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Electrochemical Determination of Tolfenamic Acid in Bulk, Tablets and Urine

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Abstract- A simple, precise, accurate and inexpensive voltammetric method was developed for the quantitative determination of tolfenamic acid at modified glassy carbon electrode in phosphate buffer of pH 7.2. Several factors such as type of buffer, type of surfactant; scan rate and accumulation time were studied to obtain the optimum conditions for the determination of tolfenamic acid. The proposed method shows linearity in concentration range of 6.0×10^{-7}-6.0×10^{-6} mol L^{-1} with mean percentage recovery of 101.2±1.99. The limits of detection and quantification were 1.43×10^{-7} mol L^{-1} and 4.34×10^{-7} mol L^{-1}, respectively. The proposed voltammetric method was successfully applied to determine tolfenamic acid in pharmaceutical formulations and human urine. The results of the proposed method were statistically compared with those of a reported method and showed no significant difference. Thus, it can be used as quality control for this drug in laboratories.

Keywords- Tolfenamic acid, Voltammetry, Modified electrode, Pharmaceutical analysis

1. INTRODUCTION

Tolfenamic acid, N-(2-methyl-3-chlorophenyl) anthranilic acid [1], is an anthranilic acid derivative, which is related to mefenamic acid, and is a nonsteroidal anti-inflammatory drug

(NSAID) used in the treatment of acute attacks of migraine. It is also given for the relief of mild-to-moderate pain in disorders such as dysmenorrhea, rheumatoid arthritis or osteoarthritis [2].

Literature survey reveals that several different analytical techniques have been developed for the determination of tolfenamic acid including spectrofluorimetric methods [3,4], thin layer chromatographic methods [5], high performance liquid chromatographic methods [5-16], and gas chromatographic methods [17-19].

Carbon based electrodes are currently in widespread use in electroanalytical chemistry, because of their broad potential window, low cost, rich surface chemistry, low background current and chemical inertness. Glassy carbon electrode (GCE) is a class of non-graphitizing carbon that is widely used as an electrode material in electrochemistry. It is also known as vitreous carbon. GCE is used very commonly because of its excellent mechanical and electrical properties, impermeability to gases, and extremely low porosity [20-25].

Polymer modified electrodes have received great attention in recent years, due to their unique physical and chemical properties, such as good reproducibility and homogeneity, high stability and selectivity and strong adherence to electrode surface. These unique characteristics make them advantageous in the fields of batteries [26], supercapacitors [27], and sensors [28].

Electropolymerization is a good choice for the preparation of polymer films. Para-aminobenzoic acid (p-ABA), a non-protein amino acid, is widely distributed in nature [23]. The obtained film has been used for electrochemical analysis [29,30].

Electrochemical analysis was quantitatively applied for the determination of pharmaceuticals in drug substances, dosage forms, human plasma, serum and urine, as the repaglinide [31], metformin hydrochloride [32], entacapone [33], gemifloxacin mesylate [34], moexipril hydrochloride [35] and simultaneous determination of indomethacin, acemethacin, piroxicam, tenoxicam [36], paracetamol, furosemide, dipyrone, cefazolin and dexamethasone [37], paracetamol, ascorbic acid and codeine [38].

In this study tolfenamic acid was determined using differential pulse voltammetry (DPV) at modified para-aminobenzoic acid glassy carbon electrode in bulk, pharmaceutical formulations and human urine.

2. EXPERIMENTAL

2.1. Pure and market samples

Tolfenamic acid was kindly supplied by Pharmakon Pharmaceuticals Company, Alexandria, Egypt. Its purity was 99.4% as stated by the supplier. Tolfenam tablets (batch no. 023, 200 mg of tolfenamic acid/tablet) were purchased from Pharmakon Pharmaceuticals Company, Egypt.

2.2. Standard solutions

Standard solutions of tolfenamic acid were prepared in acetonitrile: methanol mixture (60:40 v/v) to prepare 0.01 mol L^{-1} solution**.**

2.3. Chemicals and reagents

All reagents were of analytical grade and solvents were of spectroscopic grade. Distilled water was used throughout the work.

- Methanol, HPLC grade (Fischer Chemical, UK).
- Acetonitrile, HPLC grade (Fischer Chemical, UK).
- Sodium hydroxide (Qualikems fine chemical Pvt. Ltd).
- p-aminobenzoic acid (Sigma-Aldrich, Germany).
- Potassium dihydrogen phosphate (El Nasr Pharmaceutical Chemicals, Egypt).
- Phosphoric acid (Sigma-Aldrich, Germany).
- Acetic acid (Loba Chemie Co., India).
- Boric acid (Sigma-Aldrich)
- Britton-Robinson (BR) buffer was prepared by mixing 0.04 mol L^{-1} of phosphoric acid, 0.04 mol L^{-1} of acetic acid and 0.04 mol L^{-1} of boric acid. Buffer solutions were adjusted with the appropriate amount of 0.2 mol L^{-1} sodium hydroxide to get the desired pH values in the range of 7-11 [39].
- Phosphate buffer was prepared by adding 34.7 mL of 0.2 mol L^{-1} NaOH to 50 mL of 0.2 mol L^{-1} potassium dihydrogen phosphate and complete to 200 mL with distilled water [39].

