffraction (XRD), X-ray fluorescence (XRF), scan electron microscopy (SEM), energy dispersive X-ray analysis system (EDX), and atomic force microscopy (AFM.) The modified cathode was characterized by XRD, XRF, SEM, EDX, AFM, and contact angle measurement. The novel cell consists of modified electrodes used in the electro-Fenton oxidation process of phenolic derivatives in simulated wastewater.

MATERIALS AND METHODS

All chemicals used in the experiments were of reagent grade, and there was no need for further purification. Lead Nitrate $\text{Pb}(\text{NO}_3)_2$, Sodium Laureth Sulfate (SLS surfactant), Nitric Acid (HNO_3), phenol, sulfuric acid (H_2SO_4), and distilled water were used in the preparation of all aqueous solutions.

The electrochemical cell had a 400 mL capacity. A hot plate magnetic stirrer reserved the cell heat (LABINCO, model L-81) supplied by power by DC power supply (KA3005D Digital Control DC Power Supply 30V 5A) with outlet voltage (0–30V) and output current (0–5 A).

PbO_2 Electrode Preparation (Anode Modification)

Before the deposition process, the graphite plate with dimensions of ($3 \times 10 \text{ cm}^2$) was well cleaned and boiled in dis-

tilled water for 30 min. The graphite plate was then activated electrochemically in an open, undivided cell in a 1.44 M (H_2SO_4) solution, and a 14 mA/cm^2 current density was applied at 90 °C for 30 min. Electrode modification occurs by depositing a film of PbO_2 on electrode surfaces. The cell consists of two graphite plates as anode and a cathode used to prepare the anode electrode. The distance between the anode and the cathode in the electrodeposition cell was 3 cm. The PbO_2 film on the graphite plate was produced using an electrolyte (pH 1.6) containing 0.2 M of lead nitrate ($\text{Pb}(\text{NO}_3)_2$), 0.1 M of HNO_3 , and 0.4 ml of SLS surfactant. The electrolytic solution was heated to 65 °C, and the current density applied was 1.1 mA/cm^2 . After 3 h of electrodeposition, the electroplated electrode was washed with distilled water and kept dry for electrochemical oxidation of simulated wastewater [30].

Graphene Electrode Preparation (Cathode Modification)

Carbon fiber with a dimension of ($3 \times 10 \text{ cm}^2$) was used as the base cathode, and 0.5 g of graphene was used to modify it. Mixing 0.14 mL of Polytetrafluoroethylene (PTFE), 3 mL of ethanol, and 2 mL of deionized water, a kind of slurry was formed, coated on the carbon fiber's two sides. Then, it dried at room temperature and was calcinated for 30 min at 360 °C [36].

Electro-Fenton Oxidation Process

The electro-Fenton oxidation process degraded phenolic pollutants in simulated wastewater. The simulated wastewater was prepared with 150 ppm of phenol by adding 150 mg to 1 L of distilled water. Sodium sulfate (Na_2SO_4) with a concentration of 0.05M was used as a supporting electrolyte, and the pH of the solution was justified to 2–3 by 0.1M of H_2SO_4 . The two electrodes (anode and cathodes) were dipped into the electrolytic solution and connected to the DC power supply that applied a constant current density at 8 mA/cm^2 up to 6 h at 35 °C and 200 rpm rotation speed. Compressed air was bubbled into the solution at a flow rate of 1 liter per minute using an electromagnetic air pump (ACO-001), externally added $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ with a concentration of (0.4 mM). Finally, the samples were collected during the electrolysis process, and the concentration of phenol was determined by measuring the chemical oxygen demand (COD) using a COD reactor (Lovibond® Water Testing, MD 200 COD, tube tests, Germany) (Eq. 5).

$$\text{COD removal, \%} = \frac{\text{COD}_0 - \text{COD}_t}{\text{COD}_0} \times 100 \quad (5)$$

RESULTS AND DISCUSSION

Characterization of the Electrodes

XRD

XRD technique was used to find out the phase and structure of the prepared anode electrode in the range between 0 and 80° of 2θ for electrodeposition of PbO_2 on graphite at 65 °C, and the current density applied was 1.1 mA/cm^2 .

