



Electrochemical Sensing for Trifluoperazine Determination at a PTH/MWCNTs Film-Modified Graphite Electrode

Sura Mohammed¹, Eman A.M. Al-Jawadi^{2*}

¹College of Science, University of Mosul, Mosul, Iraq

²College of Environmental Science and Technologies, University of Mosul, Mosul, Iraq



CrossMark

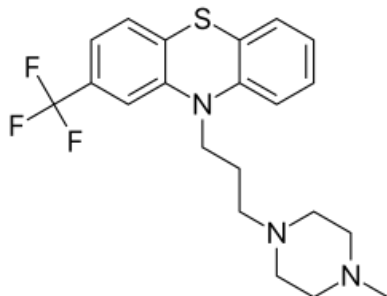
Abstract

An electrochemical approach termed cyclic voltammetry (CV) on a graphite electrode (GrE) was used to determine the antipsychotic medication Trifluoperazine (TRF). Electrochemical oxidation of TRF in phosphate buffer solution at (pH6.0) revealed a peak at (0.246) V vs. (Ag/AgCl, Sat KCl electrode). A PTH /MWCNTs / GrE composite-modified electrode was created by electropolymerized Thionin on the surface of a graphite electrode with multi-wall carbon nanotubes. The analytical curve produced under optimal conditions was linear throughout the TRF concentration range of 0.4999×10^{-11} to 521.327×10^{-11} mol L⁻¹, and the limits of detection (LOD) was 3.93×10^{-17} mol L⁻¹ (S/N=3). The linearly anodic peak current rose in proportion to the square root of the scan rate. The goal of this study is to develop a new electrode (PTH/MWCNTs/GRE) that is more sensitive and accurate at detecting TRF.

Keywords: Thionin; Carbon nanotube; Trifluoperazine; Electropolymerization.

1. Introduction

Chemical structure of (TRF) as shown in Scheme.1^[1]. Trifluoperazine is a phenothiazine derivative that, due to its neuroleptic and antidepressive effects, has been widely used in the treatment of psychotic patients^[2]. In addition, trifluoperazine has been shown to be more beneficial than a placebo in treating generalized anxiety disorder^[3]. The chemical structure of trifluoperazine (Scheme 1),



Scheme.1. The chemical structure of (TRF)

TRF is measured via spectrophotometry^[4], zone capillary electrophoresis^[5], HPLC^[6-7], and HPTLC

^[8-9], polyaminobenzene sulfonic acid/ SWCNTs-modified glassy carbon electrode^[10], among the electrochemical approaches that potentially make a substantial influence in this field, Based on boron-doped diamond electrodes, just a handful have been documented.^[11], MWCNTs modified glassy carbon^[12], Transfer of electrons between electrodes and electrically active substances is enhanced by the carbon nanotubes Inkjet-Printed CNT - Dimercaptosuccinic Acid-Capped Ferric Oxide Nanoparticles Modified Electrodes on Reduced Temperature Graphene Oxide Nanosheets for Single-Drop Trifluoperazine Determination [13] investigated the electrodes characteristics of direct electron transfer and electrocatalysis using cyclic voltammograms. Consider two different types of carbon nanotubes⁽¹⁴⁾, were deposited over a glass carbon electrode to create a carbon nanotube modified electrode using multi-walled carbon nanotubes (MWCNTs)⁽¹⁵⁾, The incorporation of CNTs into a polymer matrix containing redox mediators improved electronic and ionic transport in the polymer film.⁽¹⁶⁾, The current study intends to provide a simple, fast, sensitive, and cost-effective electrochemical technique using an unmodified

*Corresponding author e-mail: e_abd2012@yahoo.com

Receive Date: 14 July 2021, Revise Date: 31 August 2021, Accept Date: 04 October 2021

DOI: 10.21608/EJCHEM.2021.86193.4179

©2022 National Information and Documentation Center (NIDOC)

carbon electrode. As a polymer material, Polythionine (PTH) can effectively magnify signal detection as a polymer material due to its high conductivity [17], which was fabricated for analytical use when paired with MWCNTs.

2-Experimental

2.1.Apparatus

Voltammetric experiments were taken on 797 VA (Computrace Metrohm, Switzerland). A three-electrode stand with working electrodes (modified electrode & bare GC electrode), reference electrodes (Ag/AgCl with sat.KCl) and auxiliary electrode (platinum) are included. All investigations were carried out at a temperature of $25.0 \pm 0.5^\circ\text{C}$.

