



CTAB immobilized carbon paste electrode for the determination of mesalazine: A cyclic voltammetric method



Amit B. Teradale^a, Shekappa D. Lamani^b, Pattan S. Ganesh^{c,d},
Bahaddurghatta E. Kumara Swamy^{c,*}, Swastika N. Das^{a,*}

^a Department of Chemistry, BLDEA's College of Engineering and Technology, Vijayapur, Visvesvaraya Technological University, Belagavi, Karnataka 586103, India

^b Department of Chemistry, BLDEA's S.B. Arts and K.C.P. Science College, Vijayapur, Karnataka, India

^c Department of PG Studies and Research in Industrial Chemistry, Kuvempu University, Jnana Sahyadri, Shankaraghatta, 577451 Shimoga, Karnataka, India

^d Department of Chemistry, School of Mathematical and Physical Sciences, Faculty of Agriculture, Science and Technology, North-West University (Mafikeng Campus), Private Bag X2046, Mmabatho 2735, South Africa

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ABSTRACT

The electrochemical behavior of mesalazine (MSZ) was investigated at CTAB immobilized CPE in 0.2 M PBS of pH 7.4 by cyclic voltammetric technique. The modified electrode was exhibited a good electrochemical activity towards the oxidation of mesalazine, which results in the noticeable improvement of the peak currents and feasible oxidation as compared to the bare carbon paste electrode. Under optimal experimental conditions the electrochemical response to MSZ was linear in the concentration range from 60 μM to 140 μM with a detection limit of 1.9 nM by cyclic voltammetric technique. The sensitivity, long-term stability, reproducibility was shown by the modified electrode. Overall, the proposed method was successfully applied to determine MSZ in pharmaceutical samples and satisfactory results were obtained.

1. Introduction

Mesalazine (MSZ), is also known as mesalamine or 2-hydroxy-5-aminobenzoic or 5-aminosalicylic acid [5-ASA] as shown in Scheme 1. MSZ is an anti-inflammatory drug used to treat and it may also provide protection against colorectal cancer in patients suffering from inflammatory bowel disease, such as ulcerative colitis (UC) and mild to moderate Crohn's disease (CD) [1–2]. The role of MSZ is to block the production of prostaglandins and leukotrienes. It also inhibits bacterial peptide-induced, natural killer cell activity, inhibition of cyclooxygenase and lipoxygenase pathways and impairment of neutrophil chemotaxis, adenosine-induced secretion [3]. In addition, MSZ inhibits cell injury in the swollen mucosa by potent scavenging reactive oxygen metabolites, thus suppressing their toxicity [4]. Biljana Nigović et. al., [5] drug is rapidly absorbed from the small intestine when administered orally and therefore, modified-release dosage forms are designed to deliver drug in the terminal ileum and colon.

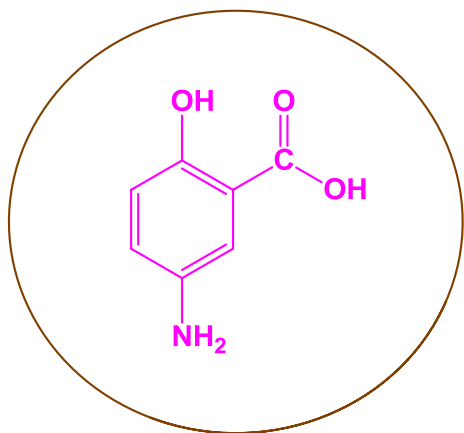
Literature survey revealed that, there are a few analytical methods for the determination of MSZ in pharmaceutical preparations and biological samples using spectrophotometry [6–7], fluorescence spectroscopy [8], liquid chromatography coupled to mass spectrometry [9], ultra-performance liquid chromatography [10], electrochemical [11],

HPLC [12], and LC-MS [13]. The main problems encountered in using such methods were reported or suffer from disadvantages for the determination of MSZ because of complicated derivatization procedures, requires tedious extraction procedure, a requirement of high-priced instruments, and lower detection capability. On the other hand, determination of MSZ using electroanalytical method is very limited although electrochemical method have attracted more attention and advantages in recent years due to their inherent specificity, sensitivity, rapid response, accuracy, low cost, and simplicity of preparation for the determination of environmental, organic, inorganic and biological molecules [14–40].

This work describes the construction of a simple voltammetric sensor for the direct, sensitive and simplicity of preparation for determination of MSZ at a surfactant immobilization on the surface of the carbon paste electrode has been proposed. Surface-active agent (surfactant) is a liner molecule with a hydrophilic head compatible with water on one side (attracted to water) and long hydrophobic tail compatible with oil on the other side (repelled by water) [41–46]. They have been extensively used in recent researches field, particularly in electrochemistry and electroanalytical chemistry for various investigations. Due to the specific amphiphilic ion or molecule structure of surfactants, these molecules can be adsorbed in the interfaces and

* Corresponding authors.

E-mail addresses: bek@kuvempu.ac.in (B.E. Kumara Swamy), drswastikandas@rediffmail.com (S.N. Das).



Scheme 1. Structure of mesalazine.

surfaces [47,48]. In general, adsorption begins well below the critical micelle concentration (CMC) of the surfactant. Adsorption of surfactants on electrodes and solubilisation of electrochemically active compounds in micellar aggregates might significantly change the charge transfer coefficients, redox potential and diffusion coefficients of electrode processes [49]. So at low concentrations, surfactants molecules immobilized on the electrode surface. Ionic surfactant adsorption on the electrode makes charged i.e., cationic surfactant give it positive charged and anionic surfactants make negative charged on electrode surface. Charged electrode scan affect the oxidation potential by charge transferring rates in electrochemical measurements. The results indicated that electrochemical responses of analysed objects were remarkably enhanced in the presence of surfactant. The surfactant-modified electrodes have been reported previously [50–54]. In the present work experimental results showed that immobilized cationic surfactant-CTAB had a distinct enhancement effect on the voltammetric responses of MSZ at a carbon paste electrode.

