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Electrochemical Behavior of Antiemetic Drug Metoclopramide at Electrochemically Pre-treated Pencil Graphite Electrode

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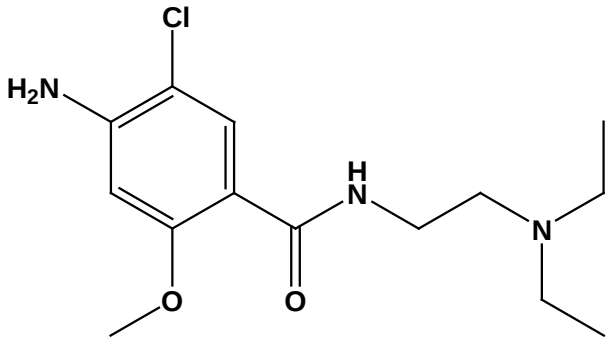
Abstract- Highly economic and selective method for the analysis of dopamine-receptor antagonist and antiemetic drug Metoclopramide is developed. In this method Metoclopramide is analyzed electrochemically by using pre-treated pencil graphite electrode (PTPGE) by differential pulse and cyclic voltammetry. The PTPGE showed very good result with significant enhancement of the peak current. The dependence of the current on pH, concentration and scan rate was investigated to optimize the experimental conditions for determination of Metoclopramide. The oxidative peak current increased linearly with the concentration of Metoclopramide in the range of 1.0×10^{-8} to 1.3×10^{-6} M. The limit of detection was found to be 1.29×10^{-11} M. The pre-treated electrode showed good selectivity, reproducibility and stability for the detection of trace Metoclopramide. The proposed method was successfully applied to Metoclopramide determination in pharmaceutical formulations and real samples.

Keywords- Metoclopramide, Voltammetry, Graphite pencil electrode, Diffusion-controlled process, Sensitivity

1. INTRODUCTION

Metoclopramide (MCP) (4-amino-5-chloro-N-[2-(diethylamino)ethyl]-2-methoxybenzamide) as shown in Scheme 1 is a benzamide dopamine-receptor Antagonist,

antiemetic drug, often used in emergency departments in the management of nausea, vomiting, and vascular-type headache, for the management of gastrointestinal motility disorders and gastrointestinal reflux and for the prevention of cancer chemotherapy induced emesis at much higher doses [1-3].



Scheme 1. Chemical structure of MCP

The higher impact of MCP in pharmaceutical sciences has resulted in extensive literature on its sensitive determination in real samples and dosage forms, by classical methods like potentiometry [4,5], reflectometry [6] spectrophotometry [7,8], LCMS [9,10], HPLC [11], spectrofluorimetry [12], have been reported for the determination of MCP. The main problems encountered in using such methods are either the need for derivatization or the need for time consuming extraction procedures. And some of voltammetric methods are also been developed for determination of MCP [2,13,14].

However, the development of a simple, sensitive, specific, and inexpensive method for the assay of the MCP is yet desirable. Electrochemical methods especially differential pulse voltammetry (DPV) makes it possible to decrease analysis time as compared to the time required by chromatographic methods and spectrophotometric methods [15].

Despite the fact that electrodes constructed from carbon based materials exhibit low background currents over a wide range of potentials and are useful for many electrochemical applications, electron transfer rates observed for redox processes at these surfaces are often slower than those at metal electrode surfaces. As a result, carbon electrodes exhibit substantial overpotentials which cause the related oxidations and reductions to take place at potentials significantly in excess of their thermodynamic potentials. In order to increase the electron transfer rates, various chemical [16,17] and electrochemical [18-20] surface treatment procedures for carbon electrodes have been developed which have been shown to produce improved electrode response compared to that of the native electrode material. The present work describes the electrochemical pre-treatment of pencil graphite electrode (PTPGE) and its application for sensitive determination of MCP in pharmaceuticals as well as real samples.

2. EXPERIMENTAL

2.1. Reagents and Chemicals

MCP purchased from Sigma-Aldrich was used as such and graphite Pencil rods (HB-0.5 mm diameter and 6 cm long) were purchased from local stationeries. A stock solution of MCP was prepared in double distilled water. Phosphate buffers from PH 3.0 to 10.4 were prepared according to method of Christian and Purdy [21]. MCP containing Tablets were purchased from local pharmacy. Other reagents used were of analytical or chemical grade. All solutions were prepared with double distilled water.