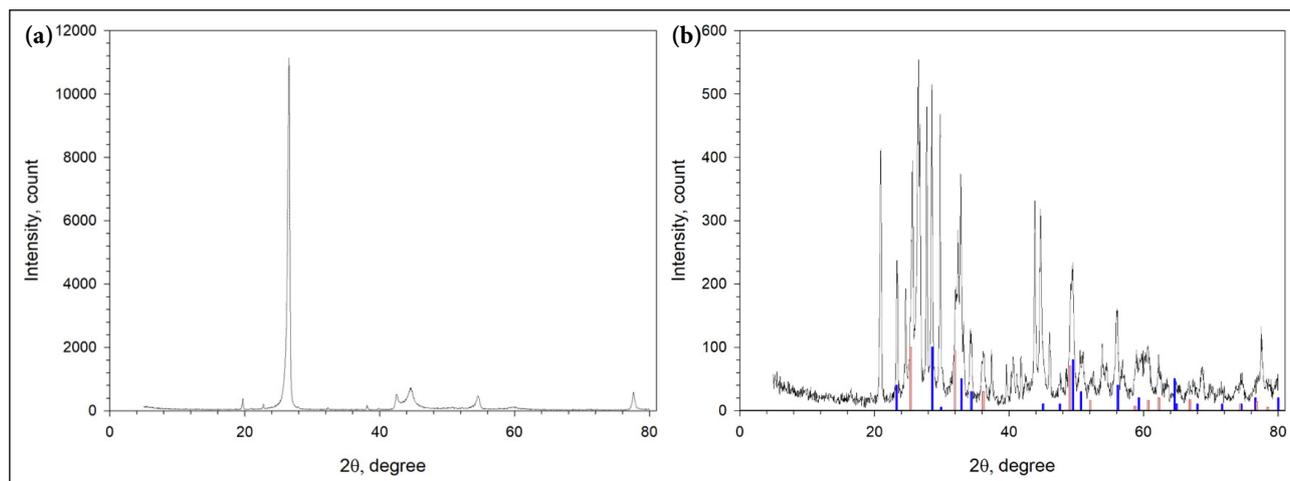


Figure 2. XRD pattern of graphite anode (a) original (b) modified by PbO_2 .

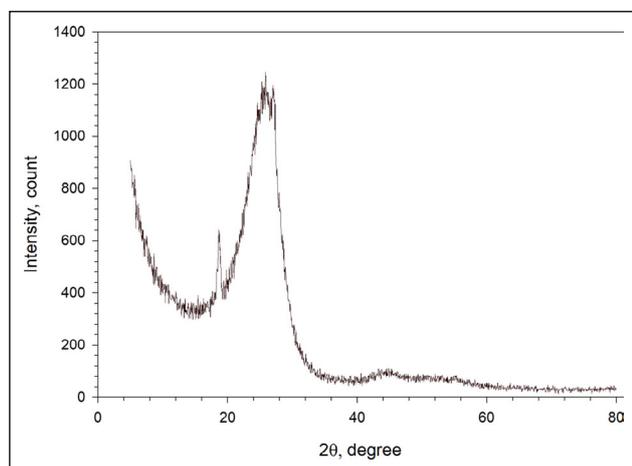


Figure 3. XRD pattern for carbon fiber cathode after modification with graphene.

Figure 2a shows the XRD patterns of the original graphite anode electrode before the electrodeposition process, and Figure 2b shows the XRD patterns of PbO_2 on the graphite anode electrode.

XRD pattern for graphite before the electrodeposition process (Fig. 2a) showed that it is identical to the standard card and has a distinctive peak at 26° of 2θ . After the deposition process, (Fig. 2b), the XRD peaks of orthorhombic PbO_2 were assigned at 2θ values of 23.402° (1 1 0), 28.549° (1 1 1), 32.611° (0 0 2), 34.3193° (0 2 1), 36.1743° (2 0 0), 40.5751° (1 1 2), 45.3306° (0 2 2), 47.6418° (2 2 0), 49.3314° (1 3 0), 50.7798° (2 2 1), 55.9957° (1 1 3) and 58.9747° (2 2 2) and these angles refer to the existence of the phase α - PbO_2 as compared with the standard card JCPDS:75-2414 and literature [37].

Furthermore, there are peaks presented in XRD patterns for the prepared electrode indicated to the presence of β phases of PbO_2 at 2θ values of 25.6413° (1 1 0), 32.0908° (0 1 1), 52.0773° (2 2 0), 54.4201° (0 0 2), 60.6214° (1 1 2), and 62.2500° (0 3 1), 66.6972° (0 2 2). XRD patterns clearly show the characteristic reflection of a mixture of α - and β phases of PbO_2 compared with the standard card JCPDS:75-2414

Table 1. XRF elemental composition report of PbO_2 deposit on graphite (normalized)

Symbol	Element	Conc., %
K_2O	Potassium	0.16
CaO	Calcium	3.26
PbO	Lead	95.97
ZrO_2	Zirconium	0.22
Ta_2O_5	Tantalum	0.39
Sum of concentration		100

for α - PbO_2 and JCPDS:75-2420 for β - PbO_2 (standard cards of α - PbO_2 and β - PbO_2 shown in Figure 2b the red and blue line, respectively) [37, 38]. The average crystallite size of electrodepositing PbO_2 on graphite was 27.05 nm, and the crystallinity was 80.02%.