To the best survey of literature revealed that, there is no report on the electrochemical oxidation of MSZ at CTAB immobilized carbon paste electrode. The aim of the present work is to develop a sensitive electroanalytical method for the determination of MSZ at carbon paste electrode modified with a cationic surfactant CTAB. Finally, this method has advantages including high sensitivity, reproducibility, rapid response, low cost, pharmaceutical formulations and good detection limit of MSZ.

2. Experimental

2.1. Instrumentation

Electrochemical studies were carried out by using an electrochemical work station CHI-660c (CH Instrument-660 electrochemical analyser) coupled with a conventional three-electrode cell. A three-electrode cell was used with saturated calomel electrode (SCE) as a reference, platinum wire as a counter electrode and a self-made bare carbon paste electrode (BCPE) or CTAB immobilized CPE as working electrode. All the potentials were given against SCE.

2.2. Reagents and chemicals

MSZ was obtained from sigma Ltd., India, ($M_{wt} = 151.16$ g/mol, purity 99%). Cetyl trimethyl ammonium bromide (CTAB) surfactant was obtained from Himedia Pvt. Ltd., were dissolved in doubly distilled water to form stock ($C_{CTAB} = 10 \times 10^{-3}$ M) solutions. The MSZ containing tablets i.e. Mesacol purchased from a local pharmacy. All chemicals were of analytical grade and used as received without any further purification. All the experiments were carried out at room

temperature. Phosphate buffer solution (PBS) of same ionic strength was prepared (0.2 M) by mixing appropriate ratio of $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ and Na_2HPO_4 . Graphite powder of average particle size $50 \mu\text{m}$ purchased from Merck and silicon oil from Himedia was used to prepare carbon paste electrode (CPE). All other reagents used were of analytical grade. All the aqueous solutions were prepared with double distilled water.

2.3. Preparation of bare carbon paste electrode

The BCPE was prepared with the composition of 70:30 (graphite powder: silicone oil) in an agate mortar and grinded for about 45 min until a homogeneous paste was formed. The paste was packed into a homemade cavity of PVC tube of 3 mm internal diameter and the surface was smoothened on a weighing paper. Unless otherwise stated, the paste was carefully removed prior to pressing a new portion into the electrode after every measurement. The electrical contact was provided by a copper wire connected to the end of the tube.

2.4. Preparation of CTAB immobilized carbon paste electrode

The paste packing procedure was same as that at bare carbon paste electrode. The CTAB immobilized MCPE was fabricated by immobilizing 20 microliter solution of CTAB on the surface of bare carbon paste electrode and allowed it for about 15 min at room temperature, after this the electrode was thoroughly rinsed with double distilled water to remove the unabsorbed CTAB [55].

2.5. Determination of MSZ in formulation tablets

A quantity of 5 tablets (equivalent to 400 mg of MSZ in each tablet) of mesacol were weighed and ground to a homogeneous fine powder in a mortar. A portion equivalent to a stock solution of concentration of about 1.0 mM was accurately weighed and dissolved in doubly distilled water. The excipient was separated by filtration and the residue was washed three times with doubly distilled water. The solution was transferred into a 100 ml calibrated flask and diluted to a final volume with same solvent. Appropriate solutions were prepared by taking suitable aliquots from this stock solution and diluted with 0.2 M PBS of pH 7.4. Each solution was transferred to the voltammetric cell and analysed by standard addition method. The cyclic voltammograms were recorded between -0.2 and 0.8 V with the scan rate of 0.05 Vs^{-1} . To study the accuracy of the proposed method and to check the interferences from excipient used in the dosage form, recovery experiments were carried out. The concentration of MSZ was calculated using standard addition method.

3. Result and discussion

3.1. Electrochemical characterization of CTAB immobilized MCPE

In order to fabricate a CTAB immobilized CPE, the different concentration of CTAB solution was immobilized on the surface of carbon paste electrode as showed in Fig. 1. The peak current response of the modified electrode increased gradually for the oxidation of 0.1 mM MSZ in 0.2 M PBS of pH 7.4 with increase in immobilization concentration. After reaching the saturation level of 20 microliter further addition in the immobilization concentration of CTAB decreases the peak current response. Therefore, 20 microliter was chosen for the diffusion of the CTAB molecule into the porous carbon paste electrode. Such a behavior is typical of a mediator based sensor. The probable immobilization mechanism of CTAB and electrocatalytic interaction with MSZ is described in Supplementary Scheme 2. Such types of mechanisms have been proposed in earlier report [56].

Fig. 2 showed the cyclic voltammograms recorded for the oxidation of 1 mM potassium ferrocyanide in 1 M KCl at both BCPE (dashed line) and CTAB immobilized MCPE (solid line) at the scan rate 0.05 Vs^{-1} .

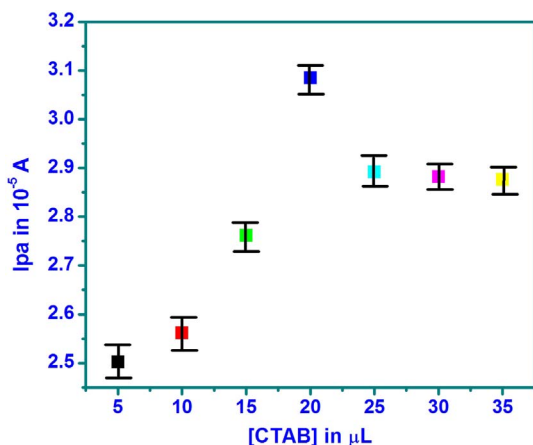


Fig. 1. Graph of anodic peak current obtained for the oxidation of 0.1 mM MSZ in 0.2 M PBS of pH 7.4 versus different concentration of CTAB immobilized modified CPE.

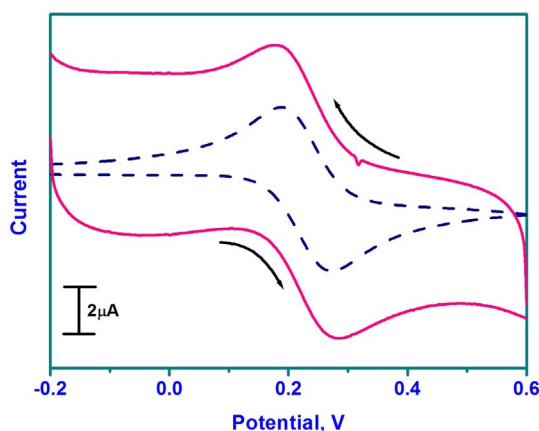


Fig. 2. Cyclic voltammograms of 1.0 mM potassium ferrocyanide at bare CPE (dashed line) and CTAB immobilized modified CPE (solid line) at the scan rate of 0.05 Vs^{-1} .

