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Indirect Determination of Diclofenac Sodium through Its Interaction with the Aniline Oxidation Peak

Rana H. Al-Hyali[1]*, Amer Th. Al-Taee[1]

[1] Department of Chemistry /College of Science/University of Mosul, Iraq

Abstract: The voltammetric measurement of diclofenac sodium was investigated using an electrochemical sensor consisting of a glassy carbon electrode (GCE) modified with aniline conducting polymer and a differential pulse voltammetric (DPV) method. Diclofenac sodium behavior was investigated through its interaction with poly aniline oxidation peak; due to diclofenac sodium adsorption on the surface of the bare glassy carbon electrode, it gives an unstable oxidation peak at 0.4V versus Ag/AgCl.saturated.KCl. We attempted to solve this issue by plating the electrode with aniline and monitoring the interaction peak between diclofenac sodium and aniline oxidation peak. The impact of pH was investigated, optimum conditions were tested, and calibration curves were constructed. Glassy carbon/poly aniline electrode (GC/PAn) results in two straight lines with R^2 values of 0.9812 and 0.9772 when current is plotted against concentrations at low concentration and high concentration, respectively. The limit of detection (LOD) and limit of quantification (LOQ) were 0.1282×10^{-7} M and 0.4275×10^{-7} M, respectively. Compared with other sensors, it was observed that the proposed electrochemical sensor has a wider linear range and lower detection limit. The suggested method was applied successfully for quantitating diclofenac sodium in tablet formulation supplied by Samaraa Drugs Industry (SDI)with accepted results of recovery of diclofenac sodium.

Keywords: Diclofenac sodium, polyaniline, differential pulse voltammetry, modified glassy carbon electrode.

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***Corresponding author.** E-mail: ranahasan@uomosul.edu.iq

1. INTRODUCTION

Non-steroidal anti-inflammatory medication diclofenac sodium (figure 1), sodium [o-(2,6-dichloroanilino) phenyl] acetate, has potent analgesic and anti-fever characteristics. (1,2). Commonly used to treat inflammatory conditions such as musculoskeletal injuries, non-articular rheumatism, rheumatoid arthritis, ankylosing spondylitis, and osteoarthritis (3-5). In veterinary medicine, it can also be used to treat animals that produce food (6).

Voltaren, cataflam, dyloject, cambia, zipsor, and zorvolex are the brand names for diclofenac. It has been effective in treatment as it causes less damage to the liver, stomach, kidneys, and heart (7).

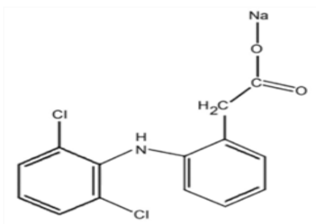


Figure 1. Structure of diclofenac sodium.

Regarding quality assurance, diclofenac is effective with minimal side effects (8). Several analytical methods have been reported to determine diclofenac in pharmaceuticals, for example, chromatography (9,10), capillary electrophoresis (11), differential scanning calorimetry (12), gravimetry (13), spectrometry (14,15) and fluorometric (16). The Brazilian Pharmacopoeia's standard method for determining diclofenac uses high-performance liquid chromatography technology (17).

Electrochemical methods have many advantages compared to other methods; they are characterized by high sensitivity, simplicity, low costs, selectivity, and low consumption as well. Therefore, it has been widely used to determine many medicinal compounds (18, 19). The bare electrodes have low selectivity and sensitivity upon electrically active compounds; the problems arise from the adsorption of the drug on the electrode surface, which causes poisoning or passivating of the electrode surface and loss of the electrode activity. To overcome these problems, the composites are designed by joining catalytic materials with exceptional conductive materials to modify the electrode surface(20-22). The applications of modified electrodes, especially carbon electrodes, have greatly progressed in the electrochemical study of biological compounds (23–25).

Many modified carbon paste electrodes (CPEs) have been described for measuring diclofenac in physiological samples and formulations of pharmaceuticals (26, 27).

Tyrosine was used to create a carbon paste electrode while investigating the oxidative behavior of diclofenac sodium (28). Cormusch et al. developed different electrodes sensitive to diclofenac by fusing the ion-pair complex formed between diclofenac, butyl rhodamine, and diclofenac with the dye safranine in a matrix of graphite (29–33). Diclofenac was electro-oxidized at a platinum electrode in 0.1M $TBAClO_4$/acetonitrile solution using a potentiometric sensor based on doped polypyrrole films (34).

Chitosan's capacity for adsorption and film formation and the significant catalytic characteristics of multi-walled carbon nanotubes (MWCNTs) were used to create an effective and straightforward sensor for detecting diclofenac sodium(35). A produced polymer with a diclofenac imprint was used to create a carbon paste electrode to develop a selective electrochemical sensor for diclofenac (MIP) (36).

