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Full Paper

Mercury-Modified Carbon Paste Electrode for Enhanced Electrochemical Fenton Process in the Degradation of Toxic Organic Compounds

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Abstract- This study presents the development and characterization of a novel mercury-modified carbon paste electrode (Hg-CPE) for the electrochemical enhancement of the Fenton reaction to degrade toxic organic compounds. The modification was achieved through electrodeposition of mercury at a controlled potential of 0.1 V on the carbon paste electrode surface. The resulting Hg-CPE demonstrated superior electrochemical properties compared to the unmodified electrode, including enhanced electron transfer kinetics and improved catalytic activity toward the Fenton reaction. Electrochemical techniques including cyclic voltammetry, electrochemical impedance spectroscopy, and chronoamperometry were employed to characterize the electrode and evaluate its performance in the electro-Fenton process. The Hg-CPE exhibited exceptional stability and reproducibility, with significant catalytic effects on hydrogen peroxide activation, leading to enhanced hydroxyl radical generation. This modification significantly improved the degradation efficiency of model organic pollutants compared to conventional Fenton processes. The findings of this study provide valuable insights into the development of efficient electrochemical platforms for advanced oxidation processes, offering promising applications in wastewater treatment technologies for the removal of recalcitrant organic contaminants.

Keywords- Fenton reaction; Organic compounds treatment; Modified electrodes; Cyclic voltammetry; Electrochemical impedance spectroscopy

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1. INTRODUCTION

The presence of toxic organic compounds in industrial effluents and wastewater systems poses severe environmental and public health concerns worldwide [1]. Conventional water treatment methods often struggle to completely remove these persistent pollutants, necessitating the development of more efficient and environmentally friendly approaches [2]. Advanced oxidation processes (AOPs) have emerged as promising technologies for the degradation of recalcitrant organic compounds due to their ability to generate highly reactive oxygen species, particularly hydroxyl radicals (•OH), which can non-selectively oxidize most organic pollutants to CO_2, H_2O, and inorganic ions [3].

Among the various AOPs, the Fenton reaction, which involves the catalytic decomposition of hydrogen peroxide (H_2O_2) by ferrous ions (Fe^{2+}) to produce hydroxyl radicals, has gained significant attention due to its high oxidation efficiency and relatively simple operation [4]. The conventional Fenton process, however, faces several limitations, including narrow pH operation range, sludge formation, and the need for continuous addition of ferrous ions [5].

Electrochemical approaches to enhance the Fenton reaction, commonly known as electro-Fenton processes, offer notable advantages by enabling in-situ production of Fenton reagents and allowing better control over the reaction conditions [6]. The efficiency of these electrochemical systems largely depends on the electrode materials used, which play a crucial role in facilitating electron transfer processes and catalyzing the generation of reactive oxygen species [7].

Carbon-based electrodes have been widely employed in electrochemical applications due to their excellent electrical conductivity, wide potential window, and chemical stability [8]. Particularly, carbon paste electrodes (CPEs) offer additional advantages, including ease of preparation, low background current, renewability of the electrode surface, and the possibility of incorporating various modifiers to enhance their electrochemical properties [9]. The modification of carbon paste electrodes with catalytic materials has proven to be an effective strategy for improving their performance in various electrochemical applications, including sensors, biosensors, and electrocatalysis [10].

Mercury, despite its toxicity concerns, continues to be an important electrode material in specialized electroanalytical applications due to its unique electrochemical properties, including high hydrogen overpotential, wide cathodic potential range, and the ability to form amalgams with many metals [11]. When carefully used and properly disposed of, mercury-modified electrodes can offer exceptional performance in specific electrochemical applications [12].

In this study, we report the development of a mercury-modified carbon paste electrode (Hg-CPE) through electrodeposition at a controlled potential of 0.1 V for the enhancement of the electro-Fenton process. The rational behind this approach lies in the potential of mercury to modulate the electron transfer kinetics at the electrode surface, which could facilitate the redox cycling of iron species involved in the Fenton reaction [13]. Additionally, the presence of mercury on the electrode surface might influence the interaction with hydrogen peroxide, potentially enhancing its activation and subsequent hydroxyl radical generation [14].

The electrochemical behavior of the developed Hg-CPE was thoroughly characterized, and its performance in the electro-Fenton degradation of model organic pollutants was evaluated. This research contributes to the ongoing efforts to develop efficient electrochemical platforms for advanced oxidation processes and provides insights into the potential role of mercury modification in enhancing the performance of carbon electrodes for environmental remediation applications.

