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Electrochemically deposited polyaniline/polypyrrole polymer film modified electrodes for determination of furazolidone drug

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A polyaniline/polypyrrole (PANI/PPy) polymer film was deposited on a tin oxide coated glass electrode, which was used to study electrochemical behaviour of furazolidone by cyclic voltammetric method. Two well-defined reduction peaks (c_1 at -0.358V and c_2 at -0.784V) and one oxidation peak were observed at 0.306 V. The results, compared with that of a glassy carbon electrode, indicate that reduction peak potential of furazolidone shifts in negative direction and reduction peak current increases significantly at PANI/PPy modified polymer film electrode. PANI/PPy polymer electrode, characterized by FT-IR spectroscopy, UV- vis spectroscopy, and SEM studies, was found stable and produced a pronounced response in long pH range (5-12). Resistance of polymer film was determined by I-V characteristics. Proposed polymer electrode gave satisfactory results in determination of furazolidone.

Keywords: Cyclic voltammetry, Furazolidone, Polyaniline (PANI), Polymer electrode, Polypyrrole (PPy)

Introduction

Chemically modified electrodes offer distinct advantages over conventional electrodes in electrocatalysis and electrochemical sensors[1-7]. Modified electrodes, which can lower over potential and increase sensitivity and selectivity of some electroactive species[8], find applications in rechargeable batteries[9-10], electrochemical devices**,** electrosynthesis[11], protective films for prevention of corrosion[12], electrochemical sensors[13], electrocatalysis[14-15,] and for electrochemical estimation of drugs and compounds of biological interest[16-21]. Conducting polymers[22] use thin films of polypyrrole (PPy) and polyaniline (PANI) due to their moderately high conductivity, low cost, relatively high stability and facile production by electrodeposition[23]. PANI shows high conductivity upon doping with simple bronstant acids[24]. PPy films doped with p-toluene sulphonate give good mechanical properties and chemical durability against aerial oxidation[25].

In present study, PANI/PPy modified polymer film has been used as electrode for investigation of furazolidone drug at lower concentrations.

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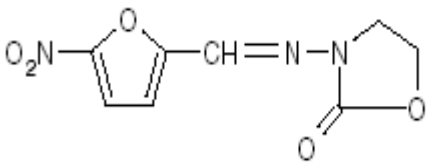
Materials and Methods

A PANI film doped with H_2SO_4 + $NaClO_4$ that improves electropolymerization efficiency[26] by electrochemical deposition on tin oxide coated glass slide was used as working electrode. On PANI film, PPy film doped with p-toluene sulphonate was deposited by electrodeposition at constant potential 0.8 V. Furazolidone (Scheme 1), is a highly effective chemotherapeutic drug, and widely used to control common infections in humans and animals. Some studies have been reported on the polarographic determination of furazolidone[27-29].

Instrumentation

Voltammetric measurements were performed using Eg & G Princeton applied research model 273 and potentiostate was controlled by electrochemistry software 4.30A. Three-electrode setup was equipped with a PANI/PPy working electrode, an Ag/AgCl reference electrode,



Scheme 1—Furazolidone

and a platinum-wire counter-electrode. pH of solutions was measured by Systonic pH meter Decibel Instrument (DB-1011). All measurements were carried out at room temperature (27-30°C).

Reagents and Solutions

Both pyrrole (99%) and aniline (99.8%) were procured from Aldrich chemicals and redistilled. All solutions and supporting electrolyte [dimethylformamide (DMF)] were of analytical grade and prepared using ultra pure water. Tin oxide was deposited on glass slide using chemical vaporization technique. Furazolidone solutions were prepared immediately before use and were purified by passing nitrogen gas. pH was adjusted with phosphate buffer solutions. Ionic strength was kept constant with aqueous 1M KCl.