A new electrochemical sensor was also developed to determine diclofenac sodium using titanium dioxide saturated with ruthenium (37). A modified gold electrode for determination of diclofenac using gold nanoparticles (AuNPs) and multi-walled functional carbon nanotubes (f-MWCNTs) / graphene oxide (GO) composite film reported by Farzaneh Nasiri and co-workers (38).

In this study, the electrochemical behavior of diclofenac was examined using a glassy carbon bare electrode, and it was modified by the electrochemical polymerization of aniline. The sensor's response signal has significantly improved, which improves the electrochemical detection of diclofenac by interacting with the peak of polyaniline oxidation.

2. EXPERIMENTAL

2.1 Materials and Techniques

2.2. Instruments

The Swiss company Metrohm provided a computrace 797VA analyzer, which was used in conjunction with a three electrodes cell made up of an auxiliary electrode, 2mm diameter Pt-wire, reference electrode, Ag/AgCl/saturated KCl, and the working electrode, 2mm diameter GCE, as to perform the voltammetric measurements. The HANNA Company, Portugal, provided a (pH211) pH meter for the pH measurements.

2.3. Reagents and Chemicals

Samaraa Drugs Industry (SDI) supplied diclofenac sodium. To make a solution of phosphate buffer pH7, 1.5 ml (0.2M) of KH_2PO_4 and 30.5 ml of (0.2 M) K_2HPO_4 were combined, and the volume was then increased to 100 ml in a volumetric vial.

2.4. Procedure

The voltammetric cell was occupied with 10 ml of pH7, dissolved oxygen was removed by Nitrogen gas passed through it for five minutes before the measurements, the voltammograms were then recorded for a series of additions of a stock diclofenac sodium, and curves of calibration were created.

2.5. Pretreatment of Glassy Carbon Electrode

GCE was cleaned and ultrasonically sonicated in water for five minutes after being polished by aluminum oxide powder (0.05 µm) (39,40).

2.6. Electrochemical Polymerization of Aniline on GCE

The electrochemical polymerization of 0.1 M pure aniline in 10 ml of 0.5 M H_2SO_4 using cyclic voltammetric technique (CV) was used to create the poly aniline film under the best optimum conditions (Fig. 2) (41). The potential was scanned between (-0.1 – 0.9) for 5 cycles using scan rate = 0.02 V/s. Three reversible oxidation peaks are shown on the voltammogram: one at potential Ep1=0.204, second at Ep2=0.478, and third at Ep3=0.787.

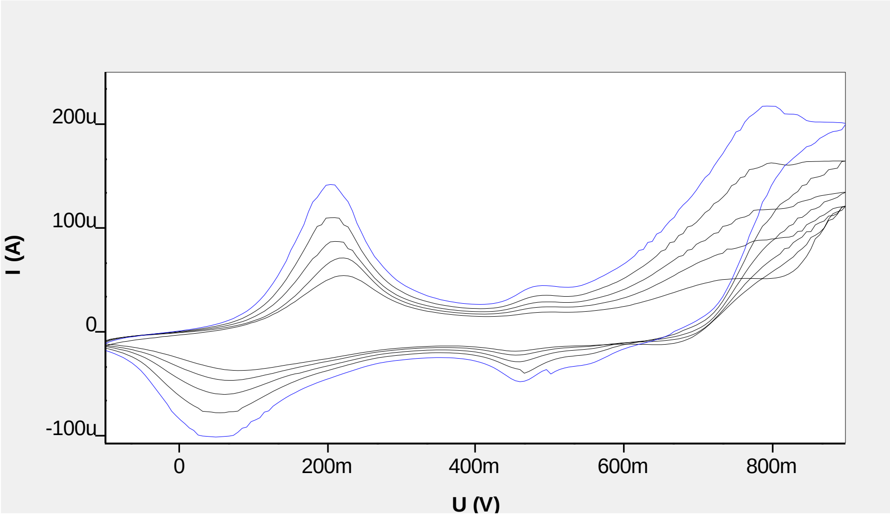


Figure 2. Electrochemical polymerization of aniline.

2 .7. Determination of Diclofenac Sodium in Pharmaceutical Dose Form:

Five tablets contents of the drug are crushed, and then a fine weight fraction equal to one tablet is dissolved in (10 ml) ethanol.

3. RESULTS AND DISCUSSION

3.1. Effect of Varying pH Levels:

Using 14.492×10^{-6} M of diclofenac sodium on GCE/PAn, various pHs were used to study the impact of pH on the diclofenac sodium oxidation peak potential (Ep) and peak current (Ip) (5-7). According to the results (Table 1), the larger diffusion current was found at pH 5, although a distortion of peak form was found at pH =4. The Plot of Ep versus pH, Figure 3, shows a straight line with a -0.064 value of intercept, which is close to the theoretical value determined by Hillson, which means the oxidation process involved one electron reduction (42).