A pH meter was used to measure the pH of the solutions (digital HANNA, Portugal). To clean the working electrode, an ultrasonic cleaner is employed (model CD-4820, China)

2.2.Reagents

SDI IRAQ supplied trifluoperazine dihydrochloride ($\text{C}_{21}\text{H}_{24}\text{F}_3\text{N}_3\text{S}_2\text{HCl}$) Before They were crushed into powder, dissolved in (0.1N) HCL, filtered into a container, and then diluted to a certain amount for analysis. The stock solution (10^{-3} mol L⁻¹) was prepared with 0.1N HCL, and working solutions were created on a daily basis by dilution of the stock solutions. As a supporting electrolyte, (0.2 M) of each of K_2HPO_4 and KH_2PO_4 was mixed into the produced Phosphate buffer P.B.S, and Thionin (TH) was acquired from (Fluka).

TH was made using distilled water and kept in the dark at $+4^\circ\text{C}$. The remaining compounds were of analytical quality and were utilized without additional purification.

2.3.Preparation of the modified electrodes

It is necessary to polish and clean the electrode. Polishing and cleaning of the electrodes are accomplished by using emery paper and alumina oxide for different minutes (1.0, 0.3, 0.05 M) and repeatedly washing well with double distilled carefully to wash after using each volume of alumina to remove alumina and then being sonicated for 15 minutes with distilled water (DSW) to obtain a mirror-like finish. After washing, the GrE was electropolymerized on the MWCNTs/GrE in PBS containing (0.1 M) Thionin, at pH 7.0, using cyclic voltammetry with 30 cycles at a scan rate of (100 mVs^{-1}) potential ranging (-0.6 to +0.2 V), previously degassed with high-quality nitrogen for 5 minutes. A polymer deposit was generated on the GrE surface and rinsed with water. Peak potential values for the anodic and cathodic peaks were (-0.189 and -0.267 V), respectively

2.4.Application to pharmaceutical product

TFP was transferred to a 5.0 ml volumetric flask and filled to capacity with (0.1N) HCL. 500 microliters were properly transferred to a 5 mL volumetric flask and the volume was finished to the mark with pH 6.0 P.B.S. Quantitatively, 10 mL of the stock preparation containing 1×10^{-3} mol L⁻¹ of TRF was supplied to the electrolytic cell and (CV) was recorded, followed by subsequent additions of the stock preparation. Standard addition was used to ascertain the substances. The usual addition technique was used to identify the medications. Using a scan rate of (100 mVs^{-1}), the peak current at the working PTH/ MWCNTs/ GrE electrode was measured. By (CV) method and the concentrations of both drugs were calculated.

3. Results and discussion

3.1.Optimization of Tirflouprazin Conditions Using (CV)

A series of (CV) Voltammogram experiments for a solution containing (79.365×10^{-9})M TRF in P.B.S. pH 6.0 was carried out. The measurements were carried out while the working circumstances were constantly changing, and the best results were obtained by achieving either the biggest peak current or the best form voltammogram. a summary at the table.1

Table 1. Influence the variant conditions for (79.365×10^{-9}) M TRF in P.B.S (6.0) to give optimum peak resolution with higher current.

Optimum Condition	Values
Deposition potential	-0.9 V
Deposition time	60.0 S
Equilibration time	4.0 S
Voltage step	0.0080 V
Scan rate	0.1 VS^{-1}

3.2. Electropolymerization of Thionin at the MWCNTs/GrE surface

Figure 1 shows voltammograms of 0.1×10^{-3} mol.dm⁻³ Thionin in pH7.0 P.B.S at the MWCNTs/GrE. With a peak potential value of (-0.189 V), anodic and cathodic peaks were recorded. Then, after continued scanning, greater peaks were observed, demonstrating the film's continuous growth. These findings revealed that TH. was electropolymerized and deposited on the surface of MWCNTs/GrE. The generated current is steady after 30 cycles. As a result, the number of cycles is chosen as the optimal effect of the Gr E electrode conversion. In the modification procedure, 30 cycles were chosen. The electrochemical behavior of TH at

MWCNTs/GrE might be described as follows^[18] The TH was oxidized.