Preparation and Activation of PANI/PPy Working Electrode

PANI films were deposited on glass slide, which is previously coated with tin oxide (deposited by chemical vapor deposition technique), by cyclic voltammetric technique in an H type cell. For electrochemical deposition, tin oxide coated glass slide was used as working electrode, Ag/AgCl reference electrode and graphite rod as counter electrode. Sulphuric acid (H_2SO_4 10^{-1} M) and sodium perchlorate ($NaClO_4$ 10^{-2} M) were used as doping agents for PANI formation. Voltage applied was (-0.3) V to (+1.4) V and aniline concentration was 0.2 M. On this pre-existing PANI film, PPy film (pyrrole concentration, 0.2 M) was deposited electrochemically by constant potential coulometry method at constant potential (0.8 V) and the film was allowed to grow till 15 coulomb charge was accumulated. Amount of supporting electrolyte, p-toluene sulphonate was 0.1 M. All films were prepared in aqueous media and stored in air at room temperature. To obtain a more sensitive and stable voltammetric response, working electrodes were cyclically scanned 20 times in the potential range of (-1.6) V to (+ 1.2) V.

Preparation and Analysis of Drug Sample

Ten furazolidone (Furoxone GSK pharmaceutical, India) tablets (100 mg each) were powdered in a mortar. Furazolidone ($1x10^{-3}$ M) were weighted and dissolved in DMF. Flask contents were sonicated for 15 min for complete dissolution. After excipients have settled down, an aliquot of clear supernatant was transferred quantitatively into a calibrated flask and diluted (10 ml) with DMF. Furazolidone was determined by cyclic voltammetric procedure.

Characterization

Particle morphology of all samples was observed by scanning electron microscopy (SEM). Current–voltage graph calculated resistance of the film. In order to make current–voltage observation contacts were taken on the polymer films with the help of silver paint, to which a DC voltage power supply was connected. Voltmeter (Multimeter Philips) was placed parallel to the polymer film and ammeter (Simpson) was placed in series with the circuit. Resistance of polymer film was evaluated from slope of I-V graph. UV-Vis absorption spectra (190-800 nm) were recorded on a Simadzu UV-240 spectrophotometer at room temperature. FTIR spectra of polymer in KBr pellets were recorded on an IR Prestige-21-FTIR (200 VCE) Shimadzu (Japan).

Results and Discussion

Scanning Electron Microscopic (SEM) Studies

SEM images indicate growth of PPy membrane along PANI chain in a granular pattern (Fig. 1). PPy (particle size, 6-10 ¼m) had globular structure. Grain size varied due to variation in PANI and PPy chain. SEM shows a rough surface, which provides large reaction surface[30].

I-V Characteristics

Electrochemically prepared PANI/PPy films with silver contacts exhibit ohmic behaviour (Fig. 2), consistency and linearity in I-V characterization. Resistance (1.66 KΩ) evaluated from the slope of I-V graph indicates semiconducting behaviour of PANI/PPy polymer film.

UV–vis Spectroscopic Studies

Polymer electrode was dissolved in 1-methyl 2-pyrrolidone. Dissolved solution was transferred to quartz tube of Shimatzu spectrometer for recording the spectrum. For the sake of comparison, spectra of all constituents [PANI (Fig. 3A), PPy (Fig. 3B) and both (Fig. 3C)] are recorded. PANI/PPy samples present characteristic bands of PANI (~263 nm, ~344 nm, and ~450 nm, which are attributed to π-π*, polaron-π* and π-polaron transitions respectively). π-π* transition corresponding to PPy shows band at ~291 nm.

FTIR

FTIR spectra of PANI/PPy polymer films are compared with PANI and PPy films separately (Fig. 4). Characteristic peaks of PANI at ~3446.78 cm^{-1}(N-H stretching) ~1591cm^{-1}(C=C stretching vibrations of the ring), ~1506 cm^{-1}(C=N stretching of the quinoid di-imine