Table 1. pH effect on the aniline oxidation peak

PH	Ep(V)	Ip(µA)
5	0.43	148
5.5	0.4	145
6	0.382	94.4
6.5	0.34	12.2
7	0.3	11

At pH=4 peak distortion was observed.

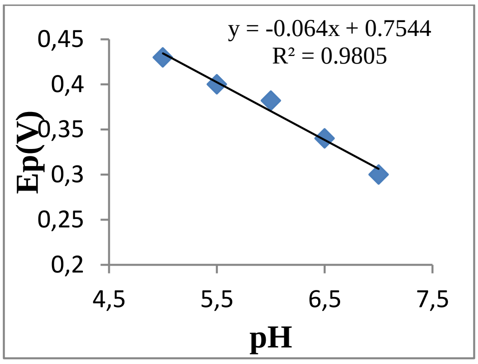


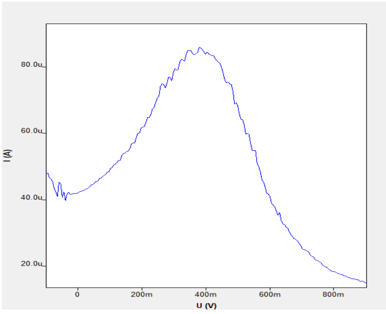
Figure 3. Effect of different pHs on the aniline oxidation peak

3.2. Optimum Conditions

Using 9.708×10^{-6} M aniline in phosphate buffer (pH 5) with GCE/PAn, optimum circumstances were studied to maximize the sensitivity of the sensor. The results are provided in table 2 provided the results, Figure 4 shows before and after optimum conditions voltammograms.

Table 2: Aniline optimum conditions in pH5 for aniline oxidation peak

Condition Values	Parameters
6×10^{-1}	Deposition Potential (V)
0.3×10^{2}	Deposition Time (s)
0.1×10^{2}	Equilibration Time(s)
7×10^{-2}	Pulse Amplitude(V)
3×10^{-2}	Pulse Time(s)
5×10^{-3}	Voltage Step(V)
4×10^{-1}	Voltage Step Time(s)
125×10^{-4}	Sweep Rate(V/s)


(a)

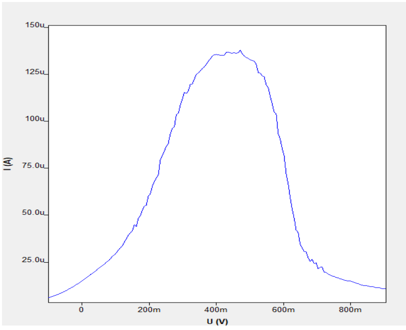

(b)

Figure 4: Differential pulse voltammograms of aniline in pH5 at GCE/Polyaniline
a-Before optimum conditions b-After optimum conditions

3.3. Aniline oxidation Peak stability at GCE/PAn

Aniline oxidation peak stability was tested. Under the aforementioned optimum circumstances, differential pulse voltammograms were acquired at various intervals. Table 3 data makes it clear that the current of the oxidation peak has remained constant throughout the measurement period.

Table 3: Aniline oxidation peak stability at GCE.

Time (minute)	Ip (μ A)
5	106
10	106
15	108
20	111
25	109
30	109
35	105
40	106
45	106
50	105
S. D	±2.02484567

3.4. Calibration Curve

The indirect determination of diclofenac sodium was done through the decrease in poly aniline oxidation peak at 0.4V with the addition of diclofenac. In order to produce the calibration curve, a series addition of 10^{-3} molar standard diclofenac sodium solution were added, and the voltammograms for each addition were recorded under the previously optimum conditions. Peak current is plotted against concentrations, and the findings show two straight lines, one at low concentrations (0.489 -5.836) $\times 10^{-6}$ molar with R^2 values of 0.9812 and second at higher concentrations (7.774-17.647) $\times 10^{-6}$ molar with R^2 values of 0.9772. The limit of determination was 0.1282×10^{-7} M (LOD=$3\sigma_{\Delta Ip}$ ×low Conc./ $\bar{x}_{\Delta ip}$) and the limit of quantitation was 0.4275×10^{-7} M (LOQ=$10\sigma\Delta Ip$ ×low Conc./ $\bar{x}_{\Delta ip}$)

Table 4: Sequence additions of diclofenac sodium in low concentration range (0.489-5.836) $\times 10^{-6}$ M using GC/PAn modified electrode

Concentration of poly aniline $\times 10^{-6}$ (M)	Ip(μA)
1.794	**139**
Concentration of diclofenac sodium $\times 10^{-6}$ (M)	**Ip(μA)**
0.489	132
0.978	129
1.955	127
2.929	125
3.902	123
4.873	121
5.836	119