2.2. Instrumentation and analytical procedures

Electrochemical measurements were carried out on a CHI 630D electrochemical analyzer (CH instruments Inc., USA). The voltammetric measurements were carried out in a 10 mL single-compartment three electrode glass cell with Ag/AgCl as a reference electrode, a platinum wire as a counter electrode and a PTPGE as a working electrode. All the potentials are given against the Ag/AgCl (3 M KCl). P^H measurements were performed with Elico LI120 pH meter (Elico Ltd., India). All experiments were carried out at an ambient temperature of 299±0.2 K.

The area of the electrode was obtained by the cyclic voltammetric method using 1.0 mM $K_3Fe(CN)_6$ as a probe at different scan rates. For a reversible process, the following Randels-Sevcik formula can be used [22].

$$I_{pa} = 0.4463(F^3/RT)^{1/2} n^{3/2} A_0 D_0^{1/2} C_0 \nu^{1/2} \quad (1)$$

where I_{pa} refers to the anodic peak current, n is number of electrons transferred, A_0 is the surface area of the electrode, D_0 is the diffusion coefficient, ν is the scan rate, and C_0 is the concentration of $K_3Fe(CN)_6$. For 1.0 mM $K_3Fe(CN)_6$ in 0.1 M KCl electrolyte, T=298 K, R=8.314 J K^{-1} mol^{-1}, F=96,480 Coulombs mol^{-1}, n=1, and $D_0=7.6 \times 10^{-6}$ cm^2s^{-1};then from the slope of the plot of I_{pa} versus $\nu^{1/2}$ relation, the electroactive area was calculated. In our experiment the slope was 4.136×10^{-5} µA $(Vs^{-1})^{1/2}$ and the area of PTPGE calculated was found to be 0.1311 cm^2 which is three times higher than that of the PGE.

2.3. Measurement procedure

A stock solution of 1 µM of MCP was prepared by dissolving the desired amount in double distilled water. The required amount of the stock solution was added to electrolytic cell containing phosphate buffer solution. Voltammograms were then recorded using voltammetric analyzer under optimized parameters. The parameters for DPV were initial potential: 0.8 V; final potential: 1.2 V; increase potential: 0.004 V; amplitude: 0.05 V; quiet time: 2 s; sensitivity: 1×10^{-6} A V^{-1}.

2.4. Pre-treatment of electrode

The electrochemical treatment of GPE was performed in aqueous media containing different supporting electrolytes by potential cycling between -2.0 V and +2.0 V with a scan rate of 50 mV s^{-1} for eight scans. The investigated supporting electrolytes were 0.1 M H_3BO_3, $NaNO_3$, $HClO_4$, H_2SO_4, H_3PO_4, HCl, $LiClO_4$, and Na_2CO_3. The results shown that the GPE electrodes pre-treated in 0.1 M HCl were the most selective and sensitive towards a MCP. So 0.1 M HCl was chosen for pre-treatment of electrodes. The prepared electrodes (PTPGE) were stored at room temperature in desiccators until their use.

2.5. Sample preparation and measurement procedures

Under optimal conditions, at pH 3.0 phosphate buffer solution (0.2 M) containing different concentrations of MCP were analyzed using PTPGE electrode and calibration curve was obtained.

Ten tablets containing metoclopramide were weighed and ground to a homogeneous fine powder in a mortar. A portion equivalent to a stock solution of a concentration of about 10 mM was weighed accurately and transferred to a 100 ml calibrated flask and completed to the volume with Millipore water. The contents of the flask were sonicated for 10 minutes to affect complete dissolution. Appropriate solutions were prepared by taking suitable aliquots of the clear supernatant liquid and diluting them with the ortho phosphate buffer solutions. Each solution was transferred to the voltammetric cell and analyzed by standard addition method. Urine samples taken from a healthy person were, at first, filtered with filter papers. Then, these samples were diluted with deionised water followed by adding an appropriate amount of standard drug solution. The resulting solution was then directly analyzed based on our proposed procedure and without any pre-treatment or extraction steps.