The XRD pattern of the modified carbon fiber cathode electrode with graphene on its surface is shown in Figure 3. The pattern showed a sharp diffraction peak at 2θ values of 26.99° (0 0 2), which was attributed to the crystalline graphitic structure. There is a weaker sharp peak at 2θ values of 18.81° , which refers to PTFE as it is used in the modification process.

XRF

The quantitative chemical composition of the electrodeposit PbO_2 on the anode electrode surface was investigated by the XRF analytical technique, and the results were listed in Table 1 as the weight percent of each component. Clearly, lead (Pb) (as oxide) had the highest weight percentage of 95.97%.

SEM

SEM images of the graphite plate coated with a layer of PbO_2 can be detected at two different magnifications (with different scales) in Figure 4. PbO_2 is coated on the graphite plate substrate uniformly and without cracking, mostly in clusters and highly compressed structures that firmly adhere to the graphite electrode surface. The layer-coated graphite

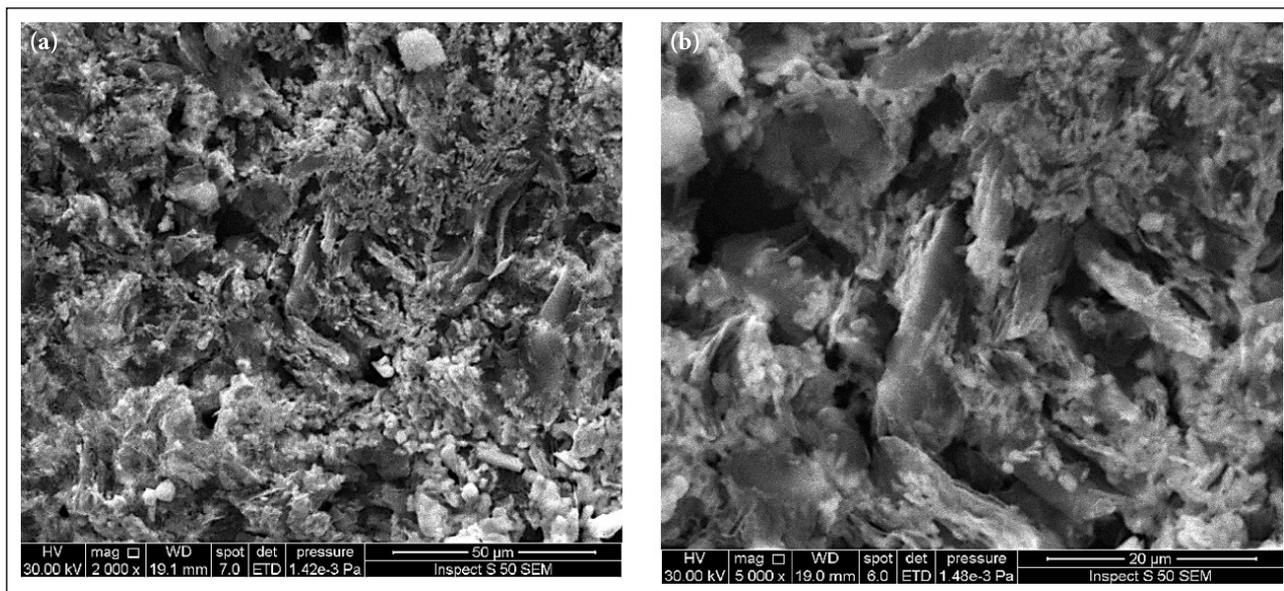


Figure 4. SEM images of PbO₂ deposit on graphite plate from an acidic electrolyte at 65 °C, 1.1 mA/cm², and 200 rpm for 3 hours (a) 50 μm and (b) 20 μm.