Due to slow electron transport phenomenon, low redox peak current response was obtained at BCPE. However, in the same identical condition the CTAB immobilized MCPE exhibited improved redox peak currents with the fast rate of electron transfer kinetics. The potential difference (ΔE_p) was found to be 0.062 V ; this is a characteristic reversible voltammogram of $\text{Fe}^{2+}/\text{Fe}^{3+}$ couple. The result suggests that the surface property of the CTAB immobilized MCPE has been significantly changed. The result confirms electrocatalytic activity of the CTAB immobilized MCPE. The available surface area for reaction of species in solution can be calculated by the Randles-Sevcik Eq. (1) [57].

$$I_p = 2.69 \times 10^5 n^{3/2} A D^{1/2} C_0 \nu^{1/2} \quad (1)$$

Where, I_p is the peak current in A. C_0 is the concentration of the electroactive species (mol cm^{-3}), n is the number of electrons involved, D is the diffusion coefficient ($\text{cm}^2 \text{ S}^{-1}$), ν is the scan rate (Vs^{-1}) and A is the electroactive surface area (cm^2). For CTAB immobilized MCPE the electroactive surface area is maximum (0.03622 cm^2) as compared with BCPE (0.02842 cm^2).

3.2. Electrochemical response of MSZ at CTAB immobilized MCPE

The cyclic voltammograms were recorded for the oxidation of 0.1 mM MSZ at BCPE (dashed line) and CTAB immobilized MCPE (solid line) in 0.2 M PBS of pH 7.4 with the scan rate 0.05 Vs^{-1} as shown in Fig. 3. At BCPE the MSZ showed broad voltammetric response with low current response and are located at 0.222 V . However, in the same identical condition the CTAB immobilized MCPE shows significant increment in current signals

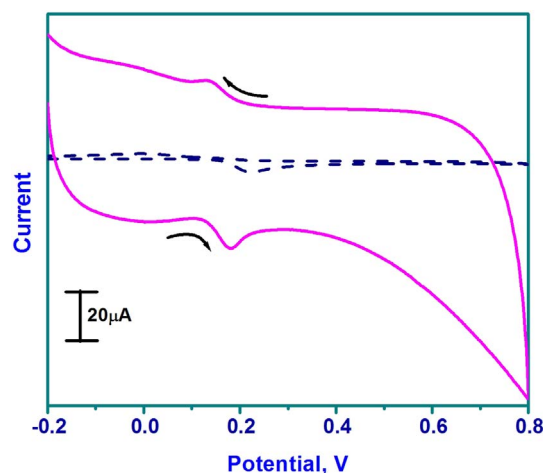


Fig. 3. Cyclic voltammograms for 0.1 mM MSZ at bare CPE (dashed line) and CTAB immobilized modified CPE (solid line) in 0.2 M PBS of pH 7.4 at scan rate 0.05 Vs^{-1} .

and the oxidation potential of MSZ was observed at 0.180 V . The increase of the current signal was almost 5 folds compared to the BCPE. This minimization of over potential and enhancement of current response confirms the electrocatalytic activity of the CTAB immobilized MCPE towards the electrochemical oxidation of MSZ in physiological pH.

3.3. Effect of scan rate on the peak current of MSZ

The effect of scan rate was studied for the redox activity of 0.1 mM MSZ at CTAB immobilized MCPE in 0.2 M PBS of pH 7.4 as a supporting electrolyte by cyclic voltammetric (CV) technique. According to Randles-Sevcik equation the redox peak current is directly proportional to scan rate. Fig. 4 showed the peak current increased with a slight positive shift in the peak potential when the scan rate was increased in the range from 0.02 to 0.3 Vs^{-1} . The graph of peak current (I_p) versus scan rate (ν) resulted in a straight line with the correlation coefficient (r^2) of 0.9993 and 0.9991 as shown in Fig. 5. The I_p versus square root scan rate ($\nu^{1/2}$) was plotted as shown in Fig. 6 with the correlation coefficient (r^2) of 0.9915 and 0.9923 . This suggests that the process of the electrode reaction is controlled by adsorption phenomenon [58,59].

The heterogeneous rate constant (k^0) values was determined from the experimental peak potential difference (ΔE_p) data's, Eq. (2) was used for such voltammograms whose ΔE_p values are greater than 10 mV [60].

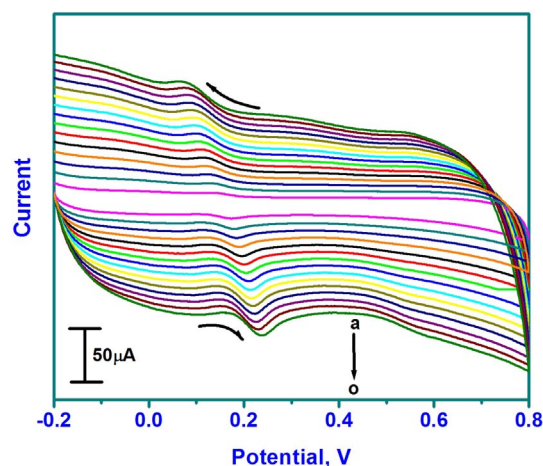


Fig. 4. Cyclic voltammograms for 0.1 mM MSZ at CTAB immobilized modified CPE in 0.2 M PBS of pH 7.4 at different scan rate (a-o; 0.02 Vs^{-1} , 0.04 Vs^{-1} , 0.06 Vs^{-1} , 0.08 Vs^{-1} , 0.1 Vs^{-1} , 0.12 Vs^{-1} , 0.14 Vs^{-1} , 0.16 Vs^{-1} , 0.18 Vs^{-1} , 0.2 Vs^{-1} , 0.22 Vs^{-1} , 0.24 Vs^{-1} , 0.26 Vs^{-1} , 0.28 Vs^{-1} and 0.3 Vs^{-1}).