3. RESULTS AND DISCUSSION

3.1. Cyclic voltammetric behavior of MCP

The electrochemical behavior of MCP at PGE and PTPGE at pH=3, were shown in Fig. 1. It can be seen that the MCP oxidation peaks at the PGE was weak and broad due to slow electron transfer, while the response was considerably improved at the PTPGE. At the PGE, the peak was at about 1.19 V (peak b), but on the PTPGE, the peaks appeared at 1.21 V (peak a), with considerable enhancement in the peak current. This was attributed to the electrocatalytic effect caused by activation of graphite surface after pre-treatment. The pre-treated electrode has no electrochemical activity in phosphate buffer solution (curve c), but the background current becomes larger, which is attributed to the fact that pre-treatment with acid can increase the surface activity remarkably. The results showed that one sharp anodic

peak was observed. After the successive scan, the peak current decreased greatly and finally remained unchanged. This phenomenon may be attributed to the adsorption of oxidative product of MCP at the pre-treated electrode surface. Therefore, the voltammograms corresponding to the first cycle and peak was generally recorded.

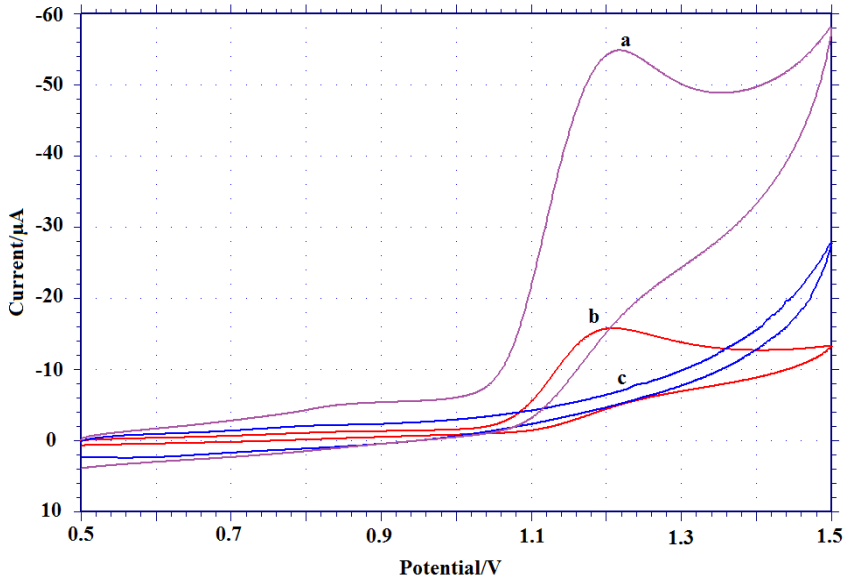


Fig. 1. Cyclic Voltammograms obtained for 1.0 µM MCP in pH 3.0,0.2 M buffer: (a)pre-treated Pencil graphite electrode with MCP (b) Pencil graphite electrode with MCP (c) pre-treated Pencil graphite electrode in pH 3.0 at υ=0.1 V s^{-1}

3.2. Effect of pH

The electrode reaction might be affected by pH of the medium. The electro-oxidation of 1.0 µM MCP was studied over the pH range of 3.0 to 10.2 in phosphate buffer solution by cyclic voltammetry. A well-defined sharp oxidation peak appeared between pH 3.0 and 9.2 (Fig. 2A), and there after the oxidation peaks observed were extremely broad. Hence, the pH study was restricted up to pH 9.2. With increase in pH of solution, the peak potential linearly shifts to less positive values and the linear relation between Ep and pH (Fig. 2B) can be expressed as:

Ep (V)=1.381-0.054 pH, r=0.987 (2)

The slope of the equation was found to be 54 mV/pH. This closeness of the slope to the expected theoretical value of 59 mV/pH suggests that the number electrons transferred is equal to that of the hydrogen ions taking part in the electrode reaction. From the plot of I_{Pa} versus pH (Fig. 2C) it is clear that peak current is affected by the pH value. However, the best

result with respect to sensitivity accompanied with sharper response was obtained with pH=3.0, so pH=3.0 was selected for further experiments.