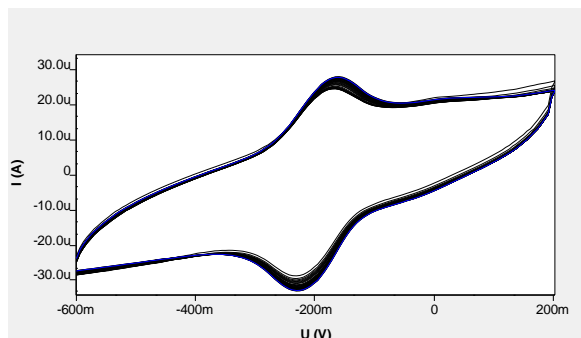


Fig. 1. Repeated cyclic voltammograms of 0.1×10^{-3} mol. dm^{-3} TH in pH 7.0 P.B.S solution; terminal potential -0.6 V; starting potential 0.2 V; scan rate: 100 mVs^{-1} .

Considering the trifluoperazine structure (Scheme 1), it may be inferred that its electrochemical activity is defined by the core phenothiazine and the associated piperazine ligand. At Thionin in P.B.S at varied pH values, cyclic voltammetric responses of (79.365×10^{-5} M) TRF solution were documented at a scan rate of (100 mV s^{-1}) (Fig. 2).

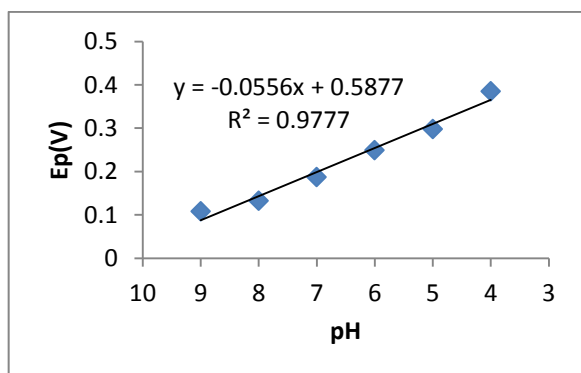


Figure 2 shows the effect of pH on TRF electrochemical oxidation at the PTH/MWCNT/GrE

For TRF analysis, however, the greatest catalytic peak current was observed at pH 6.0. By the findings of this investigation, pH = 6.0 was chosen as the optimal environment for TRF determination. As the pH of the solution rose, the anodic peak potentials shifted negatively, indicating that protons were involved in their electrodes reaction mechanisms. The relationship in Fig.2

The slope of the connection for TRF between oxidation potentials (E_p) and pH is -0.0556 mV/pH , showing that the electrochemical process includes a 2electron, 2proton transfer reaction^[19]

3.3 The Effect of Scan Rate

Scan rate exploration is possible beneficial in the research of electrochemical processes and kinetic properties of TRF. The cyclic voltammograms of TRF on PTH/MWCNT/CrE a variety of scan speeds

using P.B.S (pH 6.0) are shown in Figure 3 Up to a scan rate of 100 mVs^{-1} . With increased scan rates, the oxidation peak potential shifts toward a higher positive potential, demonstrating the electrochemical reaction's kinetic constraint. These findings indicate that at high enough overpotential, Instead than being surface controlled, the mechanism is diffusion. The inset depicts the relationship between scan rate and peak anodic currents. The linear regression equation raised the oxidation peak currents linearly as follows:

$$\text{TRF} = y = -0.2369x + 0.0851 (R^2=0.9496)$$

The drug's behavior suggests that the response is diffusion-controlled

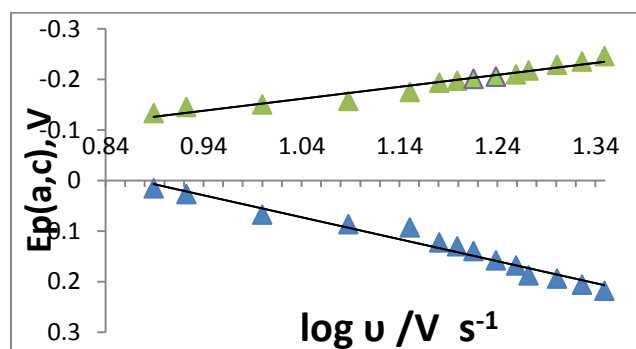


Fig. 3. liner relationship scan rate and anodic TRF peak currents

3.4. Calibration curve

The (CV) curves of the modified electrode poly/nanocomposite film in the presence of TRF in P.B.S are presented in Fig.4

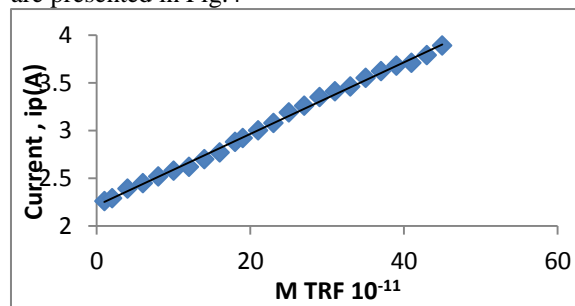


Fig.4. CV TRF on PTH/MWCNTs/GrE calibration plots of TRF.