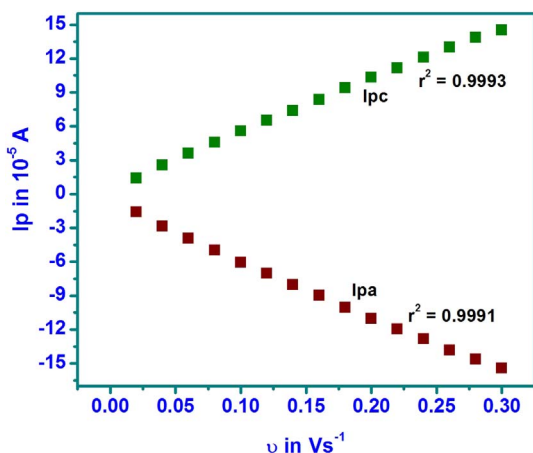


Fig. 5. The Graph of peak current (Ip) versus scan rate (v).

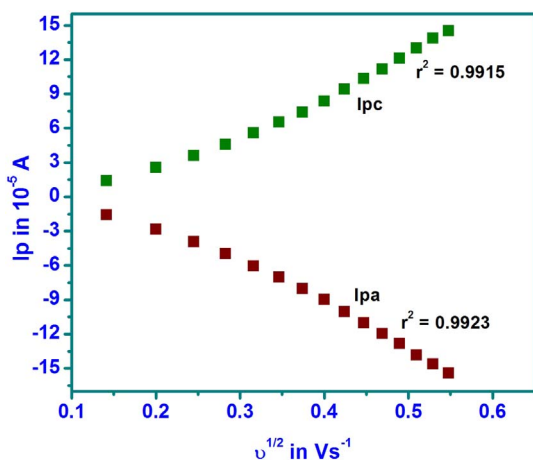


Fig. 6. The Graph of peak current (Ip) versus square root of scan rate.

$$\Delta E_p = 201.39 \log(v/k^0) - 301.78 \quad (2)$$

From the experimental ΔE_p values as shown in Table 1 and Eq. (2); the values of the k^0 for the MSZ oxidation was determined. The values of k^0 obtained at the scan rate of 0.24 Vs^{-1} for the CTAB immobilized MCPE exhibits larger heterogeneous rate constant compared with those determined in other scan rate variation studies. All the parameters are tabulated in Table 1.

Table 1
Variation of the voltammetric parameters from the plots shown in Figs. 4–6 as a function of the potential scan rate.

v (mVs^{-1})	ΔE_p (mV)	k^0 (s^{-1})
20	29.4	0.453
40	46.2	0.746
60	60.8	0.950
80	69.2	1.150
100	81.7	1.247
120	92.3	1.325
140	98.6	1.439
160	113.2	1.391
180	119.6	1.455
200	123.6	1.544
220	132.1	1.541
240	136.3	1.603
260	146.8	1.539
280	155.0	1.510
300	165.6	1.433

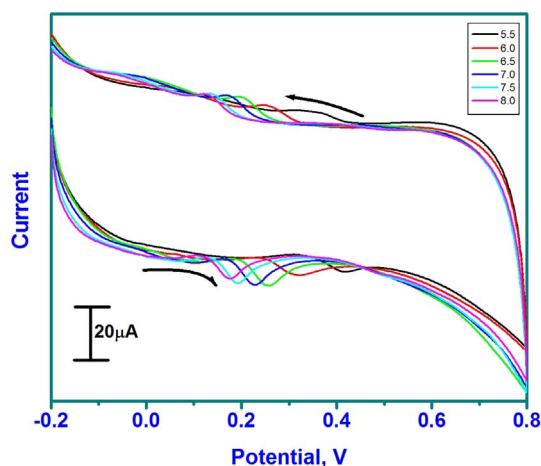


Fig. 7. Cyclic voltammograms of 0.1 mM MSZ at CTAB immobilized modified CPE in 0.2 M PBS solution of different pH values (5.5, 6.0, 6.5, 7.0, 7.5 and 8.0) at scan rate of 0.05 Vs^{-1} .

3.4. Effect of pH value on the determination of MSZ

The effect of pH on the electrochemical oxidation behavior of MSZ at CTAB immobilized MCPE was carefully studied by CV technique. Fig. 7 illustrates the peak current response of 0.2 mM MSZ at CTAB immobilized MCPE in the pH range of 5.5 to 8.0. The result shows, by increasing the pH of 0.2 mM phosphate buffer the oxidation potential was shifted to more negative side. The anodic peak potential (E_{pa}) and anodic peak current (I_{pa}) vs. pH graph clearly indicates that the catalytic oxidation potential depends linearly on pH with the slope of 0.0838 V/pH ($r^2 = 0.9571$) as showed in Fig. 8 and signifying that there is an equal number of protons and electrons involved in the redox reaction. Our experimental results were in agreement with the literature reports [61,62].

3.5. Effect of MSZ concentration

In order to develop a voltammetric method for the determination of mesalazine, The electrocatalytic oxidation of MSZ was carried out by varying its concentration at CTAB immobilized MCPE in the range of 60.0 to 140.0 μM in 0.2 M PBS of pH 7.4 at scan rate 0.05 Vs^{-1} as showed in Fig. 9A. By increasing the concentration of mesalazine I_{pa} goes on increasing with shifting E_{pa} towards less positive side. The graph of I_{pa} versus concentration of MSZ justifies the reason of increase in anodic peak current, which is due to increase in the concentration of MSZ as showed in Fig. 9B. This graph shows almost straight line with good linearity with the linear regression equation of $I_{pa}(10^{-5} \text{ A}) = 0.0167(C_0 \cdot 10^{-4} \text{ M/L}) + 2.2443$, ($r^2 = 0.9954$). The LOD were

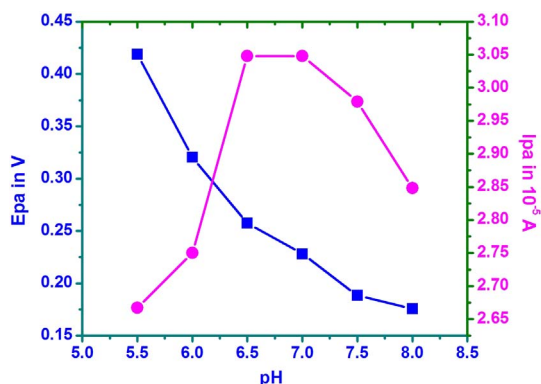


Fig. 8. The effect of anodic peak current and anodic peak potential versus pH.