2.4. Instrument

All voltammetric measurements were carried out using a computer-driven analytical electrochemical workstation (model AEW2) with ECProg3 electrochemistry software (Sycopel, England) in combination with a three-electrode configured C-3 stand. The reference electrode Ag/AgCl/ 3 mol L^{-1} NaCl (MW-2063, BAS model) and a platinum wire counter electrode (MW-1032, BAS model). A digital pH-meter (Jenway pH meter, UK) with combined glass electrode was used to carry out the pH measurements. All electrochemical experiments were performed at an ambient temperature of 25 °C.

2.5. Procedures

2.5.1. Preparation of working electrodes

The modified para-aminobenzoic acid glassy carbon electrode (MGCE) was prepared by immersing GCE in 0.01 mol L^{-1} solution of para-aminobenzoic acid and sweeping between -1300 to 1500 mV at 250 mV/s for 80 cycles [30].

2.5.2. Linearity

Aliquots of working standard tolfenamic acid solution (0.001 mol L^{-1}) were added to the electrolytic cell containing 5 mL of phosphate buffer of pH 7.2, the solutions were stirred for 5 s at open circuit conditions, voltammetric analyses were carried out using DPV and voltammograms were recorded at a scan rate 10 mV s^{-1}. Calibration curve was constructed by plotting anodic peak current against drug concentration.

2.5.3. Accuracy and precision

Three different concentrations covering the linearity range of tolfenamic acid were analyzed in triplicates within the same day for intraday and for three successive days for interday using the procedure detailed under "Linearity". Accuracy and precision were calculated.

2.5.4 Application to pharmaceutical formulations

Ten Tolfenam® tablets were accurately weighed, powdered and mixed well. A portion of the powder equivalent to 26.17 mg tolfenamic acid was introduced into a 100 mL volumetric flask containing 20 mL of acetonitrile/methanol mixture (60:40 v/v) and the flask was sonicated for 10 min, then completed to the volume with same mixture then filtered to obtain a solution claimed to contain 0.001 mol L^{-1} of tolfenamic acid. DPV method was applied using the procedure detailed under "Linearity". The drug concentrations were calculated from the corresponding regression equation. The proposed methods were further validated by using the standard addition method.

2.5.5. Analysis of tolfenamic acid in urine

For the analysis of tolfenamic acid in urine, 1 mL of urine was mixed with 9 mL phosphate buffer pH 7.2, and then successive additions of 0.001 mol L^{-1} tolfenamic acid solution were added to the voltammetric cell containing 5 mL of the previously diluted urine and the procedure detailed under "Linearity" was repeated.

3. RESULTS AND DISCUSSION

3.1. Electrochemical oxidation of tolfenamic acid

The reversibility of the oxidation process of tolfenamic acid at GCE was studied by the cyclic voltammetric technique in BR buffer of pH 8, the cyclic voltammogram showed one well defined anodic peak (anodic peak current (I)=27.905 µA at 0.683 V), and the reverse scan showed no cathodic peak indicating that tolfenamic acid oxidation is an irreversible process. The proposed oxidation mechanism of tolfenamic acid is shown in Fig. 1.