$IP (\text{A}) = 0.4999 \times 10^{-11} - 54.327 \times 10^{-11} (\text{mol L}^{-1})$ was the linear regression equation.

having a correlation coefficient of 0.9957

3.4. Stability Analysis

Investigate the stability of modified electrodes (PTH/MWCNT/graphite electrodes) by adding a concentration ($0.5 \times 10^{-7} \text{ mM}$) of TRF and measuring it using voltammetry, as shown in figure (5). The stability was quite good, as it was preserved for 92 percent after being contentiously utilized for 81

assays, and modifying the electrode surface correspondingly seems to have been beneficial.

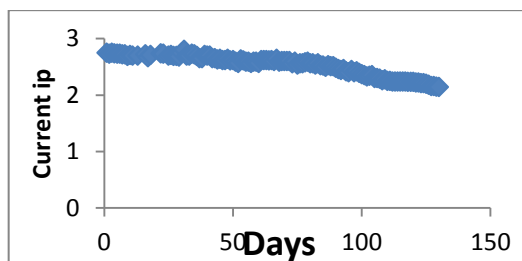


Fig. 5 . Stability of TRF

3.5. Analytical applications

The PTH/MWNTs/GrE modified electrode was used to determine TRF in tablets under optimal circumstances. The process for processing and identification was the such as detailed in the experimental section. Table 2 shows the analytical data, and the recovery rate was 97.831-100.5 percent. It was consistent with the results of the Pharmacopoeia technique (TRF UV absorbance at 256 nm in a 1:20 HCl solution)

TABLE.2 Determination of TRF in drug tablet (n=6)

Sam ple	Labele d (mg.ml ⁻¹)	Found(mg.m l ⁻¹)	R.S. D	Recover y(%)	UV metho d (mg/m L ⁻¹)
1	5	4.985	1.22	99.70	5.009
2	5	4.9778	1.28	99.557	5.007
3	5	4.9351	1.26	98	5.003
4	5	4.9133	1.33	103.5	5.008
5	5	4.946	1.29	100.5	5.005

was used as the quantitative criteria^[20], demonstrating that the offered approaches may be employed for routine analysis in an efficient manner.

4. Conclusions

Thionin has been polymerized on the MWCNTs surface, functionalizing Graphite electrodes using an electrochemical technique to create an electrochemical sensor, PTH/MWNTs/GrE. The resulting electrode was activated for surface adsorption as well as electrocatalysis TRF oxidation. Through the use of a negative poly-Thionin film, the nanocomposite film may efficiently attract TRF cations. This electrode proved sensitive, repeatable, and stable, and it may be utilized as an electrochemical sensor for routine total TRF detection in real samples.

5- Reference

[1] Prashanth, K. N., Swamy, N., & Basavaiah, K.

(2014). Extraction-free ion-pair methods for the assay of trifluoperazine dihydrochloride in bulk drug, tablets, and spiked human urine using three sulfonphthalein dyes. *Journal of Applied Spectroscopy*, 81(5), 893-902.

[2] Holroyd, S., & Seward, R. L. (1999).

Psychotropic drugs in acute intermittent porphyria. *Clinical Pharmacology & Therapeutics*, 66(3), 323-325.

[3] Ott, C. A. (2018). Treatment of anxiety disorders in patients with comorbid bipolar disorder. *Mental Health Clinician*, 8(6), 256-263.

[4] Basavaiah, K., & Krishnamurthy, G. (1998). Titrimetric micro determination of some phenothiazine neuroleptics with potassium hexacyanoferrate (III). *Talanta*, 47(1), 59-66.

[5] Madej, K., Kala, M., & Woźniakiewicz, M. (2005). LC and non-aqueous CE determination of phenothiazines in autopsy samples. *Chromatographia*, 62(9), 533-538.