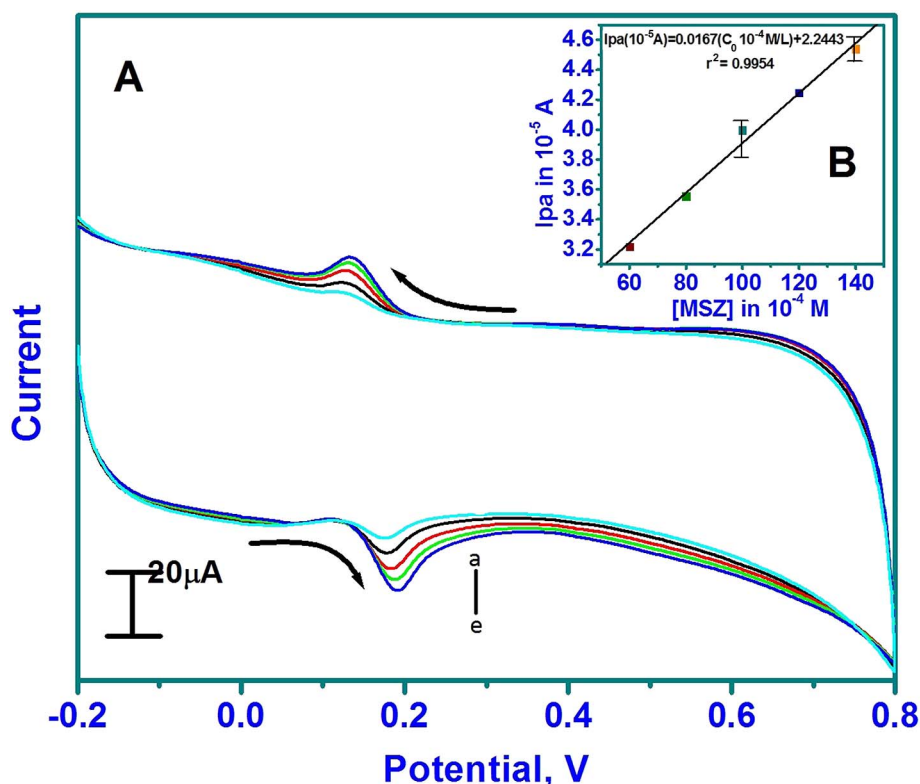


Fig. 9. (A) Cyclic voltammograms of MSZ in 0.2 M PBS solution of pH 7.4 at CTAB immobilized modified CPE at scan rate of 0.05 Vs⁻¹ with different concentrations (a–e: 60.0 μM, 80.0 μM, 100.0 μM, 120.0 μM and 140.0 μM). (B) Graph of anodic peak current versus concentration of MSZ.

Table 2
Comparison of linear range and detection limits for MSZ with different classical methods and electrodes.

Classical methods	Electrode/modifier biosensors	Linear working range	Detection limits (M)	Refs.
Ad LSV	CNT/PPY doped by 1,5-naphthalenedisulphonic acid	1.0×10^{-8} – 1.0×10^{-6}	3.0×10^{-9}	[63]
SWV	Pencil graphite electrode	9.8×10^{-7} – 7.3×10^{-5}	2.1×10^{-8}	[64]
Sona LSV	Glossy carbon electrode	1.0×10^{-6} – 5.7×10^{-5}	3.0×10^{-7}	[65]
CV	Poly(Glutamic acid) MGCE	50.0×10^{-6} – 0.5×10^{-3}	23.9×10^{-9}	[66]
DPV	Glossy carbon electrode	2.0×10^{-6} – 1.0×10^{-4}	8.2×10^{-7}	[67]
CV	CTAB immobilized modified CPE	60×10^{-6} – 140×10^{-6}	1.9×10^{-9} (nM)	Present work

calculated using the equation, $LOD = 3S/M$. Where, S is the standard deviation of six blank measurements and M is the slope of the calibration curve. The calculated detection limit of MSZ at CTAB immobilized MCPE was found to be 1.9 nM. The detection limits reported for different classical methods and electrodes are tabulated in Table 2. This method was better compared to other reported methods [63–67].

3.6. Detection of MSZ in tablets and recovery test

In order to evaluate the ability of CTAB immobilized MCPE to commercial pharmaceutical samples (400 mg mesalazine per tablet), the CTAB immobilized MCPE sensor was applied to the determination of MSZ in tablets. The procedure for the tablet analysis was followed as described in the Section 2.5. The recovery of the CV method was also studied to evaluate the accuracy of the method. The recovery test of MSZ ranging from 1.0×10^{-6} M to 2.0×10^{-5} M was performed using cyclic voltammetry. As can be seen in Table 3, good recoveries and SD ± RSD were observed which reveals the better analytical performance of the fabricated modified electrode for the determination of MSZ in pharmaceutical samples. The obtained result indicating that the CTAB immobilized MCPE can be successfully used for the selective determination of mesalazine in pharmaceutical samples.

Table 3
Determination of MSZ in commercial pharmaceutical sample.

Formulation sample	MSZ added	Detected ^a	Recovery (%)	SD ± RSD (%)
Tablet (mesacol)	1.0×10^{-6}	1.05×10^{-6}	105	0.0353 ± 0.0252
	3.0×10^{-6}	3.03×10^{-6}	101	0.0212 ± 0.0151
	5.0×10^{-6}	4.99×10^{-6}	99.8	0.0070 ± 0.0050
	7.0×10^{-6}	7.06×10^{-6}	100.8	0.0424 ± 0.0303
	9.0×10^{-6}	8.99×10^{-6}	99.8	0.0141 ± 0.0101
	2.0×10^{-5}	1.97×10^{-5}	98.5	0.0212 ± 0.0151

^a Average of five determination.