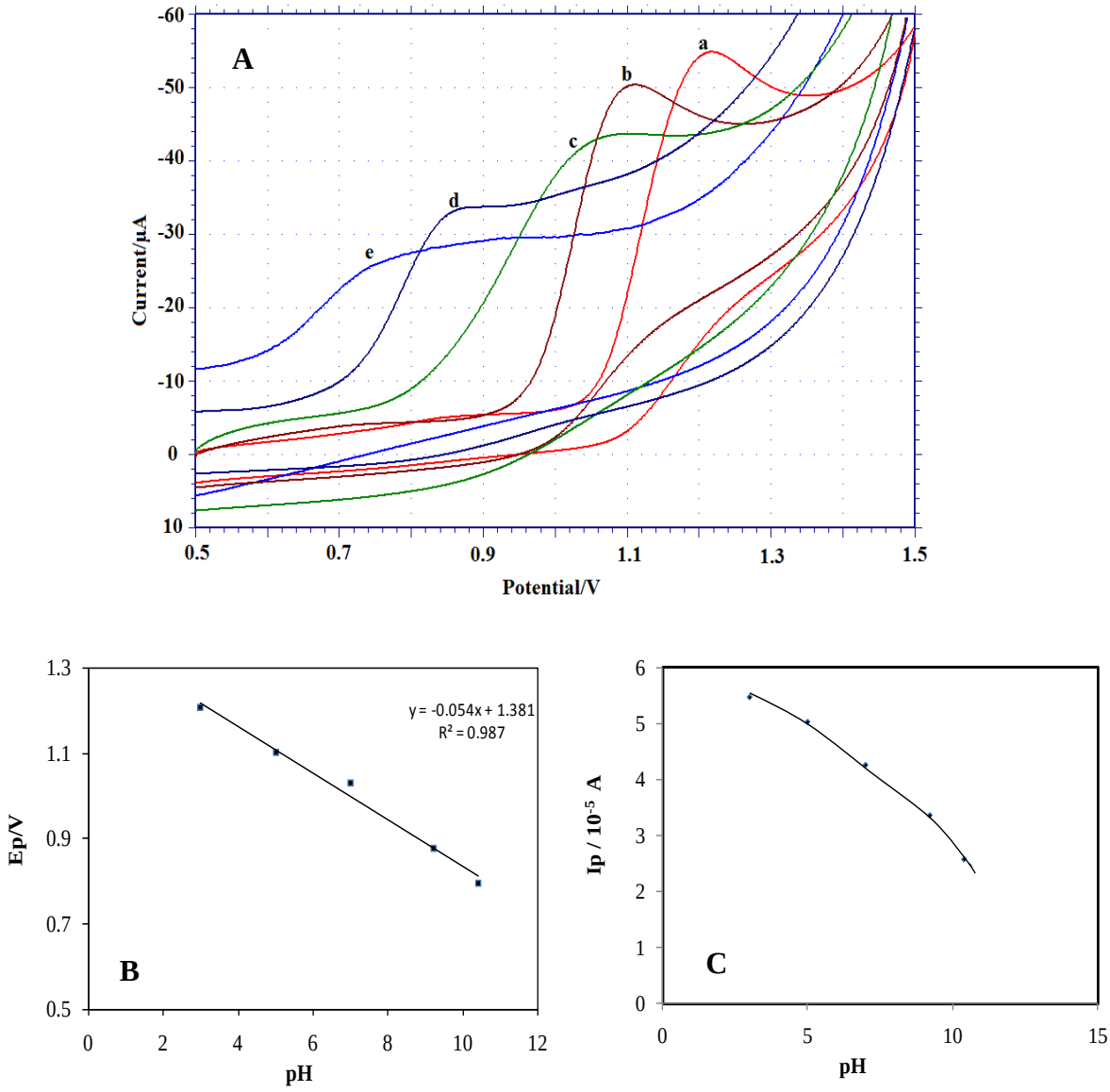


Fig. 2. A) Cyclic voltammograms obtained for 1.0 µM MCP in buffer solution at (a) pH 3.0, (b) pH 5.0, (c) pH 7.0, (d) pH 9.2 (e) pH 10.4with potential scan rate: 0.1 V s^{-1}; **B)** Variation of peak potential with pH for 1.0 µM MCP; **C)** Variation of peak current with pH for 1.0 µM MCP

3.3. Effect of the Scan rate

Useful information involving an electrochemical mechanism generally can be acquired from the relationship between peak current and scan rate. Therefore, the voltammetric behavior of MCP at different scan rates was studied using cyclic voltammetry (Fig. 3A). Scan

rate studies were carried to assess whether the process on PTPGE was under diffusion controlled or adsorption controlled.

