EXECUTIVE SUMMARY OF THE UGC MAJOR PROJECT

"INVESTIGATING THE BEHAVIOUR OF L-DOPA (LEVODOPA, 3,4-DIHYDROXY-1-PHENYLALANINE) IN THE PRESENCE OF ASCORBIC ACID(AA) BY MODIFYING THE GLASSY CARBON ELECTRODE WITH POLY ETHYLENE DIOXYTHIOPHNEN (PEDOT)/MULTI WALLED CARBON NANO TUBE (MWCNT)/MNO_2 NANO PARTICLE BY ELECTROCHEMICAL METHOD"

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1. Introduction

Generally voltammetric chemical sensor is an important class of electrochemical sensors widely used in pharmaceutical analysis because of their inherent advantages. These techniques are well suited for the determination of drugs in various samples such as syrups, tablets, creams, and ointments. The principal advantage of the modern voltammetric methods is that the precipitates do not interfere, and generally the separation and extraction procedures are not necessary. The development of chemically modified electrodes (CMEs) continues to be an area of great interest in pharmaceutical analysis owing to their ability to catalyze the oxidation or reduction of solute species that exhibits high over voltage at unmodified surfaces. Thus CMEs play an important role in reducing the high overvoltage required for the voltammetric determination of analyte without any major interference.

In the present investigation, a total of seven different nanocomposites modified electrochemical sensors have been fabricated for the determination of the drug 3,4 – di-hydroxy phenylalanine (L-dopa**)** by modification of the glassy carbon electrode surface with single or combination of PEDOT-PSS, MnO_2 and MWCNT through the technique of electropolymerization, electrodeposition and drop casting. (Table 1).

Table 1: The details of the developed electrochemical sensors for the drug 3,4 – ***di-hydroxy phenylalanine (L-dopa) are as follows:***

S.No	**Sensors (Different modified GCE)**
1.	Poly Ethylenedioxythiophene-Poly Styrene Sulfonic acid modified glassy carbon electrode (PEDOT-PSS modified GCE)
2.	Multi Walled Carbon Nano Tube modified glassy carbon electrode (MWCNT modified GCE)
3.	Manganese dioxide nano particles modified glassy carbon electrode (MnO_2 modified GCE)
4.	Poly Ethylenedioxythiophene-Poly Styrene Sulfonic acid/Manganese dioxide modified glassy carbon electrode (PEDOT-PSS/MnO_2 modified GCE)
5.	Manganese dioxide/Multi Walled Carbon Nano Tube modified glassy carbon electrode (MnO_2/ MWCNT modified GCE)

6.	Poly Ethylenedioxythiophene-Poly Styrene Sulfonic acid/Multi Walled Carbon Nano Tube modified glassy carbon electrode (PEDOT-PSS/MWCNT modified GCE)
7.	Poly Ethylenedioxythiophene-Poly Styrene Sulfonic acid/Manganese dioxide /Multi Walled Carbon Nano Tube modified glassy carbon electrode (PEDOT-PSS/MnO_2/MWCNT modified GCE)

2. The Results

2.1 Peak Currents in the modified glassy carbon electrodes.

It is observed from the Table 2 and Fig. 1 that the interaction of L-dopa with PEDOT-PSS/MnO_2/MWCNT shows highest current compared to PEODT-PSS, MnO_2, MWCNT, PEDOT-PSS/MnO_2, MnO_2/MWCNT and PEDOT-PSS/MWCNT.

Table 2: The results of peak current investigation in various sensors:

S. No	Sensors	Peak current observed for L-dopa	pH
1.	PEDOT-PSS	1.5317×10^{-4}	7.0
2.	MnO_2	1.6112×10^{-4}	5.0
3.	MWCNT	1.1800×10^{-4}	5.0

4.	PEDOT-PSS/MnO_2 modified GCE	2.3617 x 10^{-4}	7.0
5.	MnO_2/ MWCNT modified GCE	1.0533 x 10^{-4}	6.0
6.	PEDOT-PSS/MWCNT modified GCE	1.0946 x 10^{-4}	7.0
7.	PEDOT-PSS/MnO_2/MWCNT modified GCE	3.7823 x 10^{-4}	7.0