Table 4
Influence of potential interferences on the cyclic voltammetric response of 1.0 mM MSZ.

Interferents	Concentration (mM)	Signal change (%)
Ammonium chloride	1.0	4.46%
Calcium chloride	1.0	2.28%
Calcium sulphate	1.0	1.16%
Magnesium chloride	1.0	1.40%
Potassium oxalate	1.0	1.10%
Sodium chloride	1.0	1.32%
Starch	1.0	2.01%
Sucrose	1.0	1.38%

Scan rate 0.05 Vs⁻¹ at CTAB immobilized modified CPE.

3.7. Interference

Under the optimum experimental conditions, the effects of potential interferents on the voltammetric response of 1.0 mM MSZ were evaluated. The experimental results as shown in Table 4, that ten-fold excess of calcium sulphate, magnesium chloride, potassium oxalate, sodium chloride and sucrose did not interfere with the voltammetric signal of MSZ. However, ten-fold excess of ammonium chloride, calcium chloride and starch had apparent influence on the voltammetric signal of MSZ.

4. Conclusion

In the present work a CTAB immobilized modified CPE was developed for the electro oxidation of MSZ in PBS of pH 7.4 by CV technique. The oxidation peak current signifying that CTAB immobilized modified CPE exhibits noticeable enhancement effect to the determination of MSZ as well as under optimal conditions the cyclic voltammetry response to MSZ has a linear concentration over the range from 60 μM to 140 μM , with limit of detection 1.9 nM respectively. The sensitivity, long-term stability, reproducibility was shown by the modified electrode. Overall, a simple modification procedure was reported for the determination of MSZ by CV technique.

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.sbsr.2017.08.001>.