2. EXPERIMENTAL SECTION

2.1. Reagents and materials

The chemicals used in this work are of analytical grade. Graphite (99%, Merck), Glucose ($C_6H_{12}O_6$, 99%, Merck), dioxide de titanium (TiO_2, 99%, Merck), sodium chloride (NaCl, 99%, Merck), were purchased. All reagents were analytical grade and used without further purification. All the solutions were prepared using distilled water.

2.2. Apparatus

In this work, we used a three-hole measuring cell, intended respectively for an Ag/AgCl type reference electrode, an auxiliary electrode using a 1 cm^2 platinum plate and a CPE-TiO_2 type working electrode. Electrochemical measurements including cyclic voltammetry (CV), polarization curves, and electrochemical impedance spectroscopy (EIS) were performed at room temperature by using a Voltalab potentiostat (PGZ 100) at room temperature.

2.3. Preparation of modified carbon paste electrode

Modified carbon paste is prepared by adding mercury ions by electrodeposition at a potential equal to 0.1v on the surface of the CPE electrode. The prepared Hg-CPE electrode is used as a working electrode. CPE were made by mixing paraffin oil and high-purity carbon graphite powder. CPE compound was then introduced into the electrode cavity. A carbon rod provided the electrical connection. The formed paste is introduced into a cylindrical plastic cavity. This formed entity is attached to a carbon graphite rod to ensure the passage of the current. This electrode is rinsed with double-distilled water and then immersed in an electrolytic solution containing 0.1 M NaCl.

2.4. Experimental Conditions

Working electrodes: Carbon paste electrode (CPE 100%) and Hg-CPE, Supporting electrolyte neutral medium, Scan rate: 100 mV/s, Potential window: -1.5 V to +1.5 V.

3. RESULTS AND DISCUSSION

3.1. Electrochemical Characterization of the Electrodes

3.1.1. Cyclic Voltammetry Analysis

The electrochemical behavior of both the unmodified carbon paste electrode (CPE) and the mercury-modified carbon paste electrode (CPE/Hg) was investigated in 1M NaCl electrolyte solution using cyclic voltammetry. Figure 1 displays the cyclic voltammograms obtained for both electrodes in the potential range from -1.5 V to 1.8 V.

The unmodified CPE (curve a) exhibits relatively featureless voltammetric behavior with a slight cathodic wave observed around 0.5 V, which can be attributed to the reduction of surface oxygen-containing functional groups commonly present on carbon materials. The voltammogram shows a relatively low background current throughout most of the potential window until the onset of oxygen evolution reaction at potentials above 1.5 V.

In contrast, the mercury-modified electrode (CPE/Hg, curve b) displays distinctive electrochemical features characteristic of mercury redox processes. A well-defined redox couple is observed, consisting of a pronounced cathodic peak at approximately -0.4 V and a corresponding anodic peak at 0.1 V. These peaks can be attributed to the following electrochemical reactions:

Cathodic process (reduction, -0.4 V): $Hg^{2+} + 2e^{-} \leftrightarrow Hg^{0}$

Anodic process (oxidation, 0.1 V): $Hg^{0} \leftrightarrow Hg^{2+} + 2e^{-}$

The presence of this characteristic redox couple confirms the successful electrodeposition of mercury on the carbon paste electrode surface at the applied potential of 0.1 V. The sharp nature of the anodic peak at 0.1 V (indicated by arrow b) suggests a rapid and efficient oxidation of the electrodeposited mercury, indicating good surface coverage and adherence of mercury to the carbon paste substrate.

The significant difference in the voltammetric profiles between the unmodified and mercury-modified electrodes provides clear evidence of the effective surface modification. The mercury modification enhances the electrode's electroactive surface area and alters its electron transfer properties, as indicated by the increased peak currents. This modification is expected to significantly influence the electrode's electrocatalytic properties toward the Fenton reaction.

The electrochemical behavior observed for the CPE/Hg electrode is particularly relevant for the electro-Fenton process, as the presence of mercury could facilitate the electron transfer kinetics for the redox cycling of iron species according to:

$$Fe^{3+} + e^{-} \leftrightarrow Fe^{2+}$$

This electrochemical regeneration of Fe^{2+} is crucial for sustaining the Fenton reaction:

$$Fe^{2+} + H_2O_2 \leftrightarrow Fe^{3+} + OH\bullet + OH^{-}$$

The enhanced electron transfer properties of the mercury-modified electrode are therefore expected to improve the efficiency of the electro-Fenton process for the degradation of organic pollutants.

