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

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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 administrated 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

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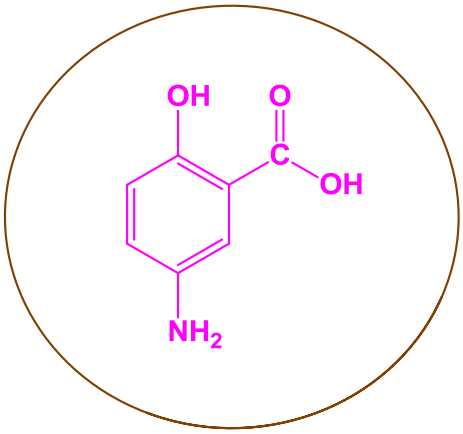

Scheme 1. Structure of mesalazine.

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 $NaH_2PO_4{\cdot}H_2O$ and Na_2HPO_4. Graphite powder of average particle size 50 μM 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}.