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References

- H. Yi, C. Li, Voltammetric determination of ciprofloxacin based on the enhancement effect of cetyltrimethyl ammonium bromide (CTAB) at carbon paste electrode, *Russ. J. Electrochem.* 43 (2007) 1377–1381.
- N.K. Sahoo, M. Sahu, P.S. Rao, G. Ghosh, Validation of stability indicating RP-HPLC method for the estimation of mesalamine in bulk and tablet dosage form, *Pharm. Methods* 4 (2013) 56–61.
- S. Kim, Ning Wang, Yijun Li, Xiwen He, Electrochemical determination of mesalazine by using graphene oxide coated with a molecularly imprinted sol-gel, *Anal. Methods* 8 (2016) 7780–7788.
- F.A. Alasha Abdalla, A.A. Elbashir, Development and validation of spectrophotometric methods for the determination of mesalazine in pharmaceutical formulation, *Med. Chem.* 4 (2014) 361–366.
- B. Nigović, M. Sadiković, S. Jurić, Electrochemical sensing of mesalazine and its N-acetylated metabolite in biological samples using functionalized carbon nanotubes, *Talanta* 147 (2016) 50–58.
- S.Y. Garmonov, Z.C. Nguyen, I.F. Mingazetdinov, L.M. Yusupova, N.S. Shitova, R.N. Ismailova, V.F. Sopin, Spectrophotometric determination of mesalazine in urine for assessing the acetylation phenotype *in vivo* in humans, *Pharm. Chem. J.* 45 (2012) 757–760.
- M.G.H. Laghari, Y. Darwis, A.H. Memon, New spectrophotometric methods for the determination of p-aminosalicylic acid in tablets, *Trop. J. Pharm. Res.* 13 (2014) 1133–1139.
- A.A. Elbashir, F.A.A. Abdalla, H.Y. Aboul-Enein, Host-guest inclusion complex of mesalazine and β -cyclodextrin and spectrofluorometric determination of mesalazine, *Luminescence* 30 (2014) 444–450.
- J. Qin, X. Di, X. Wang, Y. Liu, Development and validation of an LC-MS/MS method for the determination of mesalazine in beagle dog plasma and its application to a pharmacokinetic study, *Biomed. Chromatogr.* 29 (2015) 261–267.
- S. Nandipati, V.K. Reddy, S. Uba, A validated ultra performance liquid chromatography method for assay determination of mesalamine, *Int. J. Pharm. Pharm. Sci.* 5 (2013) 312–316.
- G. Palumbo, S. Bacchi, L. Primavera, P. Palumbo, G. Carlucci, A validated HPLC method with electrochemical detection for simultaneous assay of 5-amino-salicylic acid and its metabolite in human plasma, *Biomed. Chromatogr.* 19 (2005) 350–354.
- M. Alok Kumar, B. Mrityunjay, S. Chinmaya Keshari, S. Nalini Kanta, Development and validation of RPHPLC method for mesalamine, *Asian J. Pharm. Clin. Res.* 4 (2011) 71–73.
- E. Pastorini, M. Locatelli, P. Simoni, G. Roda, E. Roda, A. Roda, Development and validation of a HPLC-ESI-MS/MS method for the determination of 5-aminosalicylic acid and its major metabolite N-acetyl-5-aminosalicylic acid in human plasma, *J. Chromatogr. B Anal. Technol. Biomed. Life Sci.* 872 (2008) 99–106.
- V.K. Gupta, R. Ludwig, S. Agarwal, Anion recognition through modified calixarenes: a highly selective sensor for monohydrogen phosphate, *Anal. Chim. Acta* 538 (2005) 213–218.
- V.K. Gupta, S. Jain, U. Khurana, A PVC-based pentathia-15-crown-5 membrane potentiometric sensor for mercury (II), *Electroanalysis* 9 (1997) 478–480.
- V.K. Gupta, A.K. Jain, G. Maheshwari, H. Lang, Z. Ishitaiwi, Copper(II)-selective potentiometric sensors based on porphyrins in PVC matrix, *Sensors Actuators B* 117 (2006) 99–106.
- V.K. Gupta, A.K. Singh, S. Mehtab, B. Gupta, A cobalt(II)-selective PVC membrane based on a Schiff base complex of N,N'-bis(salicylidene)-3,4-diaminotoluene, *Anal. Chim. Acta* 566 (2006) 5–10.
- V.K. Gupta, A.K. Jain, P. Kumar, PVC-based membranes of N,N'-dibenzyl-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane as Pb(II)-selective sensor, *Sensors Actuators B* 120 (2006) 259–265.
- V.K. Gupta, A.K. Jain, P. Kumar, S. Agarwal, G. Maheshwari, Chromium(III)-selective sensor based on tri-o-thymotide in PVC matrix, *Sensors Actuators B* 113 (2006) 182–186.
- A.K. Jain, V.K. Gupta, L.P. Singh, J.R. Raison, A comparative study of Pb^{2+} selective sensors based on derivatized tetrapyrrole and calix [4]arene receptors, *Electrochim. Acta* 51 (2006) 2547–2553.
- R.N. Goyal, V.K. Gupta, N. Bachheti, Fullerene-C₆₀-modified electrode as a sensitive voltammetric sensor for detection of nandrolone-an anabolic steroid used in doping, *Anal. Chim. Acta* 597 (2007) 82–89.
- V.K. Gupta, A.K. Singh, M. Al Khayat, B. Gupta, Neutral carriers based polymeric membrane electrodes for selective determination of mercury (II), *Anal. Chim. Acta* 590 (2007) 81–90.
- V.K. Gupta, S. Jain, S. Chandra, Chemical sensor for lanthanum(III) determination using aza-crown as ionophore in poly(vinyl chloride) matrix, *Anal. Chim. Acta* 486 (2003) 199–207.
- V.K. Gupta, S. Chandra, R. Mangla, Dicyclohexano-18-crown-6 as active material in PVC matrix membrane for the fabrication of cadmium selective potentiometric sensor, *Electrochim. Acta* 47 (2002) 1579–1586.
- V.K. Gupta, R. Mangla, U. Khurana, P. Kumar, Determination of uranyl ions using poly(vinyl chloride) based 4-tert-butylcalix[6]arene membrane sensor, *Electroanalysis* 11 (1999) 573–576.
- A.K. Jain, V.K. Gupta, L.P. Singh, U. Khurana, Macrocyclic based membrane sensors for the determination of cobalt(II) ions, *Analyst* 122 (1997) 583–586.
- V.K. Gupta, R. Prasad, P. Kumar, R. Mangla, New nickel(II) selective potentiometric sensor based on 5,7,12,14-tetramethylbenzotetraazaannulene in a poly(vinyl chloride) matrix, *Anal. Chim. Acta* 420 (2000) 19–27.
- R. Prasad, V.K. Gupta, A. Kumar, Metallo-tetraazaporphyrin based anion sensors: regulation of sensor characteristics through central metal ion coordination, *Anal. Chim. Acta* 508 (2004) 61–70.
- V.K. Gupta, A. Nayak, S. Agarwal, B. Singhal, Recent advances on potentiometric membrane sensors for pharmaceutical analysis, *Comb. Chem. High Throughput Screen.* 14 (2011) 284–302.
- V.K. Gupta, L.P. Singh, R. Singh, N. Upadhyay, S.P. Kaur, B. Sethi, A novel copper (II) selective sensor based on Dimethyl 4, 4' (o-phenylene) bis(3-thioallophanate) in PVC matrix, *J. Mol. Liq.* 174 (2012) 11–16.
- V.K. Gupta, B. Sethi, R.A. Sharma, S. Agarwal, A. Bharti, Mercury selective potentiometric sensor based on low rim functionalized thiacalix [4]-arene as a cationic receptor, *J. Mol. Liq.* 177 (2013) 114–118.
- R. Jain, V.K. Gupta, N. Jadon, K. Radhapyari, Voltammetric determination of ceftixime in pharmaceuticals and biological fluids, *Anal. Biochem.* 407 (2010) 79–88.
- V.K. Gupta, A.K. Jain, G. Maheshwari, Aluminum(III) selective potentiometric sensor based on morin in poly(vinyl chloride) matrix, *Talanta* 72 (4) (2007) 1469–1473.
- V.K. Gupta, M.R. Ganjali, P. Norouzi, H. Khani, A. Nayak, S. Agarwal, Electrochemical analysis of some toxic metals by ion-selective electrodes, *Crit. Rev. Anal. Chem.* 41 (2011) 282–313.
- V.K. Gupta, A.K. Jain, S. Agarwal, G. Maheshwari, An iron(III) ion-selective sensor based on a μ -bis(tridentate) ligand, *Talanta* 71 (2007) 1964–1968.
- R.N. Goyal, V.K. Gupta, S. Chatterjee, Voltammetric biosensors for the determination of paracetamol at carbon nanotube modified pyrolytic graphite electrode, *Sensors Actuators B Chem.* 149 (2010) 252–258.
- V.K. Gupta, A.K. Jain, L.P. Singh, U. Khurana, Porphyrins as carrier in PVC based membrane potentiometric sensors for nickel(II), *Anal. Chim. Acta* 355 (1997) 33–41.
- A.K. Jain, V.K. Gupta, U. Khurana, L.P. Singh, A new membrane sensor for UO ions based on 2-hydroxyacetophenoneoxime-thiourea-trioxane resin, *Electroanalysis* 9 (1997) 857–860.
- S.K. Srivastava, V.K. Gupta, S. Jain, Determination of lead using a poly(vinyl chloride)-based crown ether membrane, *Analyst* 120 (1995) 495–498.
- S.K. Srivastava, V.K. Gupta, M.K. Dwivedi, S. Jain, Caesium PVC-crown (dibenzo-24-crown-8) based membrane sensor, *Anal. Proc. Incl. Anal. Commun.* 32 (1995) 21–23.
- D.W. Hatchett, M. Josowicz, Composites of intrinsically conducting polymers as sensing nanomaterials, *Chem. Rev.* 108 (2008) 746–769.
- M.A. Mhammedi, M. Bakasse, A. Chtainia, Square-wave voltammetric determination of paraquat at carbon paste electrode modified with hydroxyapatite, *Electroanalysis* 19 (2007) 1727–1733.
- J.I. Gowda, M. Mallappa, S.T. Nandibewoor, CTAB functionalized multiwalled carbon nanotube composite modified electrode for the determination of 6-mercaptopurine, *Sens. Biosens. Res.* 12 (2017) 1–7.
- A.B. Teradale, S.D. Lamani, S.N. Das, Up growth effect of cetyltrimethyl ammonium