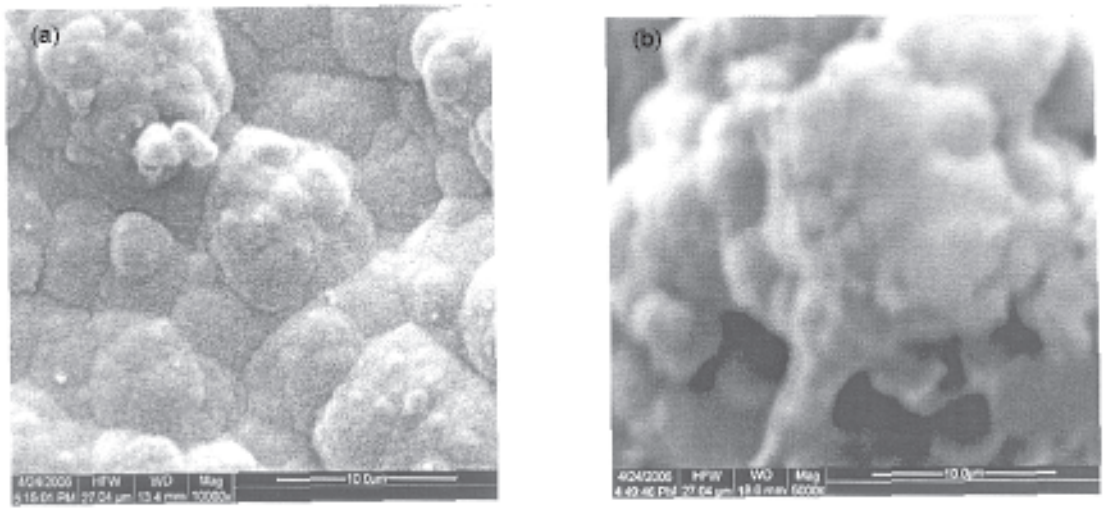


Fig. 1—SEM image of PANI/PPy composite polymer film at magnification of; a) 5000x; b) 10,000x

Fig. 2– Current–voltage characteristic of PANI/PPy polymer film

unites), ~1305 cm^{-1} (C-N radical cation stretching vibrations), ~1271cm^{-1} (C-N stretching of benzene diamine unites) and 1138 cm^{-1}(C-H bending of the qunioid ring). PPy in PANI/PPy films appear in FTIR spectra by showing characteristic peaks at ~ 3446.78 cm^{-1} (N-H stretching of polypyrrole), ~2924 cm^{-1} refer to stretching vibration of C-H, ~1445 cm^{-1} and 1384 cm^{-1} corresponding to ring vibration of pyrrole ring, and ~ 552 cm-1(N-H out of plane banding). The peaks at ~ 1036 cm^{-1} (asymmetric S (= O) $_2$ stretching) 1157cm^{-1} (symmetric S (=O) 2 stretching) and various strong bands at for S-O-C stretching confirm the presence of P toluene sulphonate. The band at ~ 658 cm^{-1} (C-Cl absorption) shows presence of perchlorate ion.

Electrochemical Behaviour of Furazolidone Drug at Polyaniline/Polypyrrole Polymer Film Modified Electrode

Cyclic voltammogram of furazolidone was examined at various pH (2.0-12.0). Furazolidone shows two reduction and one oxidation peak, a reversible peak corresponding to RNO_2 (c_1 and a_1) with a subsequent more negative 3e-irreversible peak (Fig. 5-a) due to RNHOH (C_2 without any reversible peak) according to the following mechanism:

$$RNO_2 + e^- \rightleftharpoons RNO_2^-$$

$$RNO_2^- + 3e^- + 4H^+ \rightarrow RNHOH + H_2O$$

Effect of different scan rate on electrode process was studied by recording cyclic voltammograms at various sweep rates (25-250 mV/s). Reduction peak is shifted to more negative potential and oxidation peak towards positive potential with increase in scan rate (Fig. 5b). Cyclic voltamogram of furazolidone at different concentration are shown in Fig. 5c. Peak current increased proportionally with square root of scan rate (Fig. 6), which confirmed the diffusion controlled nature of electrode process. Voltammetric response was markedly depend on pH. Furazolidone response was obtained until pH 12.0 [Fig. 7 (inset)]. A plot of peak current vs concentration (Fig. 8) was found linear in lower concentration range.