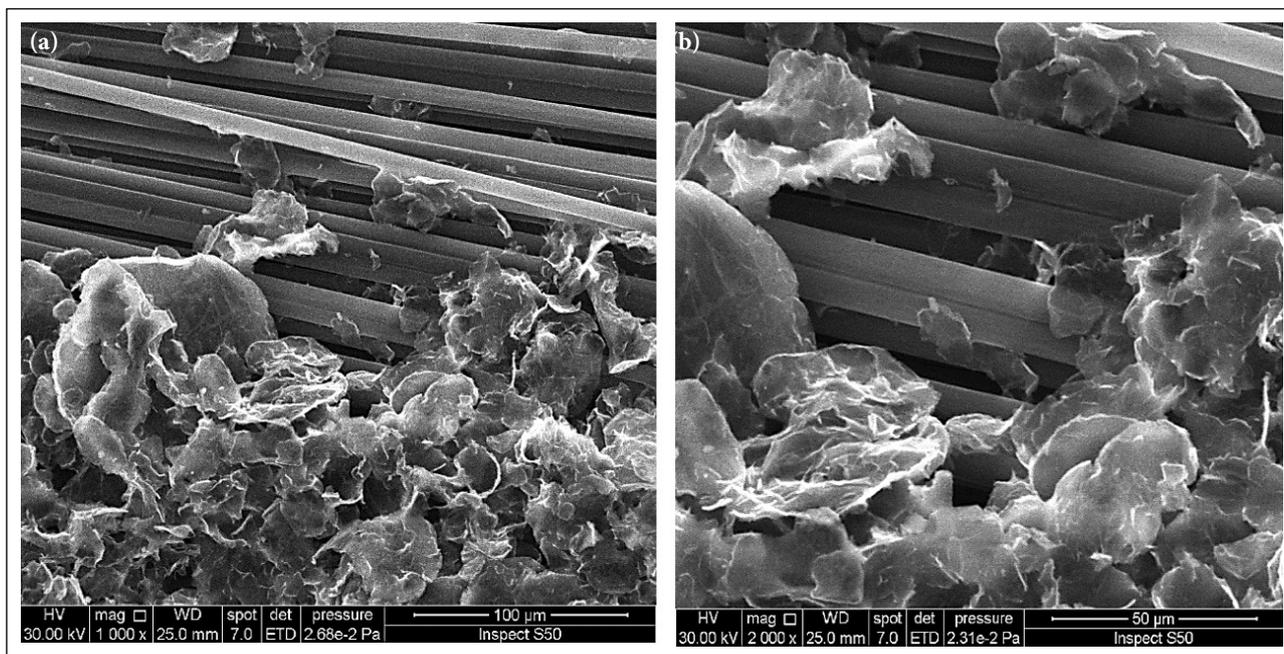


Figure 5. SEM image of graphene on carbon fiber (a) 100 μm, and (b) 50 μm.

showed tiny rough crystals of PbO₂ over the graphite plate. The crystals may have different growth rates. A more specific surface area can be obtained with the rough surface, leading to better interaction during the degradation of phenol and phenolic derivatives through the electrochemical reaction. The even surface obtained after deposition supported the adherence between the electrodeposited layer and the graphite substrate. This results in agreement with previous researchers [2, 4, 39].

The morphology of graphene on carbon fiber cathode electrode was also detected by using SEM. The SEM micrographs of the prepared cathode are shown in Figure 5.

The graphene flakes were thin sheets, and all of them were arranged on the surface of carbon fiber.

Figure 6a, b presented the original and modified carbon fiber, and the thickness of each felt in carbon fiber increases with modification. Carbon fiber has a smooth surface, and improvement with graphene made its surface rough, increasing its surface and active sites. The graphene has formed a clear layer on the carbon fiber, and penetration of graphene between the carbon fiber threads can be noticed, which increases the surface area, improves electrode performance, H₂O₂ production, and the chance of entering the reaction solution mixture between the carbon fiber threads [34].