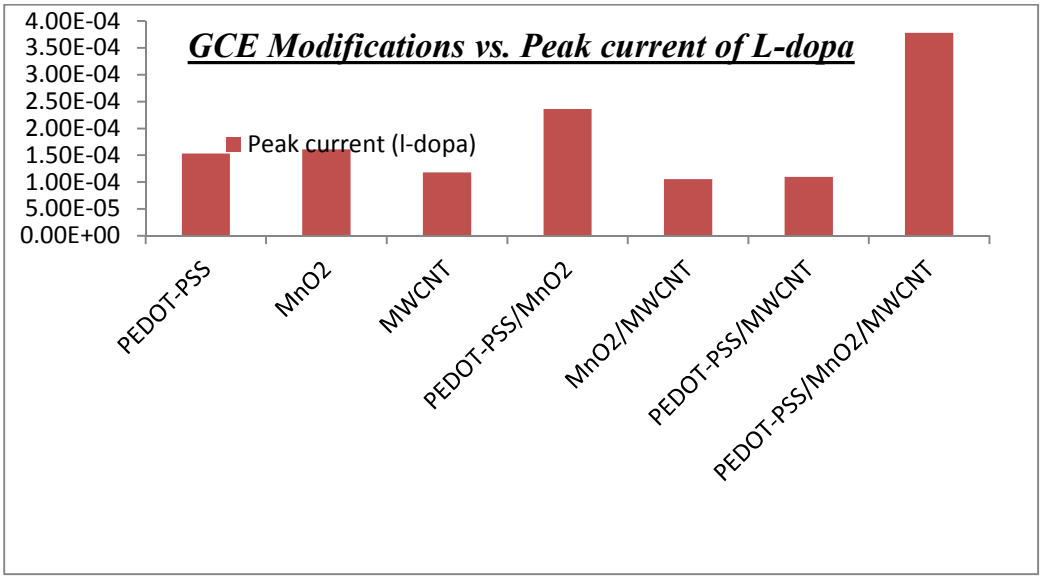


Fig. 1: Different GCE modifications vs. L-dopa peak current

Among the mono layer surfaces, the peak current increases in the order MWCNT < PEDOT-PSS < MnO_2. Among other nanocomposites, the peak

current is increasing in the order as follows MnO_2/MWCNT < PEDOT-PSS/MWCNT < PEDOT-PSS/ MnO_2 < PEDOT-PSS/ MnO_2/MWCNT.

The reason for the low current behaviour at MnO_2/MWCNT and PEDOT-PSS/MWCNT surface may be due to the adsorption properties of MWCNT. Though MWCNT has good catalytic behaviour, its surface adsorption properties may reduce the electron transfer rate in the surface by failing to produce new surface for further redox process. On the other side the reason for higher peak current behaviour for PEDOT-PSS/MnO_2 and PEDOT-PSS/MnO_2/MWCNT is due to rapid electron transaction between conduction band and valence band. Generally it is known that polymers usually have low band gap between conduction and valence band and deposition of nanomaterial over the polymer not only stabilizes the surface, it also enhances the peak current by reducing the band gap of the polymer. This makes PEDOT-PSS/MnO_2 and PEDOT-PSS/MnO_2/MWCNT nanocomposites to give higher peak currents than the other modified surfaces.

2.2. Scan Rate Investigation in the modified electrodes:

Every prepared modified GCE is subjected to the investigation of scan rate. In cyclic voltammetry the rate of voltage change over time during each phase is known as scan rate (V/s). This scan rate helps to find the whether the redox process is adsorption controlled or diffusion controlled at the surface of the electrode. If a plot is linear in the graph drawn between the anodic peak current vs. square root of the scan rate, it is a diffusion controlled redox process. For all

the modified surfaces, the anodic peak current of L-dopa was proportional to the square root of scan rate with good correlation coefficients. It is observed from the Table 3 that in our present investigation of the redox process of L-dopa follows diffusion controlled at all modified surfaces.

Table 3: Different modified GCEs R^2 value and surface process at GCE

S. No	**Sensors (Modifications at GCE)**	**R^2 value**	**Surface process at electrode**
1.	PEDOT-PSS	0.990	Diffusion
2.	MnO_2	0.999	Diffusion
3.	MWCNT	0.999	Diffusion
4.	PEDOT-PSS/MnO_2 modified GCE	0.997	Diffusion
5.	MnO_2/ MWCNT modified GCE	0.992	Diffusion
6.	PEDOT-PSS/MWCNT modified GCE	0.979	Diffusion
7.	PEDOT-PSS/MnO_2/MWCNT modified GCE	0.990	Diffusion

2.3. pH Investigations in the modified Glassy carbon electrodes:

