Curcumin/MWCNT Modified Graphite Electrode for Electrochemical Determination Of BHA

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Abstract- **CMEs, a relatively modern approach to electrode systems that finds utility in a wide spectrum implies applications in chemical sensing, energy conversion and storage molecular electronics, electrochromic displays, corrosion protection, and electro- organic syntheseis. Curcumin a bioactive polyphenolic component is the main pigment present in the rhizomes of the *Curcumina longa* possessing biological properties as anti-inflammatory, anti-angiogenic, antioxidant, etc. Surface modification of curcumin over graphite electrode and electropolymerization using cyclic voltammetry makes curcumin electroactive over sensing of several biological compounds. Application of nanomaterials like Multiwalled Cabron Nanotube (MWCNT) over CMEs enhances the catalytic current and favors the lowest detection limit. In this present investigation we used curcumin / MWCNT modified electrode to study the electro catalytic effect towards oxidation of BHA. curcumin upon electropolymerization at MWCNT immobilized graphite electrode showed well defined redox peak in 0.1 M PBS at the scan rate of 50 mV/s. Oxidation of BHA at curcumin / MWCNT modified electrode was obtained at 0.3 V. The modified electrode showed good catalytic response for the oxidation of BHA with a linear response of current with respect to the concentration.**

Keywords: CMEs, MWCNT (Multiwall Carbon Nanotube), CV, BHA (ButylatedHydroxyanisole), curcumin

I.Introduction

Chemically modified electrodes have attracted much interest for electrochemical determination of various organic and inorganic analytes. Apart from its application in quantitative determination of various analytes, the CMEs also used as tools for the study of electrocatalytic reaction of analyte over redox mediators. Many organic compound exhibit well redox behavior when modified with conducting polymers, nanomaterials, metal oxide complexation etc. Multiwalled Carbon Nanotube acts as an effective electrode material due to its intense electrocatalytic property. Many researches over curcumin, a bioactive polyphenol compound had been carried out for the past few decades. curcumin obtained from the rhizomes of ***Curcuma longa*** has a very intense biological property such as anti-oxidant, anti-inflamatory, anti-angiogenic and anti-cancer properties. Andreea LUNGUet.al had studied the electrochemical property of curcumin over free radical scavenging effect (1). This created an interest over electrocatalytic activity of curcumin, therefore there were several reports on catalytic activity of curcumin and its redox property. Ni-curcumin modified electrode was used for the electrochemical oxidation and voltammetric determination of many organic compounds such as glucose (2), Alcohol (3), Amino Acids (8). Bachar Zebib et.al had studied the stability of curcumin when complexed with different divalent ions. The each meal ion/curcumin complex shows different stoichiometry and shows different electrochemical properties (5). There were very few report on electrocatalytic activity of direct curcumin over oxidation of organic compounds. Li Zheng was the first to polymerize curcumin over CNT functionalized composite electrode as an electroactive redox mediator towards oxidation of Hydrazin (6), Balamurugan Devadas et.al electropolymerized curcumin on glassy carbon electrode and used for the electrochemical determination of epinephrine and para- acetoaminophenol, simultaneously (7). Butylated Hydroxyanisole, an effect antioxidant was fortified to food to increase its free radicle scavenging properties. BHA prevents oxidative degradation of fats and oil in foods. Although these phenolic additives has many advantages they also possess toxicity such as allergic, hyperactivity sometimes even tumor when the recommended concentration excides. Hence it is important to determine the recommended level of this antioxidant phenolic food additive. There are several modified electrode for the electrochemical determination of BHA (8, 9). Most of those modified electrode catalysis the oxidation of BHA at an oxidation potential greater than 0.4 V and the sensitivity of the electrode also hinder due to electrode surface fouling of BHA.Herein we are reporting curcumin/MWCNT electrode for the electrochemical determination of BHA with high sensitivity and reproducibility. In this paper we have polymerized curcumin over mechanically immobilized Multiwalled Carbon Nanotube functionalized paraffin wax

impregnated graphite electrode (PWIGE) and studied for its electrocatalytic oxidation for effective determination of BHA. The modified electrode showed good response for oxidation of BHA at lower potential of 0.3V at 0.1 M PBS as a background electrolyte.