[6] Patel, S., Patel, N. J., & Patel, S. A. (2009). Simultaneous spectrophotometric estimation of imipramine hydrochloride and chlordiazepoxide in tablets. *Indian journal of pharmaceutical sciences*, 71(4), 468.

[7] Prashanth, K. N., Swamy, N., & Basavaiah, K. (2014). Extraction-free ion-pair methods for the assay of trifluoperazine dihydrochloride in bulk drug, tablets, and spiked human urine using three sulfonphthalein dyes. *Journal of Applied Spectroscopy*, 81(5), 893-902.

[8] Maślanka, A., & Krzek, J. (2005). Densitometric high performance thin-layer chromatography identification and quantitative analysis of psychotropic drugs. *Journal of AOAC International*, 88(1), 70-79.

[9] El-Gindy, A., El-Zeany, B., Awad, T., & Shabana, M. M. (2002). Derivative spectrophotometric, thin layer chromatographic-densitometric and high performance liquid chromatographic determination of trifluoperazine hydrochloride in presence of its hydrogen peroxide induced-degradation product. *Journal of pharmaceutical and biomedical analysis*, 27(1-2), 9-18.

[10] Jin, G., Huang, F., Li, W., Yu, S., Zhang, S., & Kong, J. (2008). Sensitive detection of trifluoperazine using a poly-ABSA/SWNTs film-modified glassy carbon electrode. *Talanta*, 74(4), 815-820.

[11] Jin, G., Huang, F., Li, W., Yu, S., Zhang, S., & Kong, J. (2008). Sensitive detection of trifluoperazine using a poly-ABSA/SWNTs film-modified glassy carbon electrode. *Talanta*, 74(4), 815-820.

[12] Dogan-Topal, B. (2013). Electrooxidative behavior and determination of trifluoperazine at

- multiwalled carbon nanotube-modified glassy carbon electrode. *Journal of Solid State Electrochemistry*, 17(4), 1059-1066.
- [13] Ognjanovic, M., Stankovic, D. M., Jovic, M., Krstic, M. P., Lesch, A., Girault, H. H., & Antic, B. (2020). Inkjet-Printed Carbon Nanotube Electrodes Modified with Dimercaptosuccinic Acid-Capped Fe₃O₄ Nanoparticles on Reduced Graphene Oxide Nanosheets for Single-Drop Determination of Trifluoperazine. *ACS Applied Nano Materials*, 3(5), 4654-4662.
- [14] Zheng, W., Zhou, H. M., Zheng, Y. F., & Wang, N. (2008). A comparative study on electrochemistry of laccase at two kinds of carbon nanotubes and its application for biofuel cell. *Chemical Physics Letters*, 457(4-6), 381-385.
- [15] Wu, F. H., Zhao, G. C., & Wei, X. W. (2002). Electrocatalytic oxidation of nitric oxide at multi-walled carbon nanotubes modified electrode. *Electrochemistry Communications*, 4(9), 690-694.
- [16] Li, J., Yao, Y., & Shiu, K. K. (2010). Layer-by-layer assembly of Prussian blue and carbon nanotube composites with poly (diallyldimethylammonium chloride) for the sensitive detection of hydrogen peroxide. *Analytical Sciences*, 26(4), 431-435.
- [17] Yang, T., Hu, Y.W., Li, W.J. and Jiao, K., 2011. Single stranded DNA-guided electropolymerization of polythionine nanostrip to the sensing of H₂O₂. *Colloids and Surfaces B-Biointerfaces*, 83, pp.179–182.
- [18] Salimi, A., Noorbakhsh, A., & Soltanian, S. (2006). Electroless deposition of thionin onto glassy carbon electrode modified with single wall and multiwall carbon nanotubes: improvement of the electrochemical reversibility and stability. *Electroanalysis: An International Journal Devoted to Fundamental and Practical Aspects of Electroanalysis*, 18(7), 703-711.
- [19] Ensafi, A. A., Ahmadi, N., Rezaei, B., & Abarghoui, M. M. (2015). A new electrochemical sensor for the simultaneous determination of acetaminophen and codeine based on porous silicon/palladium nanostructure. *Talanta*, 134, 745-753.
- [20] Pharmacopoeia, N. C. O. C. (2005). Pharmacopoeia of the People's Republic of China. *Beijing, China: People's Medical Publishing House*.