The influence of the square root of scan rate on the peak current (Fig. 3B) showed a linear relationship in the range of 25 to 400 mV s^{-1} for cyclic voltammetry which is typical of diffusion-controlled process [23], and the equation can be expressed as

$$Ip(\mu A)=10.94v^{1/2}\ (Vs^{-1})+1.818,\ r=0.996 \quad (3)$$

A plot of logarithm of anodic peak current versus logarithm of scan rate (Fig. 3C) gave a straight line with a slope of 0.39 is close to the theoretically expected value of 0.5 for a purely diffusion-controlled current, which in turn further confirms that the process is diffusion controlled where the electro active species MCP diffuses from the bulk solution to a planar electrode surface; the equation can be expressed as:

$$\log Ip(\mu A)=0.39 \log \nu\ (Vs^{-1})+1.065,\ r=0.995 \quad (4)$$

The Ep of the oxidant peak was also dependent on scan rate. The peak potential shifted to more positive value on increasing the scan rate, which confirms the irreversibility of the oxidation process a linear relationship between peak potential and logarithmic scan rate (Fig. 3D) for cyclic voltammetry can be expressed by the following equation:

$$Ep(V)=1.239+0.022 \log \nu\ (Vs^{-1})\ ,\ r=0.989 \quad (5)$$

For an irreversible electrode process, according to Laviron, Ep is defined by the fallowing equation.

$$E_P = E^0 + \left[\frac{2.303RT}{\alpha nF}\right] log \left[\frac{RTk^0}{\alpha nF}\right] + \left[\frac{2.303RT}{\alpha nF}\right] log v \quad (6)$$

Where α is the transfer coefficient, k^0 the standard heterogeneous rate constant of the reaction, n the number of electrons transferred the scan rate and E^0 is the formal redox potential. Other symbols have their usual meanings. Thus, the value of αn can be easily calculated from the slope of Ep versus log ν. In this system, the slope is 0.022, taking T=298 K, R=8.314 J K^{-1} mol^{-1} and F=96480 C, αn was calculated to be 0.853. According to Bard and faulkner [24], α can be given as:

$$\alpha = \frac{47.7}{E_P - E_{P/2}} mV \quad (7)$$

Where $Ep_{1/2}$ is the potential where the current is at half the value. So, from this we obtained the value of α=0.4534. Further the number of electrons (n) for the oxidation was calculated to be 1.8842 ~ 2.0.

3.4. Calibration curve

In order to develop a voltammetric method for determining the MCP, we selected the differential pulse voltammetric mode, since the peaks were sharp and better defined at lower concentration of MCP than those obtained by cyclic voltammetry, with a lower background current, resulting in improved resolution. The differential pulse voltammograms were recorded between 0.9 and 1.3 V after open-circuit accumulation for 180 s with stirring.

To study the accuracy of the proposed method and to check the interference from excipients used from the dosage form, recovery experiments were carried out. The concentration MCP was calculated by using standard addition method. According to the obtained result, it was possible to apply these techniques to the quantitative analysis of MCP. The phosphate buffer solution of pH 3.0 was selected as the supporting electrolyte for the quantification MCP as it gave maximum peak current at pH 3.0.

Differential pulse voltammograms (Fig. 4) obtained with increasing amounts of MCP showed that the peak currents increased linearly with increasing concentration (Fig. 4 inset). Deviation from linearity was observed for more concentrated solutions, due to adsorption of MCP or its oxidation product on the electrode surface at higher concentrations. The linear equation was:

$$Ip(\mu A)=0.433C+10.92,\ r=0.991 \quad (8)$$

Related statistical of the calibration curves were obtained from five different determinations. The limit of detection (LOD) and quantification (LOQ) were 1.3×10^{-11} M and 4.32×10^{-11} M respectively. The LOD and LOQ were calculated on the peak current using the following equations:

$$LOD=3s/m,\ LOQ=10s/m \quad (9)$$

Where, s is the standard deviation of the peak currents of the above concentrated samples and m is the slope of the calibration curve. The detection limits reported for non-electrochemical method and electrochemical methods are shown in Table 1. The LOD and LOQ values calculated by the present method are better compared to the reported methods [4-8, 11-15].