II. Experimental Methodology

a. Chemicals and Reagents:
All the chemicals used in this experiment were of analytical grade. Graphite rod 3mm (Sigma-Aldrich), curcumin (SRL), BHA (Himedia), Dipotassium Hydrogen Phosphate , Potassium dihydrogen phosphate, Ammonium Nitrate, Barium Nitrate, Sodium nitrate, Lithium nitrate, Calcium nitrate, Potassium nitrate were purchased from Merck. All chemicals and reagents were used as such and the solutions were madeup with double distilled water. The 0.1M PBS solution pH-7 was used as a supporting electrolyte.

b. Instrument:
All electrochemical measurements were carried out in a conventional three electrode-cell powered by CH Instrument -660B Electrochemical Workstation(CH Instruments, USA).The instrument was controlled by CHI660B electrochem software accessed by data acquisition system. pH measurements were made with an Elico pH meter (model LI 120, India). All experiments were carried out at ambient temperature.

c. Electrode Preperation:
Scheme-1 represents the diagrammatic representation of modification of electrode where Multiwalled Carbon Nanotube was mechanically immobilized on the surface of Paraffin wax impregnated graphite electrode. 0.01 M ethanoic solution of curcumin (10µL) was drop casted on the MWCNT functionalized Graphite electrode. Electropolymerization of curcumin dropcasted MWCNT functionalized PIGE electrode was carried out as reported (6).

III Results and Discussion

a. Electropolymerization of curcumin over MWCNT functionalized Graphite electrode:
Polymerization of curcumin over MWCNT functionalized graphite elecrtrode was achieved by Cyclic Voltammetry. The dropcasted curcumin over MWCNT functionalized PIGE was electropolymerized by Cyclic Voltammetry using repeated scans between -0.4 to 0.6 V in 0.1 M PBS solution at pH-7 at the scan rate of 50 mVs^{-1}. The electropolymerized curcumin/ MWCNT modified electrode exhibits well defined redox peak of Hydroxyquinone/Quinone derivatives of curcumin due to two-electron and two-proton transfer processes (10, 11). Initially the oxidation peak at 0.4 V for the oxidation of curcumin was obtained at the first scan. Then upon electropolymerization, a well redox peak was obtained with an oxidation peak potential at 0.24V and reduction peak at 0.18Vin 0.1 M PBS. Fig (1) represents Cyclic Voltammograms of a) curcumin/MWCNT functionalized Graphite electrode, b) MWCNT immobilized electrode, c) curcumin modified electrode and d) bare electrode.

Scheme-1 Electropolymerization of curcumin over MWCNT functionalized PWIGE:

Step-1 Mechanical immobilized of Multiwalled carbon nanotube over PWIGE

Step-2 10 microL of 0.01 M curcumin dropcasted on to MWCNT immobilized electrode

Step-3 Electropolymerization of curcumin over MWCNT immobilized PWIGE

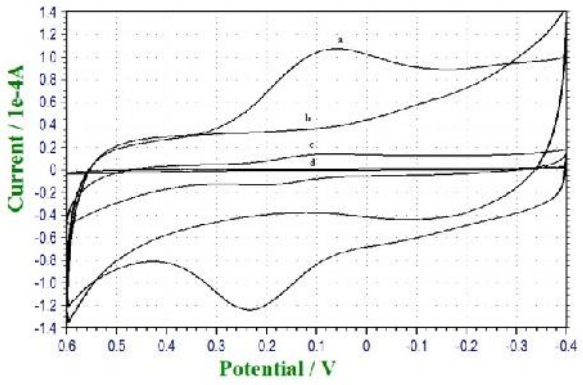

Fig:1 Cyclic Voltammetry of a) curcumin/MWCNT, b) MWCNT, c) curcumin, d) Bare modified electrode at 0.1 M PBS Buffer, pH- 7, Scan Rate- 50mV/s

b. Electrochemical behavior of Curcumin/MWCNT electrode for oxidation of Butylated Hydroxy anisol
Effect of electrolyte
The effect of different electrolytic solution was studied using cyclic voltammetry. The curcumin/MWCNT Graphite electrode exhibits a redox couple of HQ/Q derivatives at different peak potential. Fig (2) shows the cyclic voltammograms of curcumin/ MWCNT modified electrode at different electrolyte solution. Among all other electrolyte solution 0.1 M PBS exhibit a distinct redox peak at lesser potential with increase in peak current. So 0.1 M PBS was taken as a supporting electrolyte through the experiment.