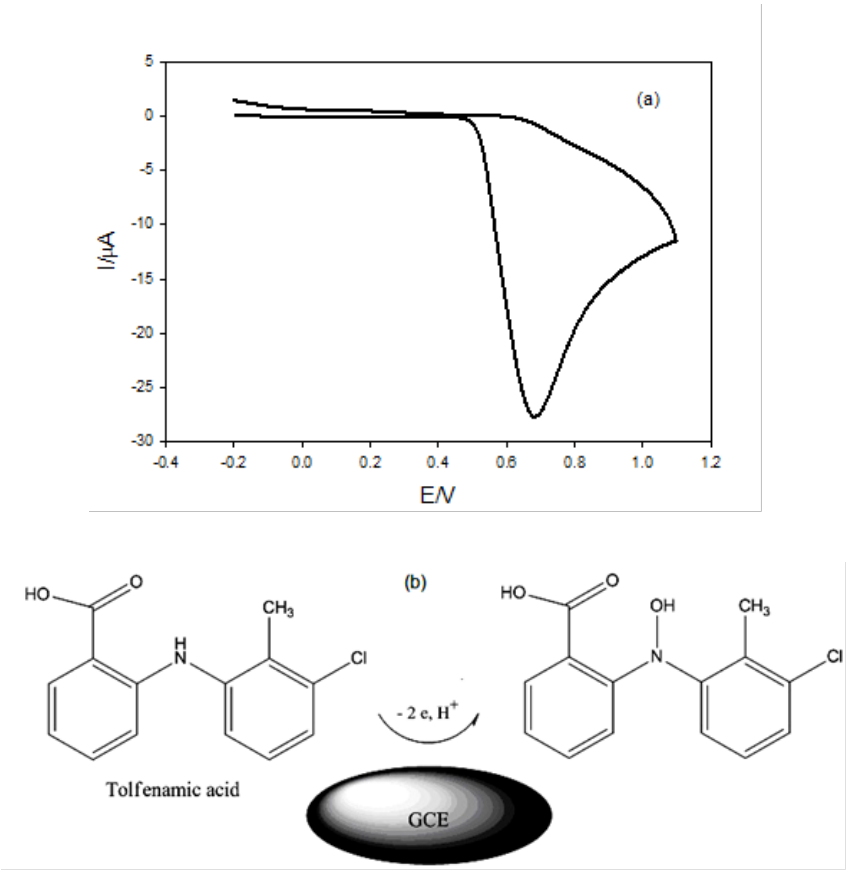

Fig. 1. Cyclic voltammogram of 0.001 mol L^{-1} tolfenamic acid in BR buffer of pH 8.0 at GCE, scan rate of 100 mV s^{-1} (a); The oxidation mechanism of tolfenamic acid at GCE (b)

3.2. Optimization of experimental conditions

3.2.1. Effect of pH

Cyclic voltammetry using scan rate of 100 mV s^{-1} at GCE was used to investigate the effect of pH on the oxidation of tolfenamic acid. 4.5 mL of BR buffer in the pH range of 7-11, 0.5 mL of 0.01 mol L^{-1} tolfenamic acid standard solution were added to the electrochemical cell, and the respective voltammetric response was recorded. This experiment was repeated using phosphate buffer to obtain the optimum buffer with the optimum pH value.

Figs 2a and 3a show that the anodic peak potential (E) was shifted negatively by increasing pH indicating that tolfenamic acid oxidation at GCE is pH dependant and those protons are involved in the reaction. Figs 2c and 3c show that higher peak current was achieved as 27.905 µA incase of BR buffer of pH 8.0 and 28.36 µA of Phosphate buffer of pH 7.2. Therefore, Phosphate buffer of pH 7.2 was used as the optimum buffer in this study.
Figs 2b and 3b show the linear relations between pH and peak potential (E) observed in the pH range (7-11) in case of BR buffer, and (6.8-8.0) for phosphate buffer with the following regression equations: E(V)=-0.0266 pH+0.8968, R^2=0.9947 and E(V)=-0.025 pH+0.870,

R^2=0.9999 for BR and phosphate buffers, respectively. Applying Nernst equation using the formula ΔEp/ΔpH (Slope)=0.059x/n [40], where x and n is the number of protons and electrons involved in the reaction, respectively. It can be concluded that number of electrons transferred is equal to the half number of protons, thus n=2 and x=1.