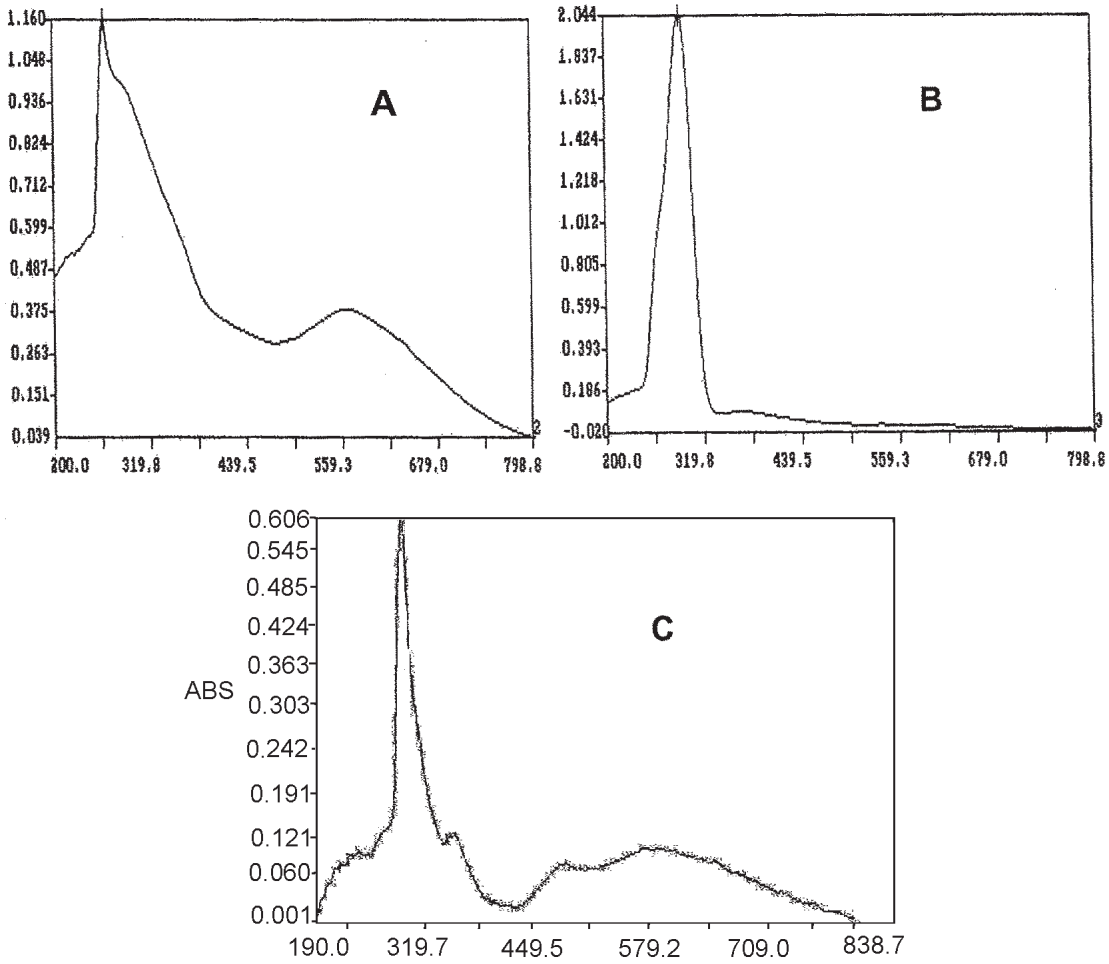


Fig. 3—UV-vis spectra of: (A) PANI deposited by CV (-0.3 V-+1.0 V) at tin oxide coated glass electrode doped with H_2SO_4 + $NaClO_4$; (B) Polypyrrole film deposited at tin oxide coated glass slide electrode at constant potential 0.8 V doped with P- toluene sulphonate; and (C) PANI/PPy polymer film successively deposited each other by electrochemical deposition