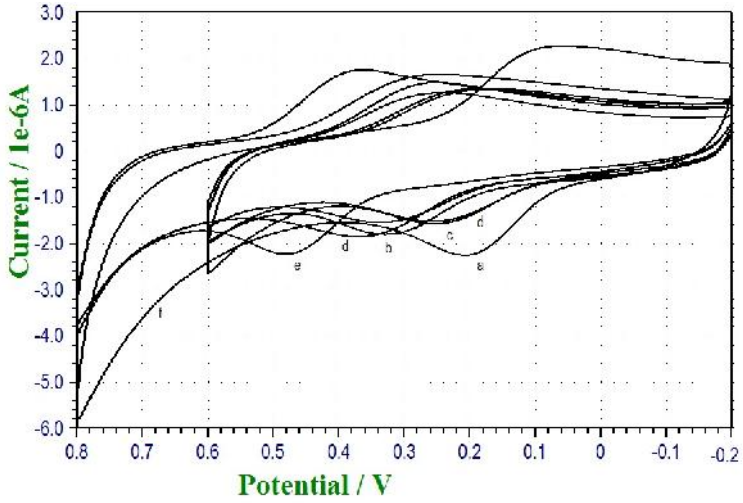

Fig:2 Cyclic voltammogram of curcumin modified electrode with the effect of 0.1 M concentration of different electrolyte a) PBS, b)Ammonium Nitrate, c)Sodium nitrate d)Lithium nitrate, e)Potassium nitrate, f)Calcium nitrate, g)Barium nitrate at the scan rate of 50 mV/s.

Effect of Scan Rate
The effect of scan rate on the performance of the modified electrode was studied with CV. Fig 3(A) represents the CV of curcumin/ MWCNT modified electrode at different scan rate from 5, 10 to 150 mV/s in 0.1 M PBS at pH 7 vs the square root of the potential. Fig 3(B) indicates the anodic and cathodic peak current increase linearly with increase in scan rate which denotes the electron transfer process is diffusion controlled.
Effect of pH over curcumin modified electrode
The reactivity site for free radicle scavenging effect of curcumin was pH dependent. The *o*-methoxyphenol group of curcumin containing OH group exhibit well redox behavior at pH-7(12). Fig-4 represents the cyclic voltammogaram of curcumin/MWCNT modified electrode in different pH containing 0.1 M PBS solution at the scan rate of 50 mV/s.

With increase in the pH the peak potential shifted towards more negative. At pH-7, the curcumin/MWCNT graphite electrode shows a well defined redox peak at lesser potential. Hence 0.1 M PBS, pH- 7 was choosen for further studies.

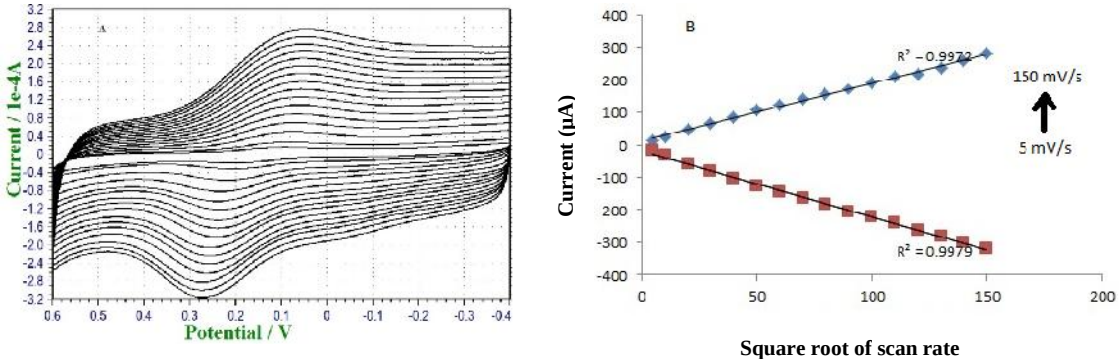

Fig: 3(A) Cyclic Voltammograms of curcumin modified electrode at 0.1 M PBS pH- 7 at different scan rate of 5, 10 to 150 mV/s and Fig: 3 (B) plot of peak currents Vs square root of scan rate.