In order to ascertain the repeatability of the analysis, five measurements of 1.0×10^{-6} M MCP were carried out using PTPGE at interval of 30 min. The RSD value of Peak current was found to be 1.21% which indicated that electrode has good repeatability. As to the

reproducibility between days, it was similar to that of within day repeatability when all conditions were kept constant.

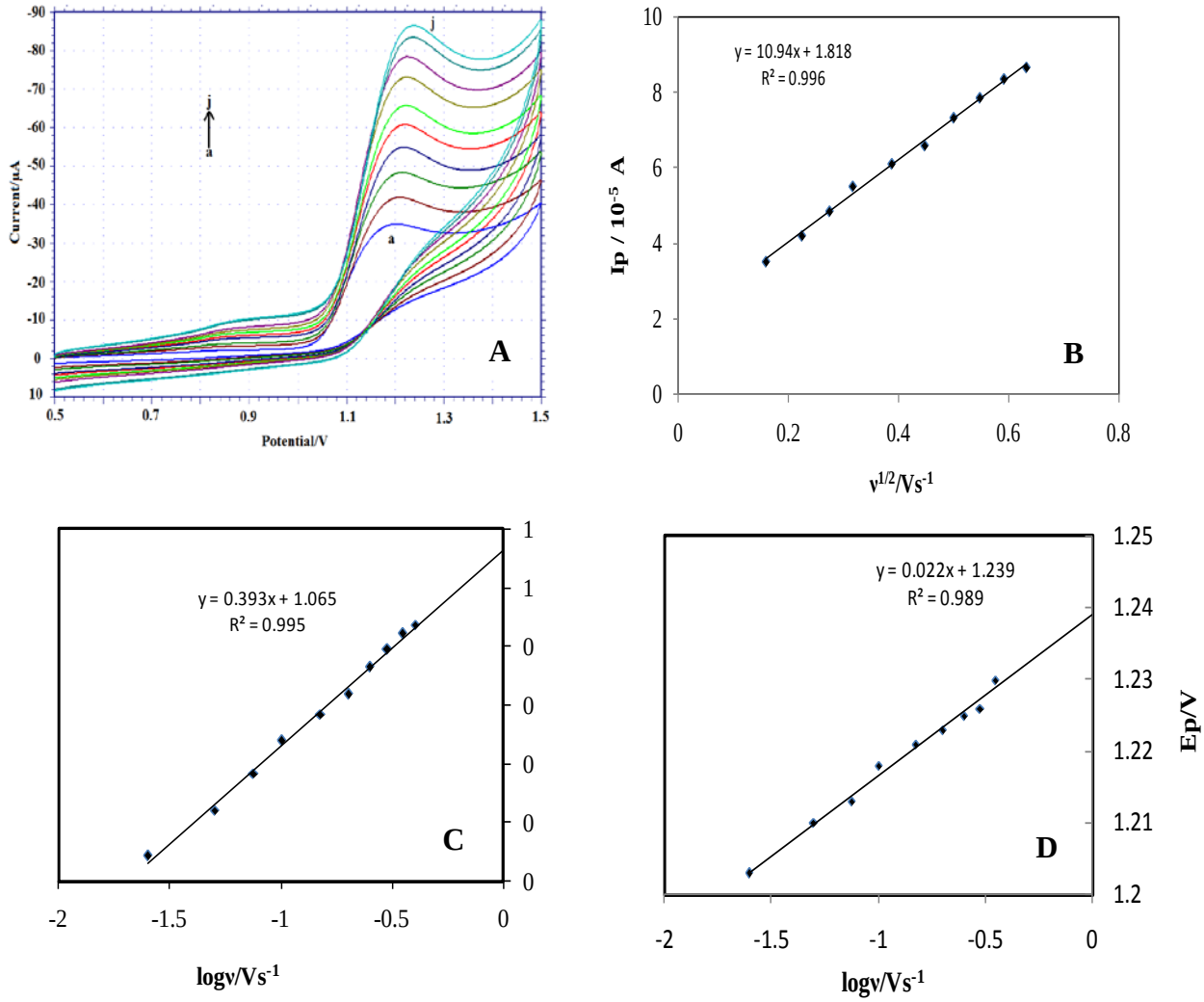


Fig. 3. A) Cyclic voltammograms of 1.0 µM MCP in 0.2 M buffer solution of pH 3.0 at scan rates of: (a) 0.025, (b) 0.05, (c) 0.075, (d) 0.10, (e) 0.15, (f)0.20 (g)0.25 (h) 0.30, (i) 0.35,(j) 0.40 Vs^{-1}; **B)** Observed dependence of peak current on the square root of scan rate; **C)** Plot of logarithm of peak current *vs*. logarithm of scan rate; **D)** Plot of variation of peak potential with logarithm of scan rate