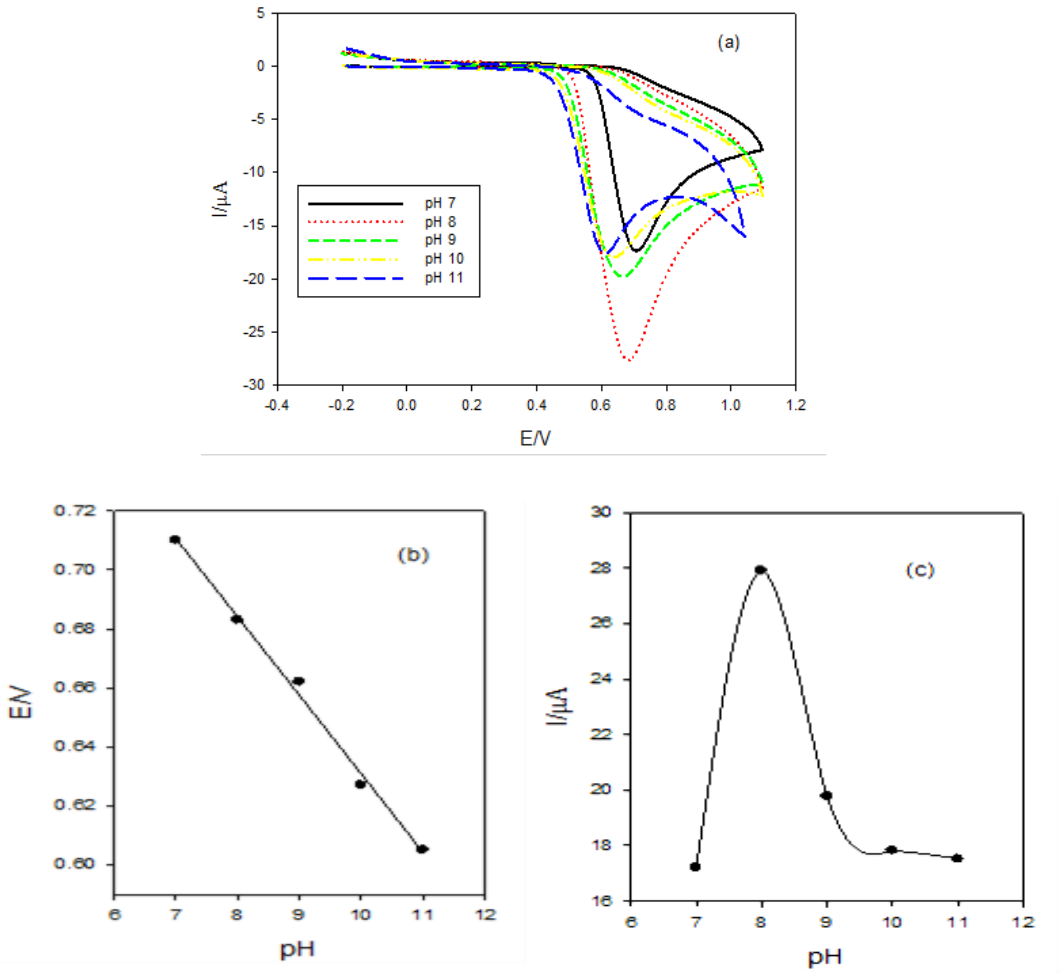

Fig. 2. Cyclic voltammogram of 0.001 mol L^{-1} tolfenamic acid in BR buffer (a) plot of the anodic peak potential as a function of pH; (b) and plot of the anodic peak current as a function of pH; (c) at GCE at scan rate of 100 mV s^{-1}