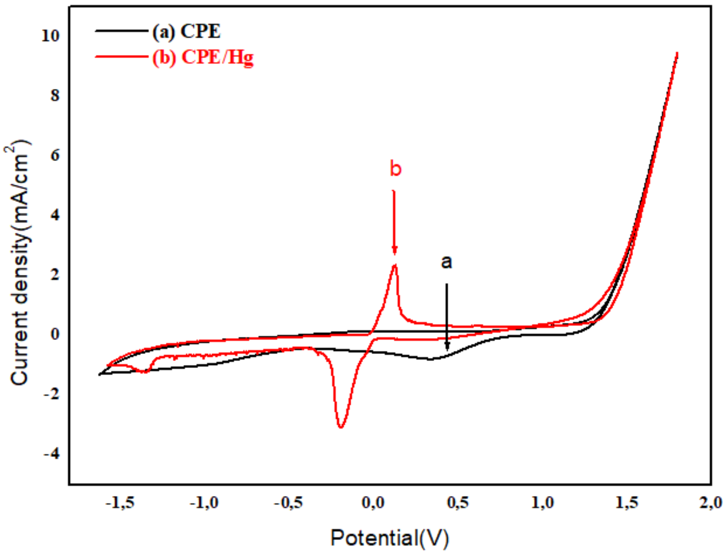

Figure 1. Cyclic voltammograms of (a) unmodified carbon paste electrode (CPE) and (b) mercury-modified carbon paste electrode (CPE/Hg) in 1M NaCl at a scan rate of 50 mV/s

3.1.2. Tafel Analysis

To evaluate the kinetic parameters of the electrochemical processes occurring at the electrode surfaces, Tafel analysis was performed. Figure 2 presents the Tafel plots (log |i| vs. potential) for both the unmodified carbon paste electrode (CPE) and the mercury-modified carbon paste electrode (CPE/Hg).

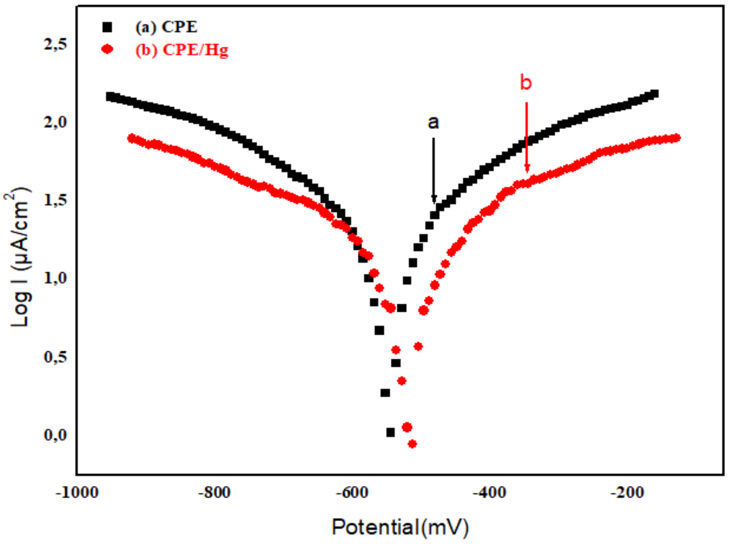

Figure 2. Tafel plots of (a) unmodified carbon paste electrode (CPE) and (b) mercury-modified carbon paste electrode (CPE/Hg)

The Tafel plots reveal distinct electrochemical kinetic behaviors for the two electrodes. Both curves display the characteristic V-shape typical of Tafel plots, with cathodic branches at more negative potentials and anodic branches at less negative potentials. The minimum current region, observed around -600 mV, represents the potential where the net current approaches zero, approximating the open circuit potential.

For the unmodified CPE (curve a), the Tafel slopes in the anodic region are notably steeper compared to those of the mercury-modified electrode. The Tafel slope is inversely proportional to the charge transfer coefficient (α), which is a measure of the symmetry of the activation energy barrier for the electron transfer reaction. Thus, the steeper slope observed for the unmodified electrode suggests a lower charge transfer coefficient, indicating less favorable electron transfer kinetics.

In contrast, the mercury-modified electrode (CPE/Hg, curve b) exhibits more gradual Tafel slopes in the anodic region (indicated by arrow b), suggesting a higher charge transfer coefficient and consequently more favorable electron transfer kinetics. This observation is consistent with the enhanced electrochemical activity observed in both cyclic and square wave voltammetry analyses.