3.5. Interference studies

MCP was formulated in single as well as multi-component Tablets. The oxidation peaks of interferents should not appear where the peak corresponds to oxidation of MCP. So in order to investigate the effect of co-formulated substances such as glucose, starch, sucrose etc. on the voltammetric response of MCP, the differential-pulse voltammetric experiments were carried out for 1.0 µM MCP in the presence of 1.0 mM of each of the interferents. The results are listed in Table 2. It was observed that none of the above mentioned excipients are

interfered in the analysis which indicates procedures were able to assay MCP in the presence of excipients, and hence they can be considered specific.

Table 1. Comparison of detection limits and linearity range for different proposed methods

Linear range (M)	**Detection limits (M)**	**Method**	**Refs.**
1.0×10^{-7}–1.0×10^{-11}	1.0×10^{-11}	FFT voltammetry	[2]
1.0×10^{-1}–1.0×10^{-6}	8.9×10^{-7}	Potentiometry	[4]
1.0×10^{-2}–6.0×10^{-5}	4.0×10^{-5}	Potentiometry	[5]
6.2×10^{-3}– 5.6×10^{-4}	1.2×10^{-4}	Reflectometric	[6]
4.4×10^{-6}–4.4×10^{-5}	1.5×10^{-6}	Spectrophotometric	[7]
1.7×10^{-4}–1.7×10^{-1}	8.9×10^{-6}	Chemiluminescence	[8]
-	7.3×10^{-9}	HPLC	[11]
1.0×10^{-6}–5.0×10^{-9}	2.0×10^{-11}	Spectrofluorimetric	[12]
4.6×10^{-7}–1.2×10^{-9}	8.0×10^{-11}	Anodic voltammetry	[14]
1.9×10^{-10}–7.9×10^{-10}	2.0×10^{-11}	Square wave voltammetry	[15]
1.3×10^{-6} –1.0×10^{-8}	1.29×10^{-11}	DPV	present work

Table 2. Influence of potential interferents on the voltammetric response of 1.0 µM MCP

Interferent	**Concentration (mM)**	**Error % in [MCP]**
Glucose	1	0.03744
Oxalic acid	1	0.04979
Sucrose	1	0.02282
Gum acacia	1	0.02697
Citric acid	1	0.03112
Talc	1	0.07468
Starch	1	0.01659
Magnesium stearate	1	0.02904

3.6. Tablet analysis and recovery test

In order to evaluate the applicability of the proposed method, the commercial medicinal sample containing MCP, (Elinorm) from,Elite pharma Pvt.Ltd India, was studied. The tablets were grounded to powder, dissolved in water and then further diluted so that MCP concentration falls in the range of calibration plot. Differential-pulse voltammograms were then recorded under exactly identical conditions that were employed while recording differential-pulse voltammograms for plotting calibration plot. It was found that MCP concentration determined for various Tablets using this method are in good agreement with the reported values. The values of experimentally determined MCP and reported MCP amounts agreed reasonably well (Table 3). The results of recovery experiments were also shown in Table 3.

Table 3. Results of the assay and the recovery test of MCP in pharmaceutical preparations using differential pulse voltammetry

Elinorm(10mg)-Metoclopramide hydrochloride	**Tablet**
Labeled claim(mg)	50.00
Amount found[a](mg)	49.68
R.S.D(%)	0.335
% of recovery in R.S.D	0.78
Added(mg)	5.00
Found(mg)	4.94
Recovered[b](%)	99.10

a Each value is the mean of five experiments
b Recovery value is the mean of five determinations

3.7. Detection of MCP in urine samples

The developed differential voltammetric method for the MCP determination was applied to urine samples. The recoveries from urine were measured by spiking drug free urine with known amounts of MCP. The urine samples were diluted 100 times with the buffer solution before analysis without further pre-treatment. A quantitative analysis can be carried out by adding the standard solution of MCP into the detect system of urine sample, and the peak linearly increased in height. The calibration graph was used for the determination of spiked MCP in urine samples. The detection results of five urine samples obtained are listed in Table 4. The recovery obtained was in the range from 97.25% to 99.5% and the standard deviation and relative standard deviations are given in Table 4.