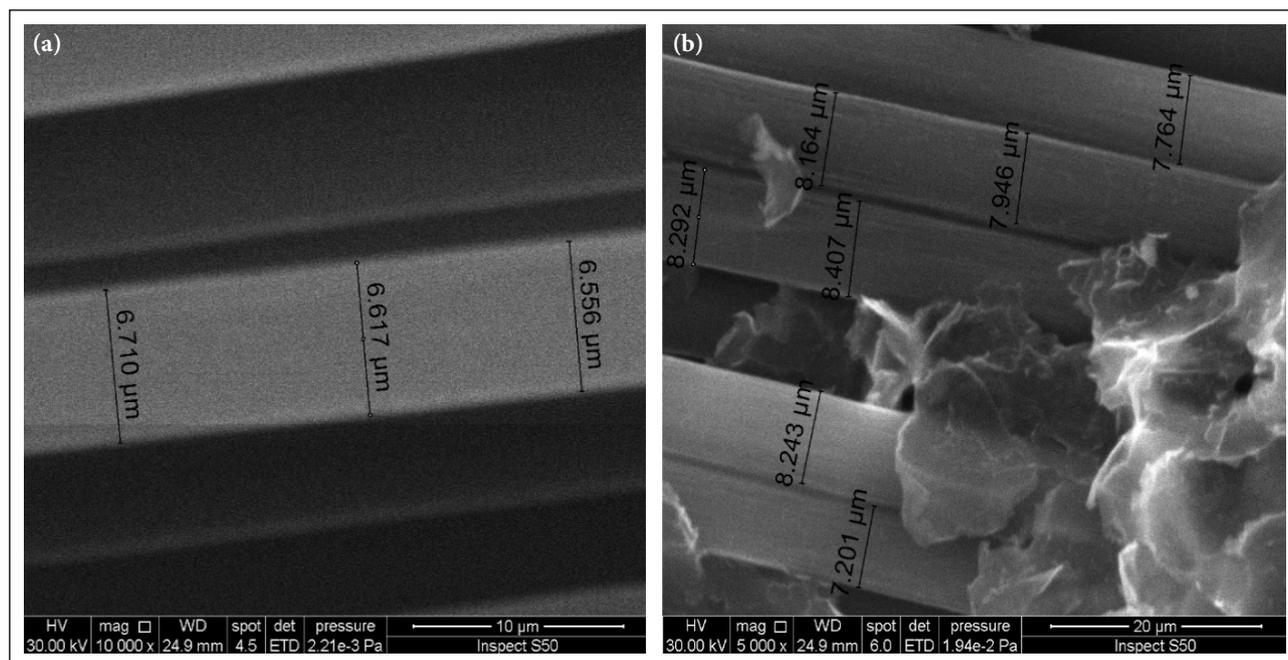


Figure 6. SEM image of carbon fiber (a) before modification with graphene and (b) after modification with graphene.

Table 2. Amplitude parameters for PbO₂ on graphite and graphene on carbon fiber

Amplitude parameters	PbO ₂ on graphite	Graphene on carbon fiber
Roughness average (Sa), nm	100.3	32.86
Root mean square (Sq), nm	123.40	48.15
Surface skewness (Ssk)	-0.097	2.219
Surface kurtosis (Sku)	2.558	10.901
Maximum peak height (sp), nm	377.8	401.6
Maximum pit height (sv), nm	379.6	97.86
Ten-point height (Sz), nm	757.4	499.5

AFM

The surface topography was evaluated quantitatively to understand the surface texture and morphology. One of the techniques used to characterize nanoscale surface topography is the AFM technique. This technique is better than other microscopic techniques because of its flexibility and facilities. AFM test made for PbO₂ on graphite anode electrode and graphene on carbon fiber cathode electrode and amplitude parameters of the obtained graphite and carbon fiber after modification on their surfaces presented in (Table 2).

The graphite statistical summary for the electrodeposit PbO₂ shows that the mean diameter was 449 nm, the minimum diameter was 242 nm, and the maximum was 772 nm.

Contact Angel Measurement

The contact angles were utilized regularly to measure the hydrophilicity of carbon materials. The contact angle of carbon fiber before modification was 90.67° and became 81.32° after modification with graphene, as shown in Figure

7. These contact angle values evidenced that the hydrophobic property of carbon fiber decayed noticeably by modification with the graphene. A Droplet of water dispersed when it contacted the modified carbon fiber surface. One of the essential features that affect the electro-Fenton oxidation process is the hydrophilicity of the cathode material. The cathode with the highest hydrophilicity provides helpfulness to O₂ diffusion and, accordingly, the highest H₂O₂ production [40, 41].

Raman Spectrometer

Raman test is considered the most active, fast, and non-destructive technique used to describe the structure and quality of carbon material and identify defects and irregular structures [42, 43]. In the Raman technique, G-band and D-bands are characteristics of ordered and disordered materials, respectively [44]. The ratio of the intensity of the D-line and G-line was used to indicate the defects in the material [43, 45, 46].

A typical Raman spectrum for the origin carbon fiber is shown in Figure 8a, and for modified carbon fiber, it is shown in Figure 8b. D-band peak at about 1350 cm⁻¹ indicates the presence of significant defects. The D band was usually correlated to a series of defects, including bonding disorders and vacancies in graphene lattice [47]. G-band at about 1600 cm⁻¹ peak corresponds to the graphitic carbon [48, 49].

The modified carbon fiber exhibited a clear D-band (as shown in Figure 8b, whereas the original carbon fiber did not have the D-band (there is a valley at about 1350 cm⁻¹, not a peak), as shown in Figure 8a. The valley in this region indicates the absence of significant defects. D-band was related to the disorder and defect in the structure because of the disorderliness in the graphene sheets [49].