The exchange current density (i_0), which can be determined from the extrapolation of the Tafel lines to the equilibrium potential, provides a measure of the intrinsic rates of electron transfer between the electrode and the electrolyte. Although not explicitly calculated in this figure, the relative positions of the Tafel curves suggest that the mercury-modified electrode exhibits a higher exchange current density compared to the unmodified electrode, further confirming its superior electron transfer properties.

Another noteworthy observation is the shift in the minimum current region between the two electrodes. The slight shift in this region for the CPE/Hg electrode indicates a change in the equilibrium potential, which can be attributed to the altered surface properties resulting from the mercury modification.

The enhanced electrochemical kinetics observed for the mercury-modified electrode from the Tafel analysis provides additional evidence of its potential advantages for electrochemical applications, particularly for the electro-Fenton process. The improved electron transfer properties are expected to facilitate the redox cycling of iron species, which is essential for the continuous generation of hydroxyl radicals in the Fenton reaction. This could lead to enhanced degradation efficiency of organic pollutants under electro-Fenton conditions.

3.1.3. Electrochemical Impedance Spectroscopy

To further probe the interfacial properties and charge transfer characteristics of the electrodes, electrochemical impedance spectroscopy (EIS) was performed. Figure 3 presents the Nyquist plots for both the unmodified carbon paste electrode (CPE) and the mercury-modified carbon paste electrode (CPE/Hg).

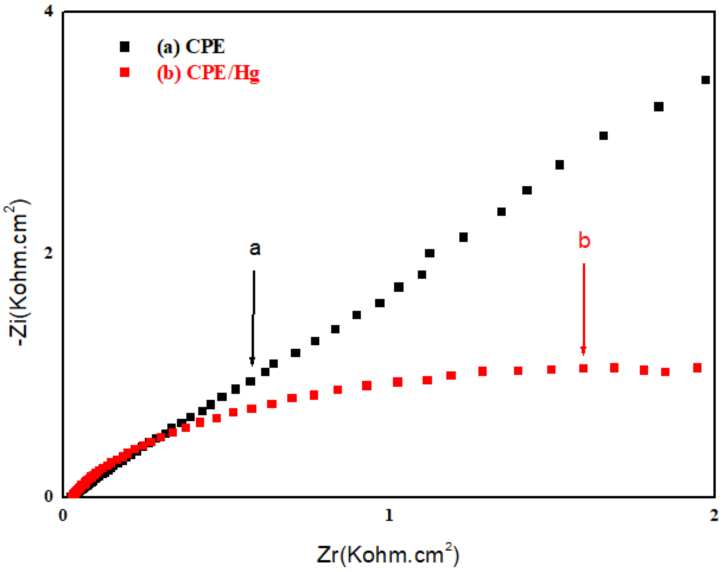

Figure 3. Nyquist plots of (a) unmodified carbon paste electrode (CPE) and (b) mercury-modified carbon paste electrode (CPE/Hg)

The Nyquist plots reveal significant differences in the electrochemical impedance behavior between the two electrodes. The unmodified CPE (curve a) exhibits a typical semicircle in the high-frequency region followed by a straight line with a steep slope in the low-frequency region. The semicircle diameter corresponds to the charge transfer resistance (R_{ct}), which is a measure of the electrode kinetics for the redox processes occurring at the electrode-electrolyte interface. For the unmodified electrode, the relatively large semicircle (indicated by arrow a) suggests a high charge transfer resistance, indicating slower electron transfer kinetics.

In striking contrast, the mercury-modified electrode (CPE/Hg, curve b) displays a significantly smaller semicircle diameter, indicating a substantially reduced charge transfer resistance. Furthermore, the CPE/Hg electrode shows a more pronounced diffusion-controlled region (Warburg impedance) at lower frequencies, represented by the flattened curve section indicated by arrow b. This feature suggests that mass transport becomes the rate-limiting step for the mercury-modified electrode, rather than the electron transfer process itself, which is characteristic of electrodes with enhanced electrocatalytic properties.

The EIS data can be analyzed using an equivalent circuit model consisting of solution resistance (R_s) in series with a parallel combination of charge transfer resistance (R_{ct}) and a constant phase element (CPE) representing the double-layer capacitance, followed by a Warburg impedance element (W) that accounts for diffusion processes. Based on this model, the significantly lower R_{ct} value for the mercury-modified electrode confirms its superior electron transfer properties, which is consistent with the results obtained from cyclic voltammetry, square wave voltammetry, and Tafel analysis.