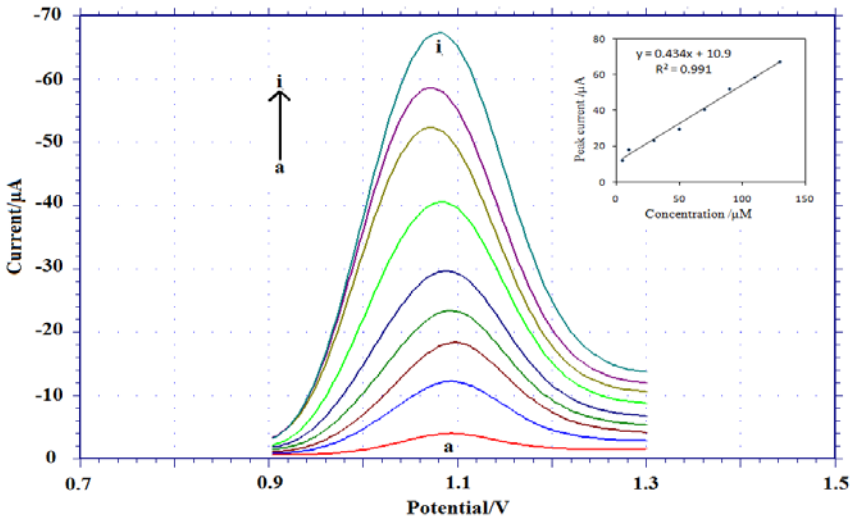


Fig. 4. Differential pulse voltammograms with increasing concentration of MCP in pH 3.0,0.2 M phosphate buffer solution on Pencil graphite electrode with MCP concentration: (a) 1, (b) 5, (c) 10,(d) 30, (e) 50, (f) 70, (g) 90, (h) 110, (i) 130×10^{-8} M, Inset: Plot of current *vs.* concentration of MCP

Table 4. Determination of MCP in urine samples

Sample	Spiked (10^{-5} M)	Found[a] (10^{-5} M)	Recovery (%)	S.D.±R.S.D (%)
0.012±0.008	98.50	0.197	0.2	1
0.011±0.004	97.25	0.389	0.4	2
0.019±0.013	98.66	0.592	0.6	3
0.102±0.006	99.50	0.796	0.8	4
0.031±0.016	97.80	0.978	10	5

a Average of five experiments

4. CONCLUSION

The voltammetric oxidation of MCP at PTPGE in phosphate buffer solution (pH=3.0) has been investigated. MCP undergoes two electron two proton changes and is a diffusion controlled process. The peak current was linear to MCP concentration over a certain range, under the selected analyte as low as 1.3×10^{-11} M and can be used to assay the drug in pharmaceutical dosage form and in spiked urine samples. The proposed method is suitable for quality control laboratories as well as pharmacokinetic studies.

NOMENCLATURE

MCP=Metoclopramide
PGE=Pencil Graphite electrode
PTPGE=Pre Treated Pencil Graphite electrode
DPV=differential pulse voltammetry
CV=cyclic voltammetry
Ipa=anodic peak current (μA)
A_0=surface area of the electrode (cm^2)
D_0=diffusion coefficient ($cm2s^{-1}$)
υ=scan rate ($mV\ s^{-1}$)
C_0=concentration ($mol\ dm^{-3}$)
n=number of electrons transferred
Ep=peak potential (V)
Ip=peak current (μA)
α=transfer coefficient
F=Faraday constant ($C\ mol^{-1}$)
R=gas constant ($J\ K^{-1}mol^{-1}$)
T=temperature (K)
LOD=limit of detection ($mol\ dm^{-3}$)
LOQ=limit of quantification ($mol\ dm^{-1}$)
s=standard deviation of the peak currents
m=slope of the calibration curve
RSD=relative standard deviation

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