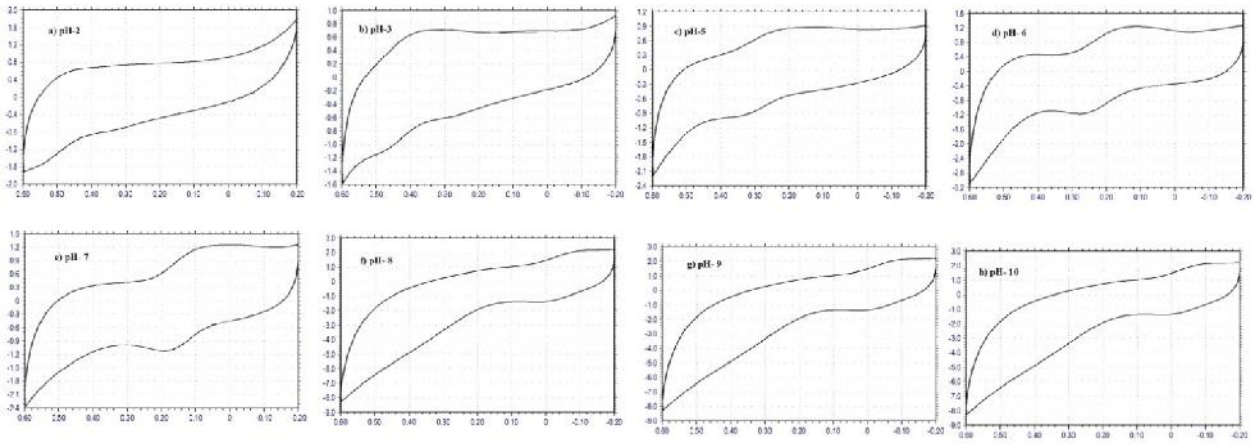

Fig: 4 Cyclic Voltammogram of curcumin/MWCNT modified Graphite Electrode at different pH in 0.1M PBS with the scan rate of 50mV/s.

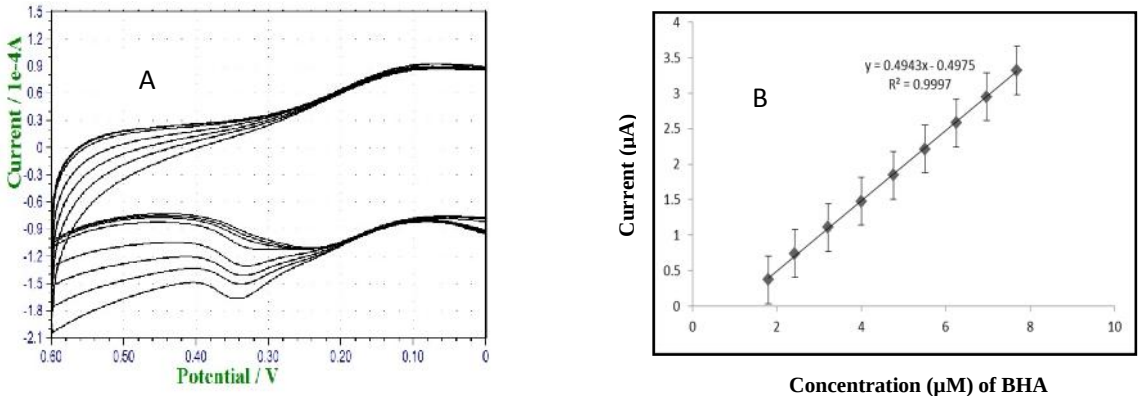

Fig: 5(A) Cyclic voltammogram of curcumin/MWCNT modified electrode in different concentration of BHA in 0.1M PBS at the Scan rate of 50 mV/s. (B) Linear calibration plot of concentration vs current.

c. Electrocatalytic oxidation of BHA using curcumin/MWCNT modified electrode

The cyclic voltammetry measurement of CME in the presence of different concentration of BHA in the potential range of 0 to 0.6V in 0.1 M PBS, pH-7 at scan rate of 50 mV/s favors the electrocatalytic oxidation of BHA was observed. An increase in the anodic peak current for the oxidation of BHA at 0.33 V was observed. Fig 5 (A) represents the Cyclic Voltammogram of different concentration of BHA in 0.1 M PBS at 50mV/s. From the result obtained from voltammogarm, a calibration plot of current vs concentration was plotted. Fig 5(B) represents the calibration plot of current against concentration of BHA ranges from $3.369X10^{-6}$ M to $3.319X10^{-4}$ M with the detection limit of $2.250X10^{-7}$ M.

d. Stability and reproducibility

The practical difficulty associated with the modified electrode exists with the stability of the electrode and reproducibility of the result. curcumin/ MWCNT modified electrode was evaluated for its stability with repeated measurement of 2.25 X 10^{-5} M BHA. The oxidation current for modified electrode for oxidation of BHA remain with the confident level of 96 %indicating that the electrode is stable towards effective measurement of BHA.

IV. Conclusion

The electropolymerization of curcumin over MWCNT functionalized graphite electrode leads to the evolution of new electrode with increased stability and reproducibility. The curcumin/MWCNT modified electrode shows good catalytic response for oxidation of BHA with the detection limit of $2.250X10^{-7}$ M. Curcumin/MWCNT modified electrode shows an excellent reproducibility with the RSD values of 2.8%. The modified electrode was stored in airtight vial and stored at ambient temperature and used for several analysis of BHA at different time interval.

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