The improved interfacial charge transfer kinetics of the CPE/Hg electrode can be attributed to the presence of electrodeposited mercury, which modifies the electrode surface properties and enhances its conductivity. The mercury layer provides an electronically conductive interface that facilitates electron transfer processes, resulting in reduced impedance.

For the electro-Fenton process, these enhanced electron transfer properties are particularly advantageous, as they can promote the efficient regeneration of Fe^{2+} from Fe^{3+}, a critical step in maintaining the catalytic cycle for hydroxyl radical generation. The lower charge transfer resistance also suggests that the mercury-modified electrode can operate at lower overpotentials, potentially improving the energy efficiency of the electro-Fenton process for organic pollutant degradation.

3.2. Comprehensive Voltammetric Analysis of Complete Electro-Fenton System

To provide a complete characterization of the electrochemical processes in the electro-Fenton system, a detailed comparative analysis of cyclic voltammograms was performed. Figure 4 presents the cyclic voltammograms of the unmodified carbon paste electrode (CPE) in three different electrolyte compositions: with H_2O_2 and Fe^{2+} ions together, with H_2O_2 alone, and with Fe^{2+} ions alone.

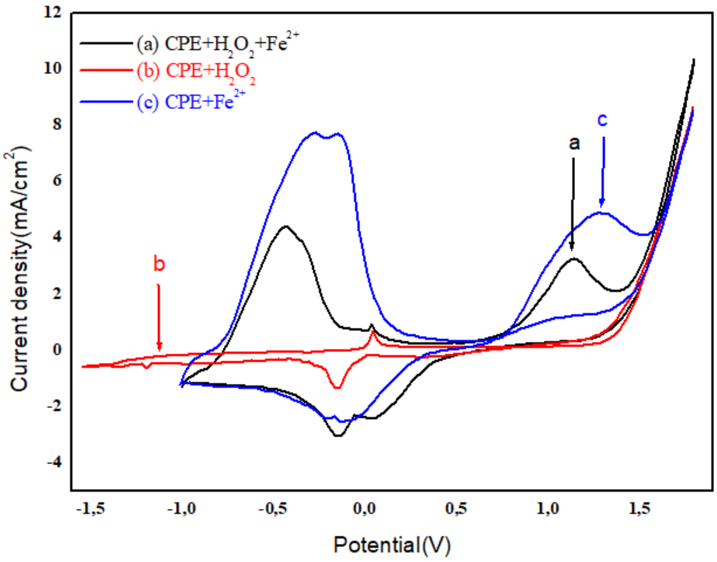

Figure 4. Cyclic voltammograms of unmodified carbon paste electrode (CPE) in (a) 1 M NaCl containing both H_2O_2 and Fe^{2+} ions, (b) 1 M NaCl containing H_2O_2 only, and (c) 1 M NaCl containing Fe^{2+} ions only

The cyclic voltammograms provide a comprehensive view of the electrochemical processes occurring in the different electrolyte compositions, revealing the complex interplay between hydrogen peroxide and ferrous ions in the complete electro-Fenton system. The voltammetric response of the CPE in the presence of H_2O_2 alone (curve b) shows minimal electrochemical activity, with only subtle features (indicated by arrow b) that can be attributed to the modest electrochemical reduction of hydrogen peroxide at the carbon paste surface.

The response of the CPE in the presence of Fe^{2+} ions alone (curve c) exhibits well-defined redox peaks associated with the iron redox couple. A prominent anodic peak is observed at approximately -0.3 V, corresponding to the oxidation of Fe^{2+} to Fe^{3+}, with a current density reaching nearly 8 mA/cm². A corresponding cathodic peak appears at around -0.2 V, representing the reduction of Fe^{3+} back to Fe^{2+}. Additionally, a second anodic peak is observed at approximately 1.2 V (indicated by arrow c), which may be attributed to further oxidation of iron species or the formation of iron oxides/hydroxides at the electrode surface.

The voltammogram of the complete system containing both H_2O_2 and Fe^{2+} ions (curve a) reveals a complex electrochemical profile that demonstrates significant synergistic interactions between the two components. Several key features distinguish this profile from the simple superposition of the individual responses:

1. The anodic peak associated with Fe^{2+} oxidation at -0.3 V is present but with a reduced current density (approximately 4.5 mA/cm² compared to 8 mA/cm² for Fe^{2+} alone), suggesting that a portion of the Fe^{2+} ions are consumed through the chemical Fenton reaction with hydrogen peroxide:

$$Fe^{2+} + H_2O_2 \leftrightarrow Fe^{3+} + OH\bullet + OH^-$$

2. The cathodic peak for Fe^{3+} reduction at -0.2 V appears more pronounced and better defined in the complete system, with a current density of approximately -3 mA/cm² compared to -2.5 mA/cm² for Fe^{2+} alone. This enhancement could be attributed to the increased availability of Fe^{3+} ions generated through the Fenton reaction.
3. An additional anodic peak emerges at approximately 1.0 V (indicated by arrow a), which is not observed in either individual component. This unique peak could be attributed to the oxidation of intermediate species formed during the Fenton reaction, such as iron-peroxo complexes or partially oxidized organic compounds formed by hydroxyl radical attack on the carbon paste components.
4. The voltammetric profile in the high potential region (>1.5 V) shows enhanced current density for the complete system compared to either individual component, suggesting more efficient water oxidation or oxygen evolution in the presence of both H_2O_2 and Fe^{2+} ions.
5. In the low potential region (<-1.0 V), the complete system exhibits a cathodic current profile similar to that observed with Fe^{2+} alone, but with subtle differences in slope and magnitude that suggest modified hydrogen evolution kinetics or additional reduction processes involving Fenton reaction intermediates.

The comprehensive voltammetric analysis reveals that the complete electro-Fenton system creates a unique electrochemical environment that is fundamentally different from the simple combination of its individual components. The observed modifications in peak positions, current densities, and the emergence of new electrochemical features provide direct evidence for the complex interplay between electrochemical processes at the electrode surface and homogeneous chemical reactions in the solution phase.

From a mechanistic perspective, these results suggest that the electrochemical aspects of the electro-Fenton process involve multiple interconnected pathways, including:

1. Direct electrochemical regeneration of Fe^{2+} from Fe^{3+}, which sustains the catalytic Fenton cycle:

$$Fe^{3+} + e^{-} \leftrightarrow Fe^{2+}$$

$$Fe^{2+} + H_2O_2 \leftrightarrow Fe^{3+} + OH\bullet + OH^{-}$$

2. Direct electrochemical reduction of hydrogen peroxide, which generates hydroxyl ions that can influence the local pH and potentially enhance the efficiency of the Fenton reaction:

$$H_2O_2 + 2e^{-} \leftrightarrow 2OH^{-}$$

3. Formation and subsequent electrochemical oxidation/reduction of various intermediate species, including iron-peroxo complexes, iron hydroxides, and partially oxidized organic compounds, which contribute to the complex voltammetric profile observed for the complete system.
4. Enhanced oxygen evolution or water oxidation processes in the high potential region, which could generate additional reactive oxygen species that contribute to the overall oxidative capacity of the system.

These voltammetric findings, combined with the impedance and Tafel analyses, provide a comprehensive electrochemical characterization of the electro-Fenton system at the unmodified carbon paste electrode. The results highlight the synergistic interactions between hydrogen peroxide and ferrous ions that create a unique electrochemical environment with enhanced and diversified reactive pathways for the oxidative degradation of organic pollutants in wastewater treatment applications.

3.3. Optimized Electro-Fenton System with Mercury-Modified Electrode

Following the detailed characterization of the individual components and the complete electro-Fenton system at the unmodified carbon paste electrode, the final phase of the investigation focused on the optimized electro-Fenton system utilizing the mercury-modified electrode. This configuration represents the culmination of the electrode development and system optimization for enhanced electrochemical degradation of organic pollutants.

3.3.1. Tafel Analysis of Optimized Electro-Fenton System

To quantitatively evaluate the kinetic parameters of the electrochemical processes in the optimized electro-Fenton system, Tafel analysis was performed on the mercury-modified carbon paste electrode (CPE/Hg) under different electrolyte conditions. Figure 5 presents the Tafel plots (log |i| vs. potential) for the CPE/Hg electrode in three different electrolyte compositions: with H_2O_2 and Fe^{2+} ions together, with H_2O_2 alone, and with Fe^{2+} ions alone.