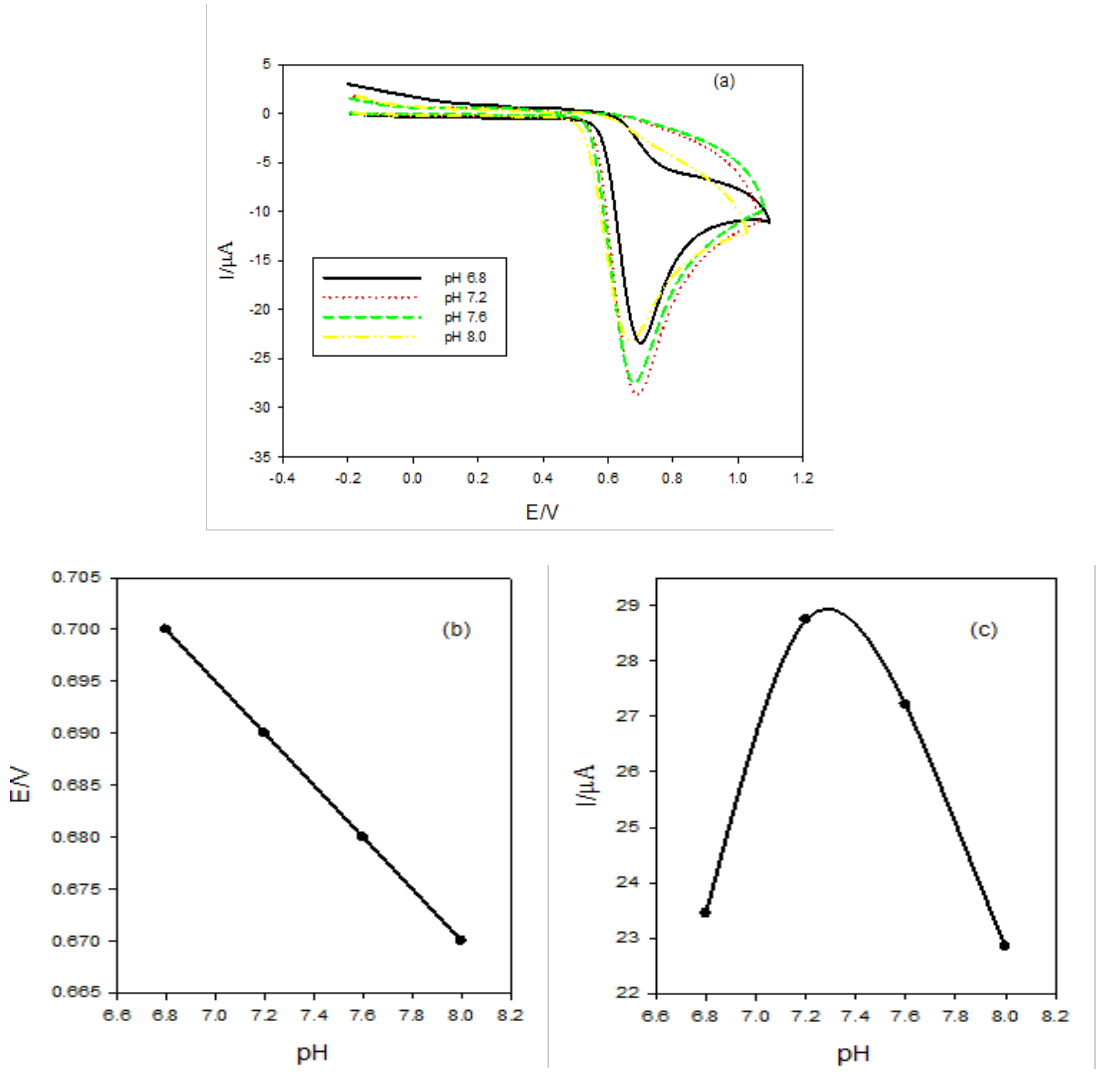

Fig. 3. Cyclic voltammogram of 0.001 mol L^{-1} tolfenamic acid in Phosphate buffer (a), plot of the anodic peak potential as a function of pH; (b) and plot of the anodic peak current as a function of pH; (c) at GCE at scan rate of 100 mV s^{-1}

3.2.2. Effect of para-aminobenzoic acid

Para-aminobenzoic acid (*p*-ABA) was used as a modifier to fabricate polymer modified electrode by electropolymerization method. The polymeric film is negatively charged containing electron-rich nitrogen atoms and high electron density carboxyl groups, attracting the tolfenamic acid cations from solution. This effect leads to the enhancement of the anodic peak current. The anodic peak current was found to be 28.36 µA in phosphate buffer pH 7.2 at bare GCE and 264.4 µA at MGCE as shown in Fig. 4.

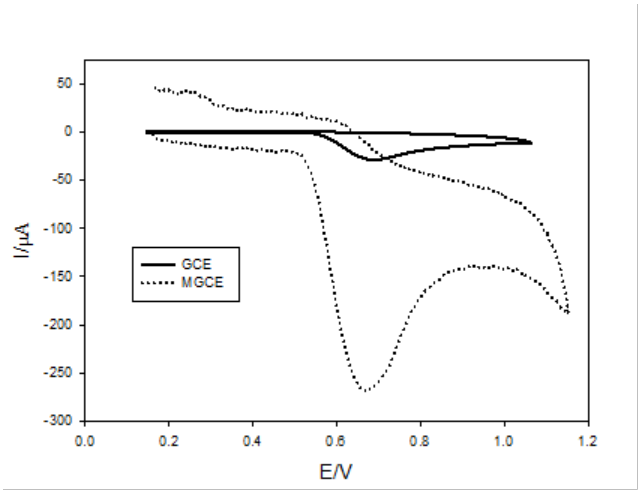

Fig. 4. Cyclic voltammograms of 0.001 mol L^{-1} tolfenamic acid in phosphate buffer of pH 7.2 at GCE and MGCE and scan rate of 100 mVs^{-1}

3.2.3. Effect of number of cycles of p-amino benzoic acid

The effect of the number of cycles of *p*-amino benzoic acid on the anodic peak current of tolfenamic acid was studied; it was found that as the number of cycles increased the anodic current increased up to 80 cycles. After 80 cycles the anodic current decreased, so 80 cycles was chosen as the optimum number of cycles as shown in Fig. 5.

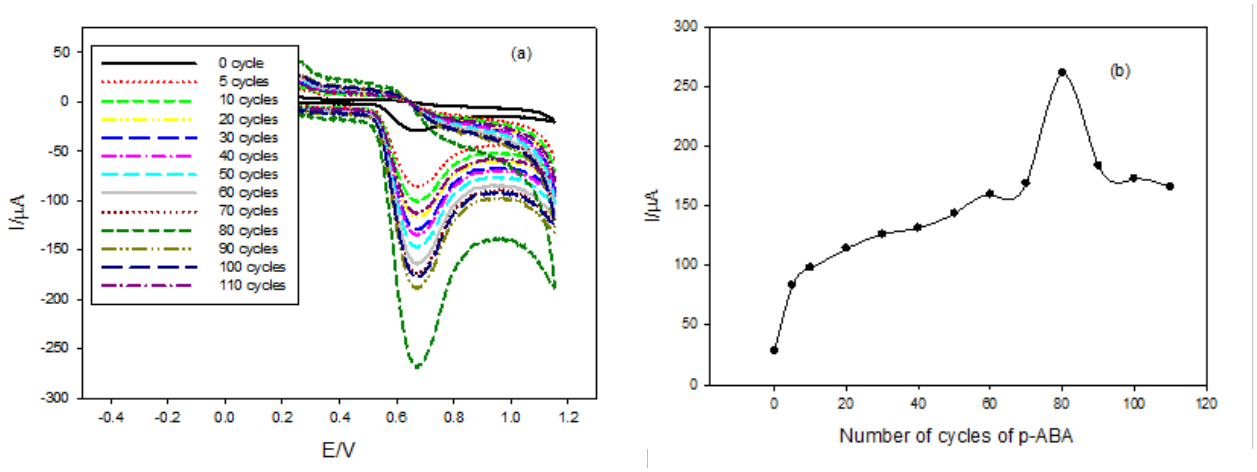

Fig. 5. Cyclic voltammograms of 0.001 mol L^{-1} tolfenamic acid in phosphate buffer of pH 7.2 at MGCE and scan rate of 100 mVs^{-1} as a function of number of cycles of *p*-aminobenzoic acid (a); Plot of the anodic peak current versus the number of cycles of *p*-aminobenzoic acid (b)