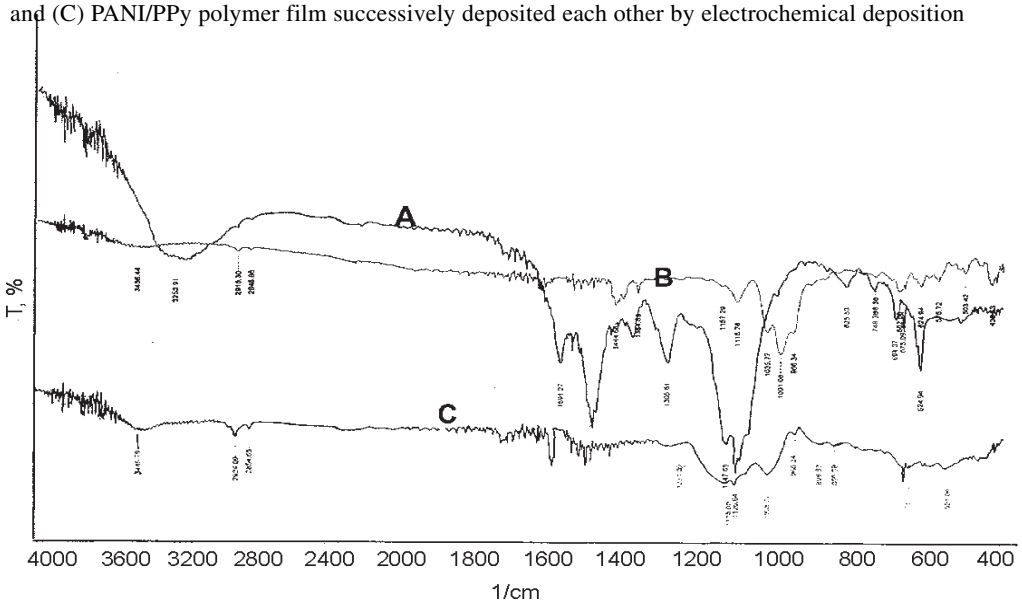
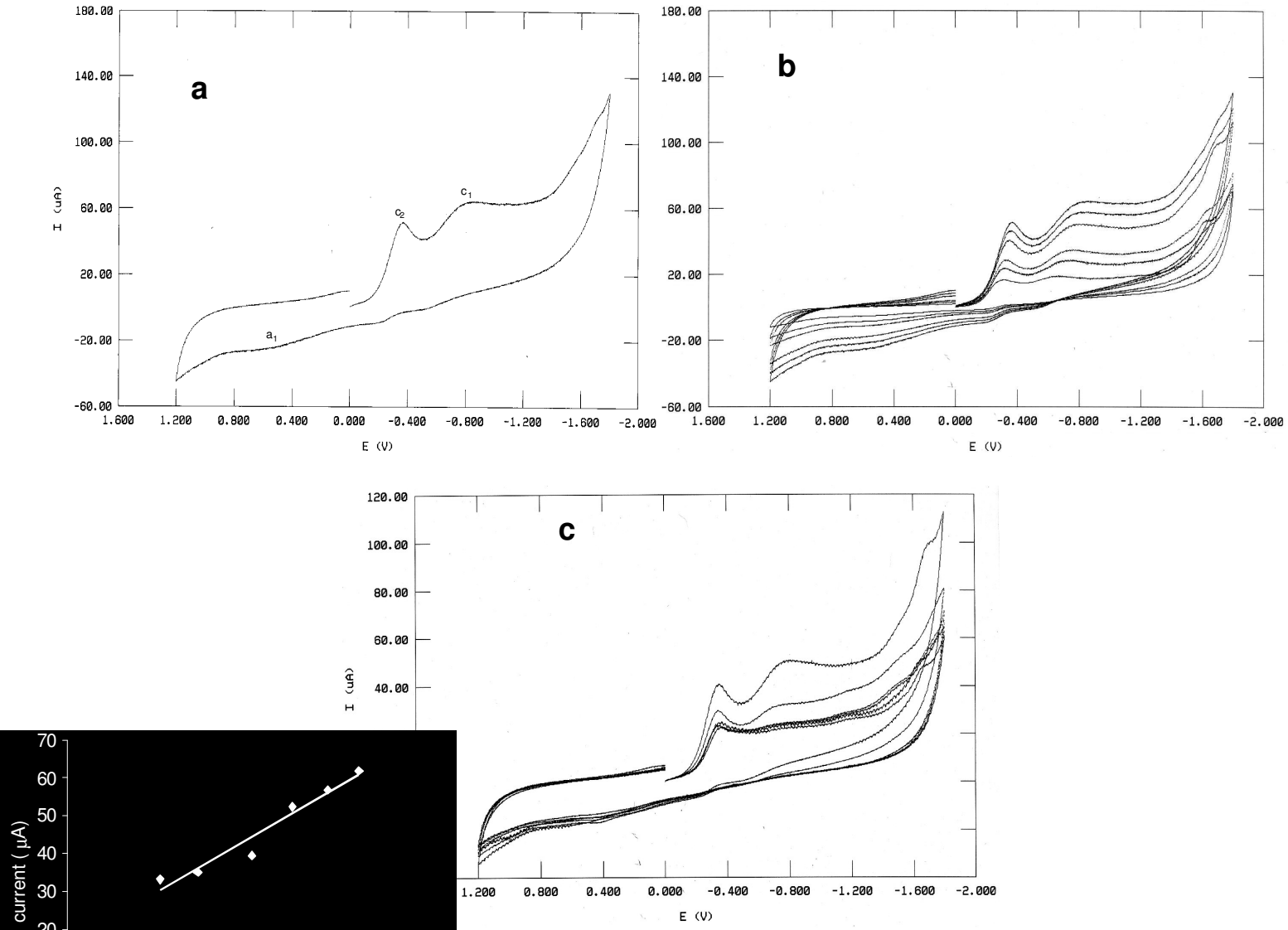