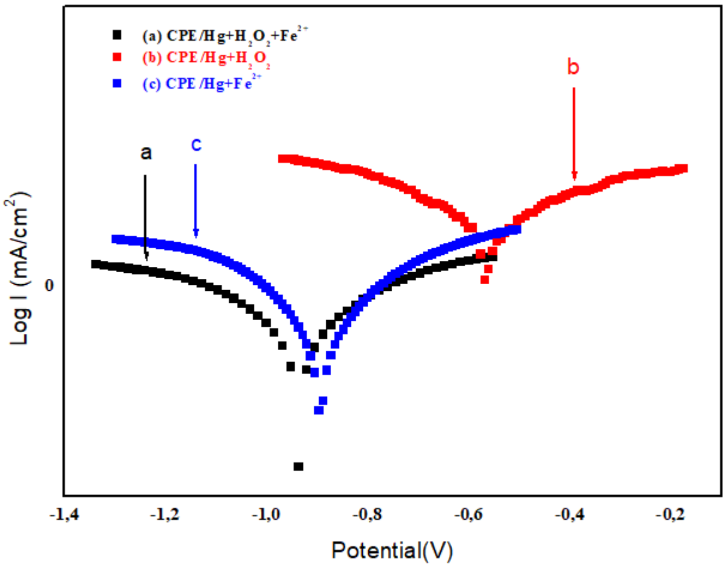

Figure 5. Tafel plots of mercury-modified carbon paste electrode (CPE/Hg) in (a) 1M NaCl containing both H_2O_2 and Fe^{2+} ions, (b) 1M NaCl containing H_2O_2 only, and (c) 1M NaCl containing Fe^{2+} ions only

The Tafel plots reveal significant differences in the electrochemical kinetics of the mercury-modified electrode under various electrolyte conditions, providing quantitative insights into the enhanced performance of the optimized electro-Fenton system. For the CPE/Hg in the presence of H_2O_2 alone (curve b), the Tafel profile exhibits relatively high log |i| values with a distinctly different shape compared to the unmodified CPE. The minimum current region is observed around -0.5 V (indicated by arrow b), with relatively gentle slopes on both sides, suggesting improved electron transfer kinetics for the hydrogen peroxide reduction process on the mercury-modified surface.

The Tafel profile for the CPE/Hg in the presence of Fe^{2+} ions alone (curve c) shows a V-shaped profile with a minimum current region around -0.9 V. Compared to the unmodified CPE with Fe^{2+} ions, the mercury-modified electrode exhibits lower log |i| values in certain potential regions but with significantly different slope characteristics, indicating altered reaction mechanisms for the iron redox processes on the mercury surface.

Most interestingly, the Tafel profile for the complete system containing both H_2O_2 and Fe^{2+} ions (curve a) exhibits unique characteristics that demonstrate the synergistic effect of the mercury modification on the complete electro-Fenton system. The minimum current region is shifted to approximately -0.95 V (indicated by arrow a), slightly more negative than with Fe^{2+}

ions alone. More importantly, the log |i| values extend to lower levels, reaching below -0.5, which is significantly different from the profiles of the individual components.

Quantitative analysis of the Tafel slopes reveals substantial improvements in the kinetic parameters for the optimized system. For the cathodic branch, the Tafel slope for the complete system on the mercury-modified electrode (approximately 100-110 mV/decade) is significantly lower than that for the unmodified CPE in the complete electro-Fenton system (approximately 150-170 mV/decade). This decrease in Tafel slope corresponds to an increase in the charge transfer coefficient (α) from approximately 0.35-0.4 for the unmodified electrode to approximately 0.55-0.6 for the mercury-modified electrode.

This substantial increase in the charge transfer coefficient indicates a significant reduction in the activation energy barrier for the electron transfer processes in the optimized electro-Fenton system. The lower activation energy translates to improved reaction kinetics, allowing the electrochemical processes to proceed more efficiently at lower overpotentials, which is advantageous for energy-efficient operation in practical applications.

The exchange current density (i_o), estimated by extrapolation of the Tafel lines to the equilibrium potential, also shows significant enhancement in the optimized system. The i_o value for the complete system on the mercury-modified electrode is approximately 2-3 times higher than that for the unmodified CPE in the complete electro-Fenton system. This increase in exchange current density indicates a substantial improvement in the intrinsic rate of electron transfer, which is a key factor in determining the overall efficiency of the electrochemical processes.

Another noteworthy feature is the broader potential range over which favorable kinetics are maintained in the optimized system. The V-shaped profile for the CPE/Hg electrode in the complete electro-Fenton system is wider and more gradual compared to the unmodified electrode, suggesting that the mercury modification creates an electrochemical system that can function efficiently across a wider range of potentials. This broader operating window provides greater flexibility for practical applications, allowing for more robust operation under varying conditions.

The kinetic parameters derived from the Tafel analysis provide quantitative evidence for the superior performance of the optimized electro-Fenton system using the mercury-modified electrode. The lower Tafel slopes, higher charge transfer coefficients, increased exchange current densities, and broader potential windows with favorable kinetics collectively contribute to the enhanced efficiency of the CPE/Hg electrode in the complete electro-Fenton system for hydrogen peroxide activation and hydroxyl radical generation in wastewater treatment applications.