3.2.4. Effect of scan rate

The effect of different scan rates (υ) ranging from 10-250 mV s^{-1} on the cyclic voltammetric response of tolfenamic acid in phosphate buffer (pH 7.2) was investigated, with increasing scan rates, the anodic peak was shifted to the positive potential direction and the peak current increased remarkably with increasing scan rates (Fig. 6a). It was found that the logarithm of anodic peak current (log I) is linear to the logarithm of scan rate (log υ), with the linear regression equation as log I=0.6616 log υ+1.098, R^2 (correlation coefficient)=0.9985. From the value of the slope, 0.6616, it can be deduced that the electrochemical oxidation process of tolfenamic acid at MGCE is a diffusion controlled process with an adsorption contribution (Fig. 6b) [41].

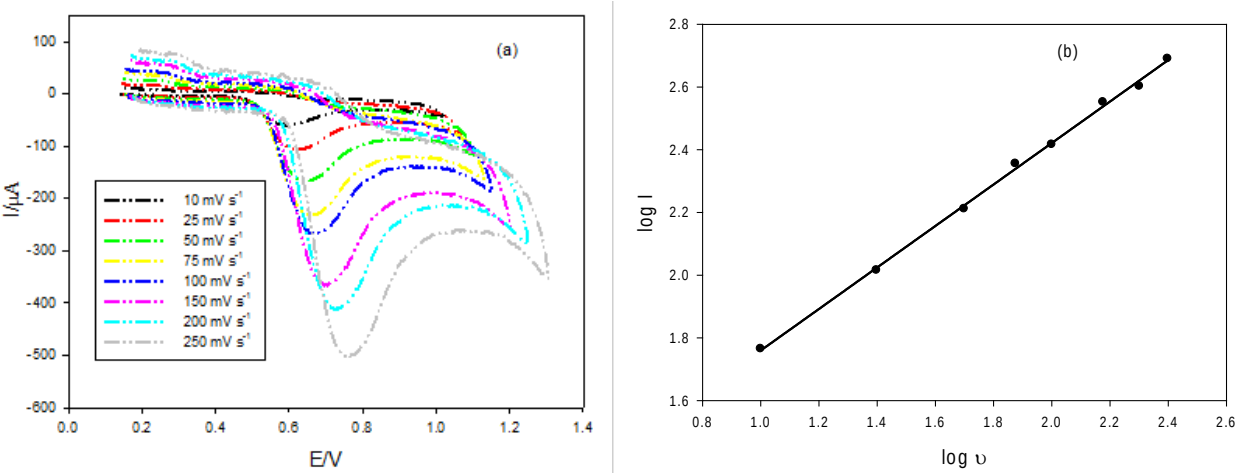

Fig. 6. Cyclic voltammograms of 0.001 mol L^{-1} tolfenamic acid at MGCE in phosphate buffer (pH 7.2) as a function of scan rate (a); Plot of log (I) versus log (υ) (b)