- bromide with carbon paste electrode for the electrochemical determination of allopurinol and its biological activities, *Anal. Bioanal. Electrochem.* 8 (2016) 814–829.
- [45] J.C. Abbar, S.T. Nandibewoor, Voltammetric oxidation and determination of atorvastatin based on the enhancement effect of cetyltrimethyl ammonium bromide at a carbon paste electrode, *Colloids Surf. B Biointerfaces* 106 (2013) 158–164.
- [46] A.T. Buddanavar, J.I. Gowda, S.T. Nandibewoor, Voltammetric behavior of isoniazid and its electroanalytical determination at carbon nanotubes CTAB modified glassy carbon electrode, *Anal. Bioanal. Electrochem.* 8 (3) (2016) 329–344.
- [47] J.I. Gowda, D.G. Gunjiganvi, N.B. Sunagar, M.N. Bhat, S.T. Nandibewoor, MWCNT–CTAB modified glassy carbon electrode as a sensor for the determination of paracetamol, *RSC Adv.* 5 (2015) 49045–49053.
- [48] R. Vittal, H. Gomathi, K.-J. Kim, Beneficial role of surfactants in electrochemistry and in the modification of electrodes, *Adv. Colloid Interface Sci.* 119 (2006) 55–68.
- [49] R. Hosseinzadeh, R.E. Sabzi, K. Ghasemlu, Effect of cetyltrimethyl ammonium bromide (CTAB) in determination of dopamine and ascorbic acid using carbon paste electrode modified with tin hexacyanoferrate, *Colloids Surf. B Biointerfaces* 68 (2009) 213–217.
- [50] L. Fernandez, C. Borrás, H. Carrero, Electrochemical behavior of phenol in alkaline media at hydrotalcite-like clay/anionic surfactants/glassy carbon modified electrode, *Electrochim. Acta.* 52 (2006) 872–884.
- [51] P. Manisankar, G. Selvanathan, C. Vedhi, Determination of pesticides using heteropolyacidmontmorillonite clay-modified electrode with surfactant, *Talanta* 68 (2006) 686–692.
- [52] R. Vittal, H. Gomathi, K.J. Kim, Beneficial role of surfactants in electrochemistry and in the modification of electrodes, *Adv. Colloid Interface Sci.* 119 (2006) 55–68.
- [53] L. Fernandez, H. Carrero, Electrochemical evaluation of ferrocene carboxylic acids confined on surfactant–clay modified glassy carbon electrodes: oxidation of ascorbic acid and uric acid, *Electrochim. Acta.* 50 (2005) 1233–1240.
- [54] S. Yuan, W. Chen, S. Hu, Fabrication of TiO₂nanoparticles/surfactant polymer complex film on glassy carbon electrode and its application to sensing trace dopamine, *Mater. Sci. Eng. C* 25 (2005) 479–485.
- [55] P.S. Ganesh, B.E. Kumara Swamy, Voltammetric investigation of catechol and hydroquinone at triton X-100 modified carbon paste electrode, *Anal. Bioanal. Electrochem.* 8 (2016) 615–628.
- [56] A.B. Teradale, S.D. Lamani, B.E. Kumara Swamy, P.S. Ganesh, S.N. Das, Electrochemical investigation of catechol at poly(niacinamide) modified carbon paste electrode: a voltammetric study, *Adv. Phys. Chem.* 2016 (2016) 8092860 (8).
- [57] P.S. Ganesh, B.E.K. Swamy, Simultaneous electroanalysis of norepinephrine, ascorbic acid and uric acid using poly(glutamic acid) modified carbon paste electrode, *J. Electroanal. Chem.* 752 (2015) 17–24.
- [58] S. Skrzypek, W. Ciesielski, A. Sokolowski, S. Yilmaz, D. Kazmierczak, Square wave adsorptive stripping voltammetric determination of famotidine in urine, *Talanta* 66 (2005) 1146–1151.
- [59] B. Dogan, S.A. Ozkan, Electrochemical behaviour of carvedilol and its adsorptive stripping determination in dosage forms and biological fluids, *Electroanalysis* 17 (2005) 2074–2083.
- [60] S. Reddy, B.E. Kumar Swamy, H. Jayadevappa, CuO nanoparticle sensor for the electrochemical determination of dopamine, *Electrochim. Acta.* 61 (2012) 78–86.
- [61] S. Mehretie, S. Admassie, M. Tessema, T. Solomon, Voltammetric determination of paracetamol with poly(3,4-ethylenedioxythiophene) modified glassy carbon electrode, *Anal. Bioanal. Electrochem.* 3 (2011) 38–50.
- [62] H. Filik, G. Cetintas, A.A. Avan, S.N. Koc, I. Boz, Electrochemical sensing of acetaminophen on electrochemically reduced graphene oxide-nafion composite film modified electrode, *Int. J. Electrochem. Sci.* 8 (2013) 5724–5737.
- [63] A. Akkaya, C. Altug, N.K. Pazarlioglu, E. Dinckaya, Determination of 5-aminosalicylic acids by catalase-peroxidase based biosensor, *Electroanalysis* 21 (2009) 1805–1810.
- [64] C.V. Uliana, H. Yamanaka, G.S. Garbellini, G.R.S. Banda, Determination of 5-aminosalicylic acid in pharmaceutical formulations by square wave voltammetry at pencil graphite electrodes, *Quim Nova* 33 (2010) 964–967.
- [65] E.L. Beckett, N.S. Lawrence, R.G. Evans, J. Davis, R.G. Compton, Sono-electrochemically enhanced determination of 5-amino salicylic acid, *Talanta* 54 (2001) 871–877.
- [66] A. Anil Kumar, T. Shobarani, B.E. Kumar Swamy, P.S. Ganesh, Electrochemical oxidation of mesalazine drug at poly(glutamic acid) modified CPE, *Anal. Bioanal. Electrochem.* 9 (3) (2017) 328–339.
- [67] B. Negovic, B. Simunic, Determination of 5-aminosalicylic acid in pharmaceutical formulation by differential pulse voltammetry, *J. Pharma. Biomed. Anal.* 31 (2003) 169–174.