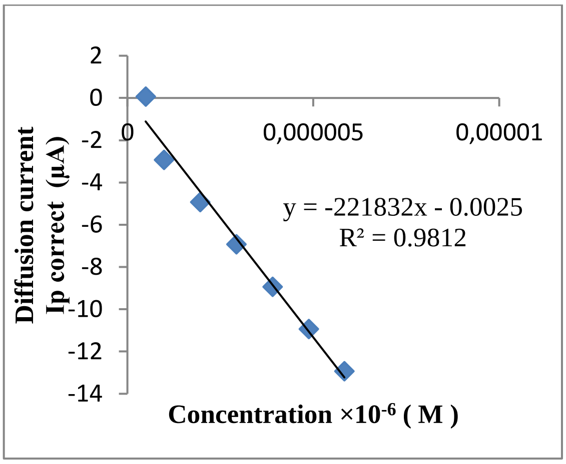


Figure 5. Calibration curve of diclofenac sodium at low concentration.

Table 5: Sequence additions of diclofenac sodium in high concentration range (7.774 -17.647) $\times 10^{-6}$ M using GC/PAn modified electrode.

Cocentration$\times 10^{-6}$ M	Ip (μA)
7.774	116
8.737	115
9.689	113
11.605	112
13.514	110
17.647	107

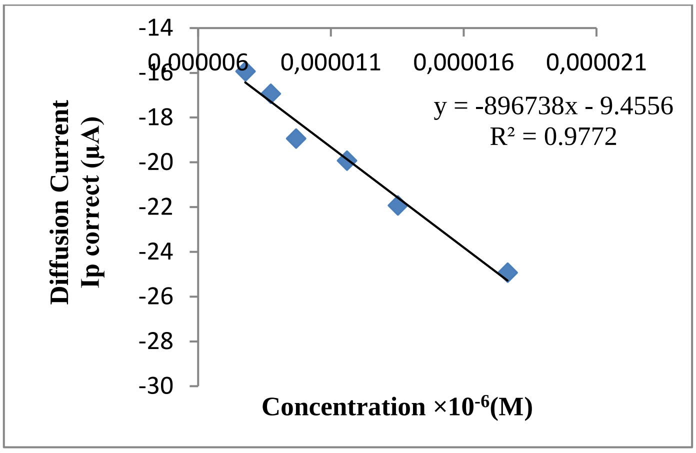


Figure 6: Calibration curve of diclofenac sodium at high concentration

Table 6: Determination of diclofenac sodium in pharmaceutical formulation tablets.

Taken Conc.$\times 10^{-6}$ (M)	Found Conc. $\times 10^{6}$(M)	Ip (Tablet) (µA)	Ip (Pure) (µA)	% Recovery	% Error
0.9794	0.9946	131	129	101.5	-1.55
1.9569	1.9877	129	127	101.5	-1.57
7.7821	8.0504	120	116	103.4	-3.44
8.7463	8.8984	117	115	101.7	-1.73
13.5397	13.7858	112	110	101.8	-1.81
17.341	17.8272	110	107	102.8	-2.80

The results show a good agreement between the taken (concentration of diclofenac sodium in tablets) and found (concentration of diclofenac sodium measured) concentrations with a good recovery obtained.

4. CONCLUSION

The glassy carbon electrode suffers from losing activity due to the adsorption of diclofenac sodium on its surface; the electrochemical plating of aniline on the bare glassy carbon electrode caused an enhancement and stabilization of electrode response, The indirect determination of diclofenac sodium through its interaction with aniline oxidation peak increased the sensitivity and stability of developed detector.

The developed electrode was applied to estimate diclofenac sodium in pharmaceutical formulations with acceptable percentage recoveries.

Table 7: Comparison of the proposed method with the methods mentioned in the literature.

Electrode	Linear Range (µM)	Detecton Limit (M)	References
Polyaniline/Reduced Graphene Oxide Nano-composite	16.9–270	3.71×10^{-6}	(36)
IL - modified CNT paste electrode	0.5-300	0.2×10^{-6}	(43)
F - MWCNTs / Au - PtNPs / Au	0.5–100	0.3×10^{-6}	(44)
f-MWCNTs /GCE	2–15	0.1×10^{-6}	(45)
PANI / rGO molecular imprinter	17–270	3.7×10^{-6}	(47)
Zinc / Fe-PANI / CPE	1–30	0.235×10^{-6}	(48)
GC / PAn	0.489-17.647	0.1282×10^{-7}	present work

The comparison of the suggested method with the methods reported in the literature shows that the present work has a better limit of detection with good linearity.

5. ACKNOWLEDGMENTS

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