All the sensors have been subjected to the study of L-dopa redox process at pH range from 3.0–8.0. Though it may be important to fix biological buffer pH 7.0

for the L-dopa redox process, there is also a need to consider other factors like good peak separation and better reversibility which help to analyse any other interference in the potential range and also enhance the rate of the reaction at the surface of the electrode. The Table 4 and Fig. 2 summarise the results of the solution pH fixed for L-dopa oxidation at various modified GCEs

Table 4: pH for L-dopa oxidation at various modifications

S. No	**Sensors (Modifications at GCE)**	**pH fixed for L-dopa oxidations**
1.	PEDOT-PSS	**7.0**
2.	MnO_2	**5.0**
3.	MWCNT	**5.0**
4.	PEDOT-PSS/MnO_2 modified GCE	**7.0**
5.	MnO_2/ MWCNT modified GCE	**6.0**
6.	PEDOT-PSS/MWCNT modified GCE	**7.0**
7.	PEDOT-PSS/MnO_2/MWCNT modified GCE	**7.0**

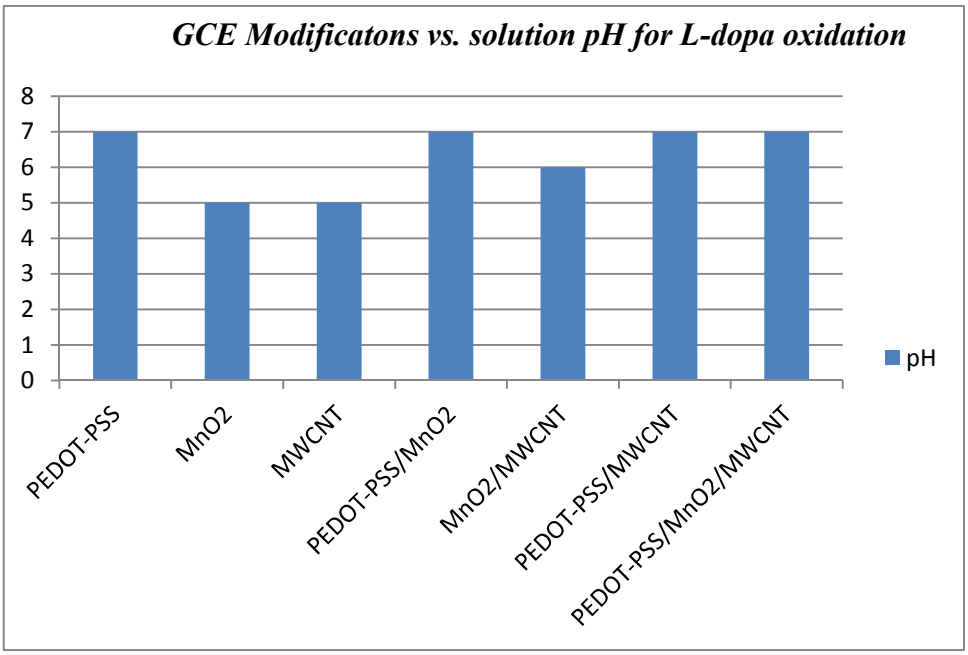


Fig. 2: Various GCE modifications vs. solution pH for L-dopa oxidations

Further pH plays a major role in determining the oxidation mechanism of L-dopa. It is observed from (Fig.3) that while varying the pH from 3.0 to 8.0 there is a shift in the oxidation peaks of L-dopa towards low oxidation potential in all modified GCEs.

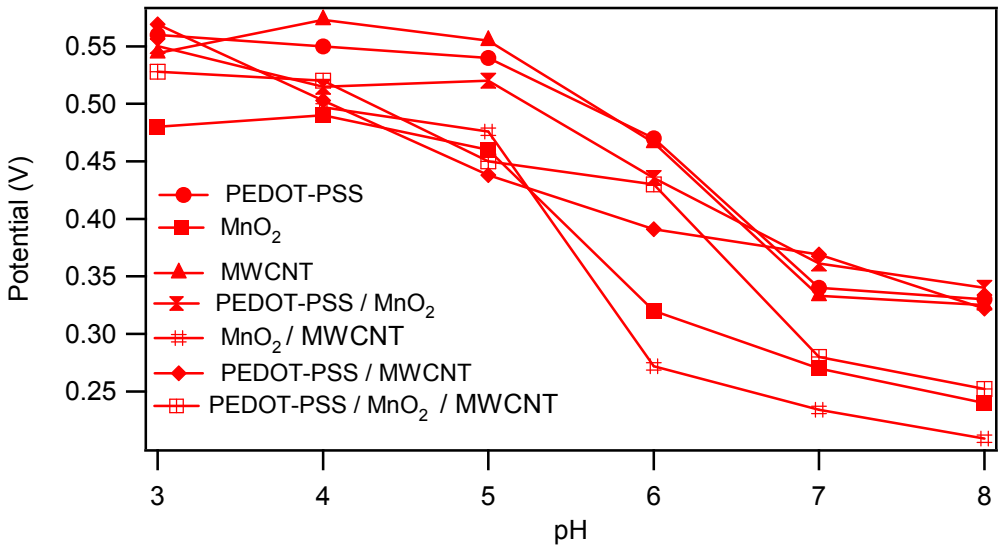
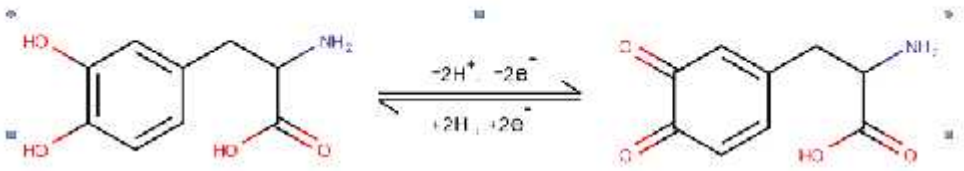