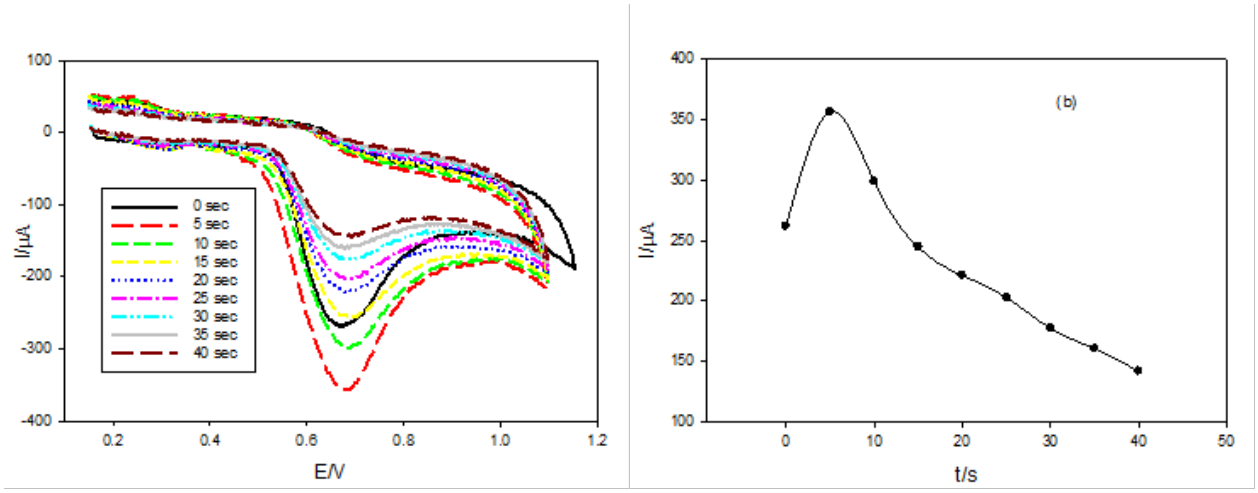

Fig. 7. Cyclic voltammograms of 0.001 mol L^{-1} at MGCE in phosphate buffer (pH 7.2) at scan rate of 100 mV s^{-1} as a function of accumulation time from 0 to 40 s (a); Plot of the anodic peak current versus accumulation time (b)

3.2.5. Effect of accumulation time

Effect of accumulation time on the anodic peak current of of 0.001 mol L^{-1} tolfenamic acid at MGCE was studied at open circuit conditions. It was found that the peak current depended on the accumulation time (T_{acc}). Sharp increase was observed at 5 s reaching its maximum value, and then decreased with increasing time. Thus the preconcentration time of 5 s was chosen as the optimum time for determination of tolfenamic acid (Fig. 7).

3.3. Method validation

3.3.1. Linearity

Linear relationship between the peak current and the drug concentration was found in the range of (6.0×10^{-7}-6.0×10^{-6} mol L^{-1}) using the proposed DPV method (Fig. 8). The regression parameters were computed and presented in Table 1.

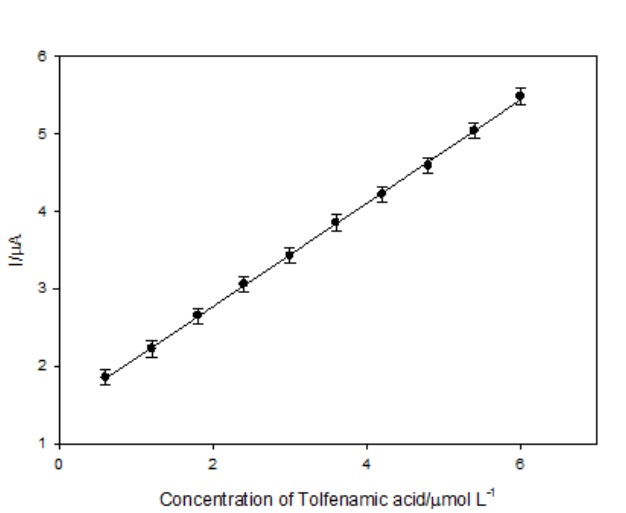

Fig. 8. Calibration curve of the anodic peak current to the corresponding concentration of tolfenamic acid

Table 1. Regression parameters for the determination of tolfenamic acid by proposed electrochemical method

Parameter	**Values**
Linearity range (mol L^{-1})	6.0×0^{-7}-6.0×0^{-6}
Slope±SD	0.6663±2.1
Intercept±SD	1.442±0.032
SD of residual	0.029
Correlation coefficient (R^2)	0.9995
LOD (mol L^{-1})	1.43×0^{-7}
LOQ (mol L^{-1})	4.34×0^{-7}

Limit of detection and limit of quantitation were found to be 1.43×10^{-7} mol L^{-1} and $4.34x10^{-7}$ mol L^{-1}, respectively The experimental limit of detection (LOD) and limit of quantitation (LOQ) were determined according to International conference on harmonization (ICH) guide lines [42] using the standard deviation of multiple blank samples and the slope of the calibration curve (Table 1).

3.3.2. Accuracy and precision

Table 2 shows the intraday and interday accuracy and precision for different concentrations of tolfenamic acid. The recovery (R%), the standard deviation (SD) and the relative standard deviation (RSD%) values indicate to good accuracy, indicating to good precision.

Table 2. Intraday and interday accuracy and precision for the determination of tolfenamic acid by the proposed electrochemical method

Taken	**Intraday**			**Interday**		
(mol L^{-1})	**Found*±SD* (mol L^{-1})**	**R*%**	**RSD*%**	**Found*±SD* (mol L^{-1})**	**R*%**	**RSD*%**
1.8×10^{-6}	$1.84\times10^{-6}\pm2.83\times10^{-8}$	102.2	1.54	$1.82\times10^{-3}\pm7.07\times10^{-9}$	101.1	0.39
3.0×10^{-6}	$3.01\times10^{-6}\pm5.66\times10^{-8}$	100.3	1.88	$2.97\times10^{-3}\pm7.07\times10^{-9}$	99	0.24
4.2×10^{-6}	$4.26\times10^{-6}\pm7.07\times10^{-8}$	101.4	1.66	$4.26\times10^{-3}\pm8.83\times10^{-9}$	101.4	2.07

*Mean value of three determinations

3.3.3. Robustness

The robustness of proposed DPV method was evaluated by variation in the number of cycles of p-(ABA) and pH of phosphate buffer. Results in Table 3 show that the DPV method was not affected by deliberate changes in the optimum parameters of the method.