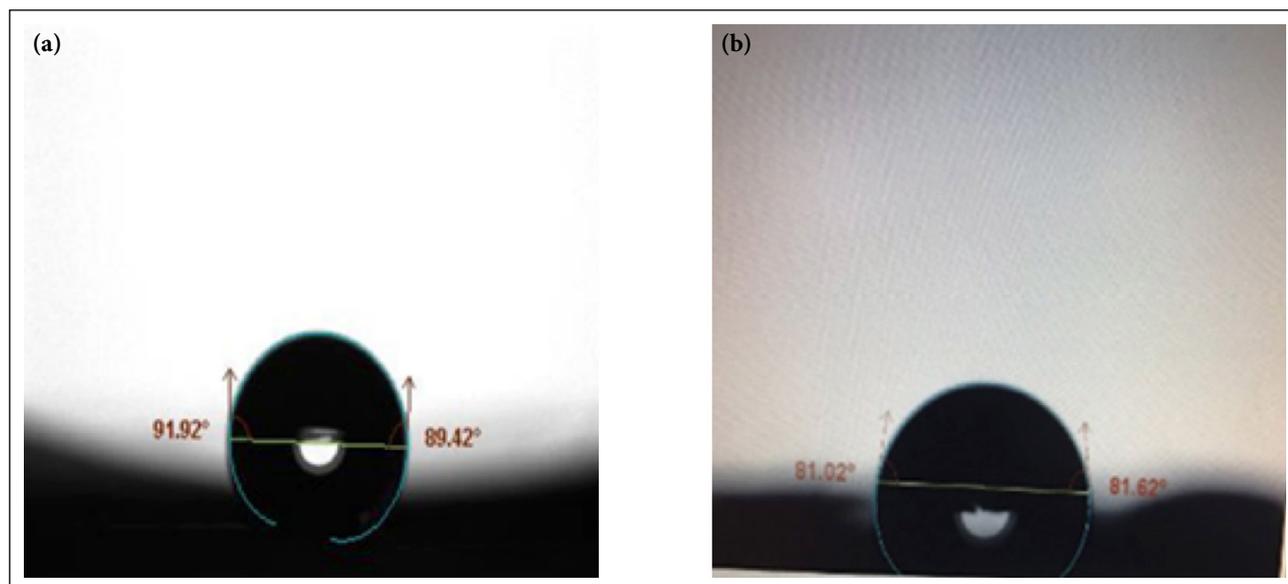


Figure 7. Contact angle for carbon fiber cathode (a) before modification (b) after modification with graphene.

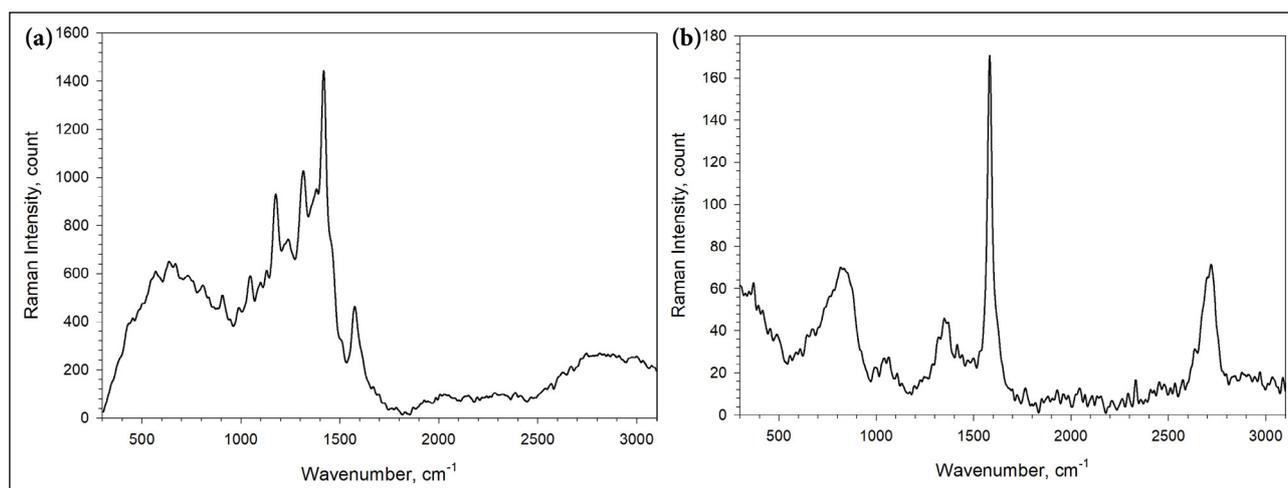


Figure 8. A typical Raman spectrum of carbon fiber (a) before modification (b) after modification with graphene.