Fig. 4—FTIR spectra of: (A) PANI doped with H_2SO_4+$NaClO_4$; (B) PPy doped P-toluenesulphonate; and (C) PANI/PPy polymer film



of furazolidone at PANI/PPy polymer film modified electrode in phosphate buffer
n rate 50 mV/ S (b) different scan rate on pH 7.0 at $5x10^{-4}$ M concentration
t concentration $5x10^{-3}$ - $2x10^{-4}$ M at pH 7.0 and scan rate 50 mV/ S

Fig. 6—Dependence of peak current on square root of scan rate ($v^{1/2}$) at PANI/PPy modified polymer electrode of $1x10^{-4}$ M solution of furazolidone at pH 7.0

Comparison of PANI/PPy Polymer Film Modified Electrode with Different Electrode Materials

Four different types of electrode materials were used to study electrochemical behaviour of furazoliodne. PANI film doped with H_2SO_4 + $NaClO_4$ was not found stable against DMF solution, which was used as solvent for furazolidone drug. PPy film doped with p-toluene sulphonate did not reveal any peak and indicates no electrochemical behaviour against furazolidone. Glassy carbon (GC) electrode exhibits good electrochemical response against furazolidone in cyclic voltammetry, but on comparing current response at different concentrations (Figs 8 and 9), PANI/PPy polymer electrode shows better response than GC electrode.