Table 3. Robustness results of the proposed DPV method

Parameter	**RSD*%**	**R*%**
pH 7.0	0.37	99.7
pH 7.4	0.80	99.3
72 cycles	1.75	101.7
82 cycles	1.32	99.12

*Mean value of three determinations

3.4. Application to pharmaceutical dosage form

The proposed method was successfully applied for the determination of tolfenamic acid in pharmaceutical dosage form in the presence of excipients and additives in the same concentration range as in the bulk without interference with a recovery of 100.385±1.336. The standard addition technique was used to determine the recovery of the proposed method as shown in Table 4.

Table 4. Recovery of the proposed electrochemical method for the determination of tolfenamic acid in its pharmaceutical preparation

Formulation	**Standard addition**			
	Taken (mol L^{-1})	**Added (mol L^{-1})**	**Found (mol L^{-1})**	**Recovery %**
Tolfenam ® tablets	1.2×10^{-6}	6.0×10^{-7}	6.10×10^{-7}	101.66
		1.2×10^{-6}	1.23×10^{-6}	102.50
		1.8×10^{-6}	1.81×10^{-6}	100.55
		2.4×10^{-6}	2.38×10^{-6}	99.16
		3.0×10^{-6}	2.97×10^{-6}	99.00
		3.6×10^{-6}	3.62×10^{-6}	100.55
		4.2×10^{-6}	4.17×10^{-6}	99.28
Mean%± RSD%		100.385±1.336		

Table 5. Determination of tolfenamic acid in its pharmaceutical dosage form

Parameters	**Electrochemical method**	**Reported method [43]**
Linearity range(mol L^{-1})	6.0×10^{-7}-6.0×10^{-6}	3.82×10^{-5}-4.77×10^{-4}
No. of experiments	10	6
Mean%	101.2	99.4
SD	1.99	1.96
Variance	3.96	3.8
t-test*	1.77 (2.145)	
F-test*	1.04 (3.48)	

*Figures in parenthesis are theoretical t and F values at p = 0.05

Statistical analysis of the results obtained by the proposed method compared with those obtained by the reported method [43] revealed that there is no significant difference between the proposed and reported method confirming accuracy and precision at 95% confidence limit [44] as shown in Table 5.

3.5. Determination of tolfenamic acid in urine

Aliquots of 0.001 mol L^{-1} tolfenamic acid solution covering the linearity range (6.0×10^{-7}-6.0×10^{-6} mol L^{-1}), were added to the voltammetric cell containing 5 mL of diluted urine and voltammograms were recorded at a scan rate 10 mV s^{-1} using DPV at MGCE, percentage recoveries were calculated from regression equation (Table 6), where they showed that there is no interference occurred upon addition of diluted urine.

Table 6. Determination of tolfenamic acid in spiked human urine

Concentration (mol L^{-1})	Recovery%
6.0×10^{-7}	101.3
1.2×10^{-6}	99.8
1.8×10^{-6}	101.6
2.4×10^{-6}	101.6
3.0×10^{-6}	101
3.6×10^{-6}	100.4
4.2×10^{-6}	99.5
4.8×10^{-6}	100.3
5.4×10^{-6}	101.3
Mean*%±RSD*%	100.8±0.78

*Mean value of three determinations

Table 7. Comparison of some methods for the determination of tolfenamic acid in bulk, dosage forms, human plasma and human urine

Formulation	Method	Linear range (mol L^{-1})	Ref.
Bulk drug	Spectrofluorimetry	2.5×10^{-8}-5.0×10^{-5}	[4]
Bulk drug	Chromatography	3.82×10^{-5}-3.82×10^{-4}	[5]
Human plasma	Chromatography	7.64×10^{-7}-1.91×10^{-5}	[7]
Animal serum and plasma	Chromatography	4.77×10^{-7}-5.73×10^{-6}	[13]
Dosage form	Chromatography	1.27×10^{-4}-6.38×10^{-4}	[15]
Bulk drug, Dosage form and human urine	DPV	6.0×10^{-7}-6.0×10^{-6}	This work

The proposed method is more sensitive than chromatographic methods [5,7,15] for the determination of tolfenamic acid in bulk, dosage form and in biological fluids as shown in Table 7.

4. CONCLUSION

In the present work a modified electrode, was fabricated by modifying the surface of the glassy carbon electrode with electropolymerization of p-aminobenzoic acid. The advantage of the modified electrode is the significant enhancement of the GCE sensitivity. The proposed DPV method could be used simply for the determination of tolfenamic acid in bulk, dosage form and human urine with good accuracy and precision. The proposed can be successfully applied in routine analysis as quality control method.

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