Defects and distortion were efficiently enhanced by modification of carbon fiber with graphene, which will improve the activity of oxidation-reduction reaction and provide more active sites and, thereby, H_2O_2 generation [50–54].

The intensity ratio of the D-band to G-band (ID/IG) obtained from Raman spectra results after modification with graphene was about 0.314.

Anodic Polarization

The electrochemical performance of the PbO_2 electrode was studied by linear sweep voltammetry in an acidic solution of 0.1 M H_2SO_4 in the potential window of 0–3V versus SCE at a scan rate of 50 mV/s. The anodic linear sweep voltammograms for phenol oxidation on graphite and PbO_2 on graphite anodes were shown in Figure 9. A higher anodic current was detected when utilizing the PbO_2 anode electrode than the graphite anode electrode in the oxidation of phenol and its derivatives in simulated wastewater. A higher current of the PbO_2 electrode, perhaps because of the electrodeposited

layer of PbO_2 , improves the anode electrode's performance in the electro-Fenton oxidation technique. Consequently, PbO_2 anode denotes a capable anode electrode material for wastewater treatment comprising phenolic compounds compared to graphite or carbon-based materials.

Cod Removal

Figure 10 shows the effect of using modified electrodes (anode and cathodes) on the COD removal efficiency by the electro-Fenton oxidation process. Figure 10 shows that the COD removal after 6 h was 62.33% using unmodified electrodes (anode and cathode). COD removal was 81.23% using a modified anode (PbO_2 on graphite) and unmodified cathode (carbon fiber) and 79.87% by using an unmodified anode (graphite) and modified cathode (Graphene on carbon fiber). Using the two modified electrodes, the COD removal reached 94.02%. Oxidation efficiency using an unmodified anode electrode increased slightly after four hours of electrolysis. Modified anode by deposition layer of PbO_2 on it led to increase oxidation efficiency of organic pollutants.

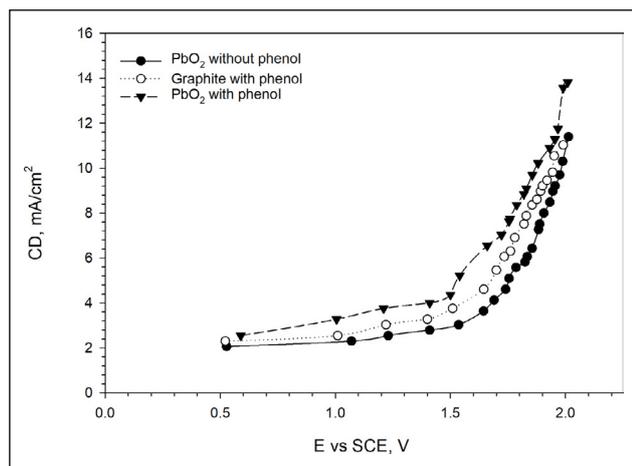


Figure 9. Anodic polarization curves (a) H_2SO_4 (0.1M)- PbO_2 anode (b) phenol (150 ppm) - H_2SO_4 (0.1M) - graphite anode (c) phenol (150 ppm) - H_2SO_4 (0.1M)- PbO_2 anode.

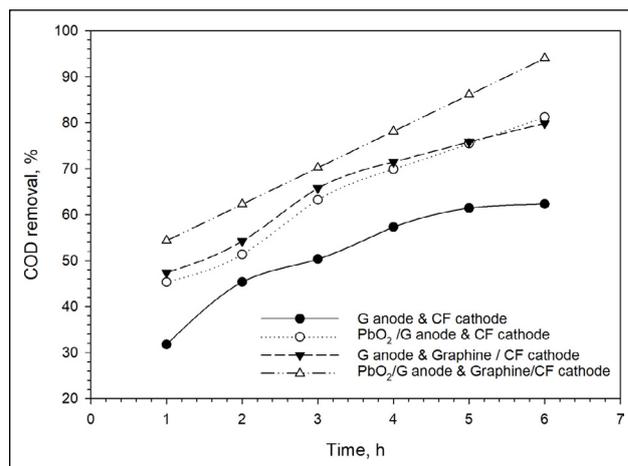


Figure 10. Comparison of COD removal between modified and unmodified electrodes by the electro-Fenton oxidation process.