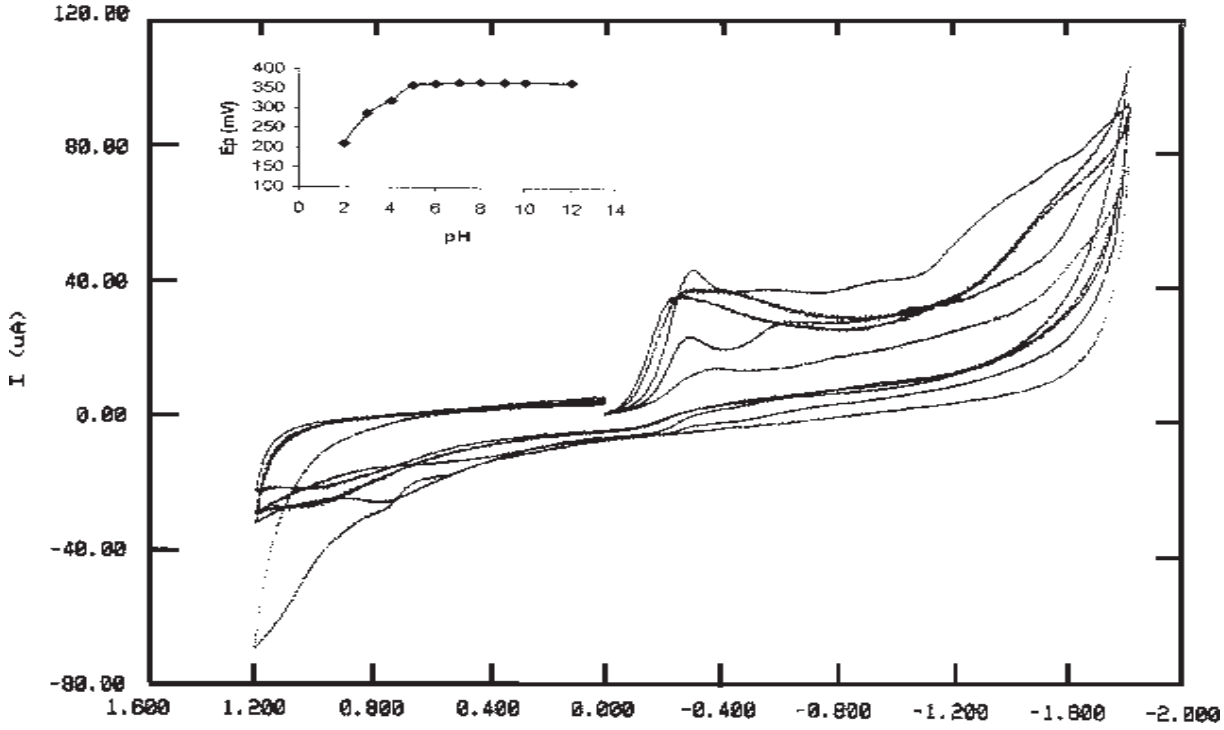


Fig. 7—Cyclic voltamogram of furazolidone at PANI/PPy polymer film modified electrode in phosphate buf fer at different pH

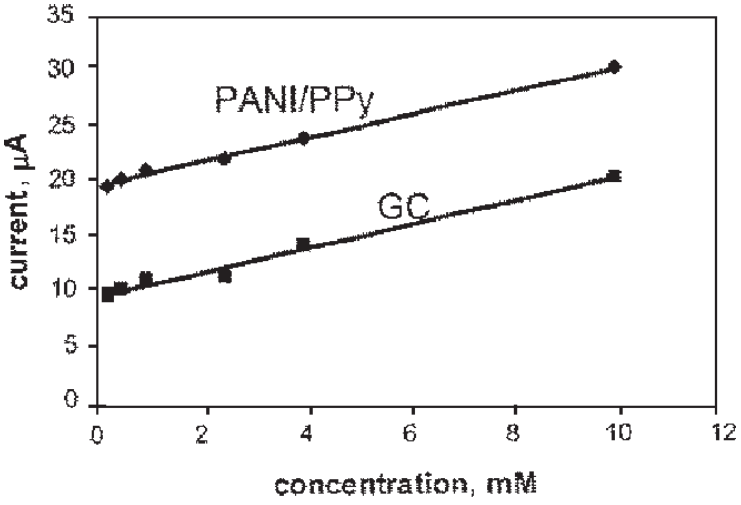


Fig. 8—Comparative behaviour of furazolidone current response at different concentration on PANI/PPy polymer film modified electrode with GC electrode at pH 8.0