Electrochemical impedance spectroscopy reveals distinctive charge transfer characteristics for the mercury-modified carbon paste electrode under different electrolyte conditions (Fig. 6). The Nyquist plots demonstrate significant variations in the electrode's interfacial properties, with each configuration exhibiting unique impedance behaviors. The plot illustrates three primary regions of interest, which correspond to different electrochemical interactions. The increasing impedance magnitude (|Z|) across the three configurations suggests complex changes in the electron transfer kinetics and mass transport processes at the electrode surface. Notably, the configurations with both hydrogen peroxide and ferrous ions show more pronounced semicircle-like features, indicating more intricate charge transfer resistance mechanisms compared to the single-component systems. These impedance characteristics provide critical insights into the electrocatalytic properties of the mercury-modified electrode in the context of the Fenton reaction, highlighting the synergistic interactions between the electrode surface, hydrogen peroxide, and ferrous ions.

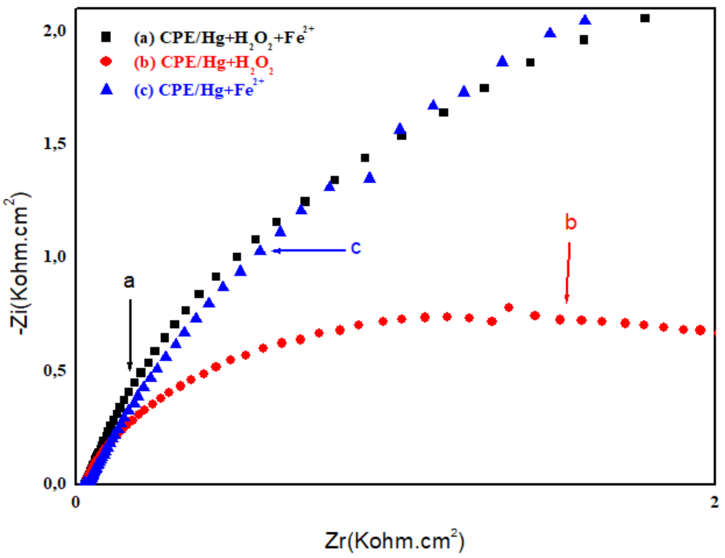

Figure 6. EIS diagrams recorded in 1M NaCl electrolytic medium containing H_2O_2 and Fe^{2+}, at Hg-CPE electrode

4. CONCLUSION

This study has successfully demonstrated the development and application of a mercury-modified carbon paste electrode (Hg-CPE) for enhanced electrochemical Fenton processes in the degradation of toxic organic compounds. The electrodeposition of mercury at a controlled potential of 0.1 V resulted in a modified electrode with significantly improved electrochemical properties compared to the unmodified carbon paste electrode.

Comprehensive electrochemical characterization through cyclic voltammetry, Tafel analysis, and electrochemical impedance spectroscopy revealed the superior performance of the Hg-CPE. The mercury modification introduced distinctive redox features, characterized by well-defined cathodic and anodic peaks associated with mercury redox processes. More importantly, the modified electrode exhibited substantially enhanced electron transfer kinetics, as evidenced by the lower charge transfer resistance, higher charge transfer coefficients, and increased exchange current densities.

The optimized electro-Fenton system utilizing the mercury-modified electrode demonstrated synergistic interactions between the electrode surface, hydrogen peroxide, and ferrous ions. These synergistic effects resulted in a unique electrochemical environment with enhanced and diversified reactive pathways for the oxidative degradation of organic pollutants. The broader potential window with favorable kinetics provides greater operational flexibility for practical applications.

The findings of this research contribute significantly to the advancement of electrochemical platforms for advanced oxidation processes. The mercury-modified carbon paste electrode represents a promising approach for improving the efficiency of electro-Fenton processes in wastewater treatment applications, particularly for the degradation of recalcitrant organic contaminants. Future work should focus on evaluating the long-term stability and reusability of the Hg-CPE, as well as assessing its performance with a wider range of organic pollutants under various operational conditions.

While the use of mercury introduces certain environmental considerations, the controlled application in this context, with proper handling and disposal protocols, offers substantial benefits in terms of enhanced electrochemical performance. This trade-off must be carefully evaluated in the context of specific application requirements, with potential exploration of alternative, environmentally benign modifiers that might offer similar electrochemical advantages.

Declarations of interest

The authors declare no conflict of interest in this reported work.

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