Oxidation efficiency was still increasing noticeably after four hours because the modified anode has high stability and resistance to corrosion. Also, the deposition of PbO_2 on graphite gives an anode electrode with good electrochemical oxidation of COD removal because it has high electrical conductivity and increases the overpotential for oxygen evolution. PbO_2 layer deposit increases the hydroxyl radical yield, decreases the energy consumption, and increases the current efficiency [30, 32, 55]. Modified cathode using graphene increases the COD removal efficiency because graphene has a high surface area and excellent conductivity. It leads to an increase in the electron transfer rate and thereby improves the production of (H_2O_2) from the reaction of oxygen reduction that occurs on the cathode electrode [34, 36, 47]. The generation of H_2O_2 controls the rate of Fenton reaction and the formation rate of homogeneous $\cdot\text{OH}$ in the medium [36, 56, 57].

Organic pollutants in real wastewater from one of the Iraqi refineries were also treated by using this cell sand electro-Fenton oxidation process at 8 mA/cm^2 CD, 35°C operating temperature, 0.4 mM of Fe^{2+} up to 6h. Figure 11 compares the COD removal results for simulated and real wastewater. It was evident from Figure 11 that the removal efficiency for simulated wastewater is higher than that of real wastewater and that, perhaps because of the formation of intermediate, many side reactions occur when treating real refinery wastewater. Real wastewater contains different contaminants that might participate in unknown reactions or act as a catalyst to improve the unwanted reactions or increase the indirect electrochemical oxidation process because of existing highly dissolved salts that need higher current applied.

Using PbO_2 /Graphite and Graphene/Carbon Fiber as the anode and cathode, respectively, the electro-Fenton process was applicable for treating simulated wastewater at the best conditions. After 6 hours of electrolysis, a 94.02% COD removal efficiency was possible by starting with an initial COD concentration of about 320 ppm. The current research results were encouraging and were in the same

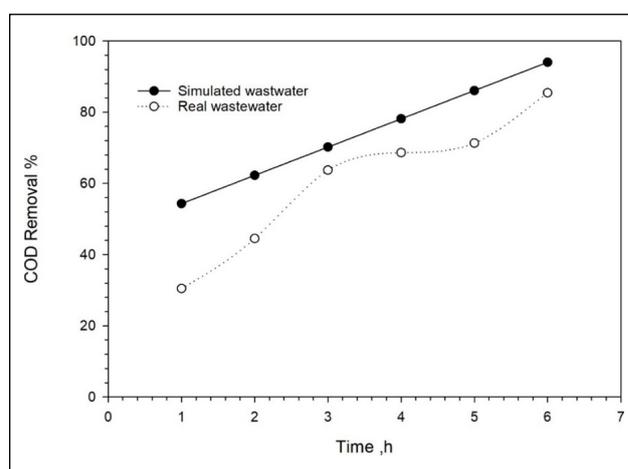


Figure 11. Comparison of COD removal between simulated and real wastewater by the electro-Fenton oxidation process.

magnitude for removing organics pollutants and COD from wastewater of petroleum refineries compared to the results of removal using electro-Fenton [36, 40, 58] or Fenton using heterogeneous catalysts [59–61].

CONCLUSION

A PbO_2 on graphite anode electrode was prepared for COD removal from phenolic wastewater. Characterization of the prepared anode electrode showed a mixture of α and β phases of PbO_2 with an average crystal size of 27.05 nm and an average particle size of 449 nm. Pb was the primary element in the electrodeposited material, with 95.97 weight %. (As oxide). Analysis of the morphology of the PbO_2 film deposit on graphite showed that the particles were well crystallized to form a uniform surface. Carbon fiber was modified using graphene, and morphology analysis showed that the graphene flakes were thin sheets. All of them were arranged on the surface of carbon fiber with an average particle size of 322 nm. Contact angle measurement presents that it increases with modification from 81.32° to 90.67° ,

and that improves the oxidation-reduction reaction. Raman test showed that the (ID/IG) for the modified carbon fiber cathode was about 0.314, which enhanced the oxidation-reduction reaction. The mechanism of the electro-Fenton oxidation process depends on $\cdot\text{OH}$ generated from H_2O_2 decomposition in the presence of Fe^{2+} . COD removal reached 94.02% using a modified anode and cathode at 8 mA/cm^2 and 0.4 mM of Fe^{2+} after 6 h of electrolysis at 35°C .

DATA AVAILABILITY STATEMENT

The author confirm that the data that supports the findings of this study are available within the article. Raw data that support the finding of this study are available from the corresponding author, upon reasonable request.

CONFLICT OF INTEREST

The author declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

USE OF AI FOR WRITING ASSISTANCE

Not declared.

ETHICS

There are no ethical issues with the publication of this manuscript.

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