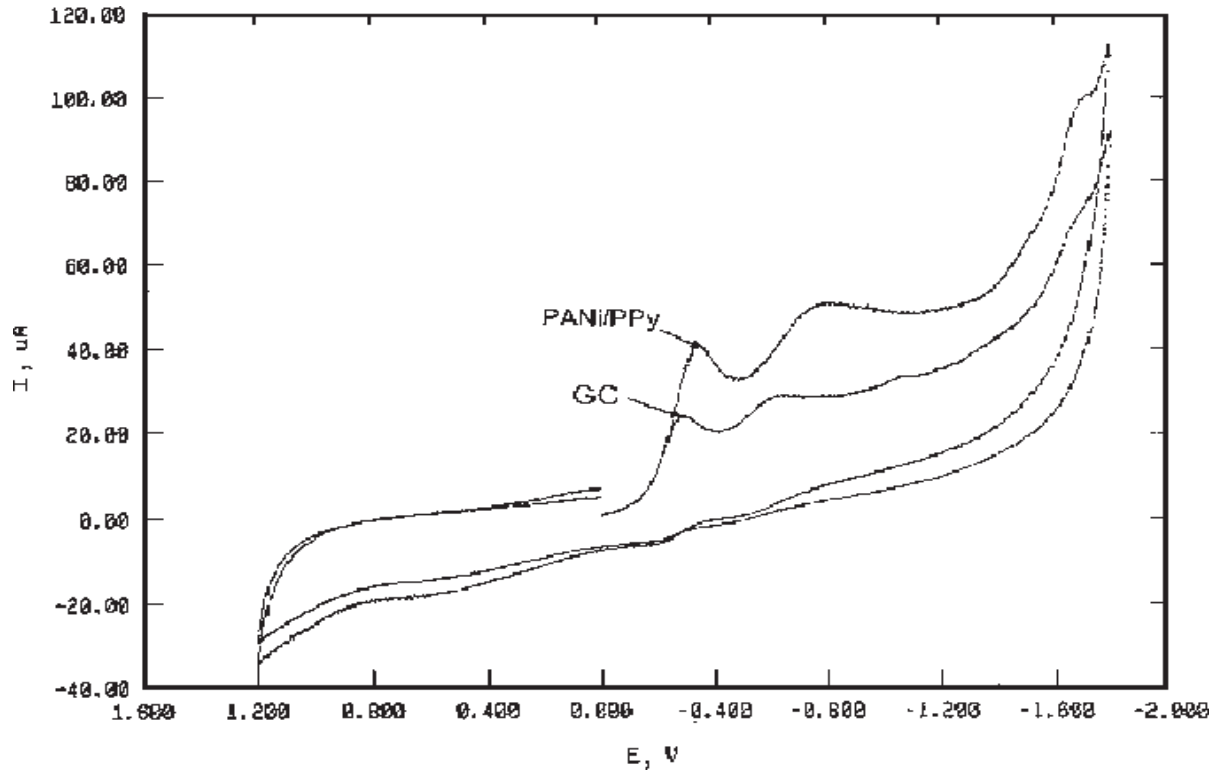


Fig. 9—Behaviour of furazolidone at PANI /PPy polymer film modified electrode and with GC electrode at pH 8.0

Analytical Application

Two reduction peaks (c_1 -0.358 V and c_2 at -0.784 V) and one oxidation peak (+0.306 V) can be obtained by GC electrode, but better current response is achieved by PANI/PPy polymer electrode. Peak current of reproducible c_1 depended directly on furazolidone concentration up to lower concentration. Peak c_1 is therefore chosen as the analytical signal and a voltammetric method for determination of furazolidone was proposed.

Conclusions

Electrochemically deposited PANI/PPy on tin oxide coated glass slide indicates good current response for voltammetric determination of furazolidone drug over GC electrode. SEM studies show rough surface with increase in surface area for electrochemical reactions. I-V characteristic of composite film was linear indicating semiconducting behavior of newly developed electrode, which also shows good adherence to the substrate. PANI/PPy polymer film modified electrode provides a sensitive and selective method of furazolidone analysis, and become good analytical alternative for determining furazolidone in pharmaceutical formulations.

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