Fig. 3: Peak potentials vs. pH for all modified GCEs

This indicates the participation of two protons in the oxidation mechanism. It is known that catechol derivatives prefer to follow equal number of protons and electrons transfer in redox process; thus the total number of electrons participated in the L-dopa oxidation mechanism is predicted to be two. The possible electro oxidation mechanism for L-dopa is given below (as mentioned in Scheme 1).



L- dopa **L-dopaquinone**

Scheme 1: Electro oxidation Mechanism of L-dopa

2.4. Concentration Variation of L-dopa

The concentration variation of L-dopa needs high sensitivity; this can be achieved by Differential Pulse Voltammetry (DPV) technique. The DPV curves at different concentrations of L-dopa at all the modified glassy carbon electrodes, (PEDOT-PSS, MnO_2, MWCNT, PEDOT-PSS/MnO_2, MnO_2/MWCNT, PEDOT-PSS/MWCNT and PEDOT-PSS/MnO_2/MWCNT) clearly show that the anodic peak current increases linearly with increasing the concentrations of L-dopa in the presence of 5mM ascorbic acid (AA), and this clearly indicates that AA has no influence in the determination of L-dopa. The

linear range, R^2 and limit of detection (LOD) values of all the modified Glassy carbon electrodes are summarized below in Table 5.

Table 5: Summary of modified GCEs linear range, r^2 value and LOD

S. No	Sensors (modified GCEs)	Linear range (con variation of L-dopa in 5mM AA)	R^2	LOD
1.	PEDOT-PSS	50 µM – 247 µM	0.998	50 µM
2.	MnO_2	285 µM – 985 µM	0.995	285 µM
3.	MWCNT	2.75 x 10^{-4}M – 8.0 x 10^{-4} M	0.999	2.75 x 10^{-4}M
4.	PEDOT-PSS/MnO_2	12 µM – 40 µM	0.989	12 µM
5.	MnO_2/MWCNT	4.50 x 10^{-4} M – 2.25 x 10^{-3} M	0.992	4.50 x 10^{-4} M
6.	PEDOT-PSS/MWCNT	30 µM – 575 µM	0.994	30 µM
7.	PEDOT-PSS/MnO_2/MWCNT	2 µM – 217 µM	0.995	2 µM

2.5. Analytical Application of the Developed Sensor

By comparing the peak currents, scan rate, linear range, and LOD of the entire modified GCEs (PEDOT-PSS, MnO_2, MWCNT, PEDOT-PSS/MnO_2, MnO_2/MWCNT, PEDOT-PSS/MWCNT, PEDOT-PSS/MnO_2/MWCNT), the PEDOT-PSS/MnO_2/MWCNT modified GCE has been fixed for the L-dopa determinations in real (tablet) samples, because of its higher peak current for

L-dopa oxidation in comparison with other modified GCEs. Moreover this modified GCE also shows a long linear range in L-Dopa concentration variation and low detection limit as seen in DPV. All these make PEDOT-PSS/MnO_2/MWCNT modified GCE is best among all the modified electrodes.

The concentration of L-Dopa in tablets was determined using PEDOT-PSS/MnO_2/MWCNT modified GCE in DPV technique. The standard addition method was followed to find the unknown concentrations. The average recovery was 98%, indicating applicability and reliability of the proposed method.

Acknowledgement

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