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Original Article

A novel poly (glycine) biosensor towards the detection of indigo carmine: A voltammetric study

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ABSTRACT

The electrochemical behavior of indigo carmine (IC) at poly (glycine) modified carbon paste electrode (PGMCPE) was investigated by cyclic and differential pulse voltammetry. The oxidation peak of IC was observed in phosphate buffer of pH 6.5. The influence of different pH, scan rate, and concentration were analyzed. The probable reaction mechanism involved in the oxidation of IC was also proposed. Results showed that PGMCPE a remarkable electrocatalytic activity for the oxidation of IC under optimal conditions. The electrocatalytic response of the sensor was proportional to the IC concentration in the range of $(2 \times 10^{-6} - 1 \times 10^{-5} \text{ M})$ and $(1.5 \times 10^{-5} - 6 \times 10^{-5} \text{ M})$ with a limit of detection $11 \times 10^{-8} \text{ M}$ and limit of quantification $3.6 \times 10^{-7} \text{ M}$. The modified electrode demonstrated many advantages such as simple preparation, high sensitivity, low detection of limit, excellent catalytic activity, short response time, and remarkable antifouling property toward IC and its oxidation product.

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1. Introduction

Indigo carmine (5,5'-indigodisulfonic acid sodium salt) dye is used in food industry, cosmetics industries and also for dyeing of denim and polyester fibers [1,2]. Indigo carmine is a highly toxic which might cause irritations vomiting and diarrhea to human beings. Waste water from textile industries frequently contains significant amounts of non-biodegradable dyes [3,4]. Most of these dyes are toxic and potentially carcinogenic in nature and their removal from the industrial effluents is a major environmental concern [5].

Monitoring trace or ultra trace IC in natural environment, biological and other real samples is very important, since the

ingestion of IC can lead to toxicosis, affecting first the liver and later the central nervous system, kidneys and eyes. Because the concentration of IC is extremely low in various natural samples, a selective and sensitive method for reliable determination of IC would be of great interest [6,7].

Cyclic voltammetry (CV) is the most widely used technique for acquiring qualitative information about electrochemical reactions. The power of CV results from its ability to rapidly provide considerable information on the thermodynamics of redox processes and the kinetics of heterogeneous electron transfer reactions and on coupled chemical reactions or absorption processes [8–21]. CV is often the first experiment performed in an electrochemical study. In particular, it offers a rapid location of redox potentials of the electroactive

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species, and convenient evaluation of the effect of media on the redox process [22,23].

The carbon paste electrode has been used to determine some chemical compounds in different literatures, as modified electrode to enhance electrochemical study [24–28]. An electrochemical detection used to analysis most compounds in the previous studies [29–33].

Development of a new method capable of determining IC amount in pharmaceutical and biological dosage forms is important. Electroanalytical techniques have been used for the determination of a wide range of biomolecules compound with the advantages that there is no need for derivatization and that these techniques are less sensitive to matrix effects than other analytical techniques. Additionally, application of electrochemistry includes the determination of electrode mechanism. Redox properties of molecules can give insights into their metabolic fates or their in vivo redox processes or pharmacological activity. The goal of this work was the development of new voltammetric method for direct determination of IC. This paper describes fully validated, simple rapid and sensitive procedures for the determination of IC employing DPV and CV. This work was also aimed to study the voltammetric behavior and oxidation mechanism of the cited IC using this technique.

2. Experimental

2.1. Reagents

All chemicals were used as received without further purification. Indigo carmine received from Moly Chem Mumbai, Silicone oil, Glycine, Monosodium phosphate, Disodium phosphate, Graphite (150 mesh) were obtained from Nice chemicals, Cochin, India. Stock solution of IC (25×10^{-4} M), Glycine (25×10^{-3} M) were in double distilled water. Phosphate buffer solution was prepared by mixing the suitable amount of 0.2 M monosodium phosphate and 0.2 M disodium phosphate.

2.2. Apparatus

Voltammetric experiments were performed using a model EA-201 Chemilink system (EA-201 Chemilink system, Mumbai, India). A conventional three-electrode system was used with a carbon paste electrode (3 mm diameter CPE), a KCl-saturated calomel reference electrode (SCE), and a Pt wire as the counter electrode. A digital pH meter (Equiptronics, Mumbai, India) was employed for the preparation of the buffer solutions which were used as the supporting electrolyte in voltammetric experiments. All experiments were carried out at room temperature (25 °C).

2.3. Preparation of bare carbon paste electrode

The bare carbon electrode was prepared by hand mixing of graphite powder and silicon oil in the ratio of 70:30 (w/w) in an agate mortar until a homogenous paste was obtained. The prepared carbon paste was tightly packed into a PVC tube (3 mm internal diameter) and the electrical contact was provided by a copper wire connected to the paste at the end of the tube.

2.4. Preparation of poly (glycine) modified CPE

Electrode construction was the electropolymerization of the 1 mM glycine was placed in the electrochemical cell containing 0.2M PBS (pH 5.7). The BCPE (bare carbon paste electrode) was pretreated by scanning in the solution from 500 to 1800 mV at 100 mV s^{-1} for 10 times. The electropolymerization of poly (glycine) film was carried out with CV and the voltammograms, as shown in Fig. 1. The poly (glycine) modified CPE after polymerization was rinsed with water and used for the determination of IC.

3. Results and discussions

3.1. Characterization of the modified electrodes

The surface morphology of bare carbon paste electrode and poly (glycine) modified carbon paste electrode is characterized by Field Emission Scanning Electron Microscopy. The surface of BCPE (Fig. 2a) was irregularly shaped. However, the PGMCPPE (Fig. 2b) is more compact and uniform because of the covering of thin poly (glycine) film on the CPE.

3.2. Optimization of experimental parameters

The number of electropolymerization cycles was investigated (data not shown). The oxidation current increased dramatically as the polymerization cycles were raised from 6 to 10 and then decreased after 10 cycles. The phenomenon could be associated with the increasing thickness of the composite film, which hindered the transfer of electron on the electrode surface. Therefore, 10 electropolymerization cycles were selected in this work.

3.3. Repeatability and long-term stability of the modified electrode

The repeatability of the analytical signals was studied and relative standard deviation (RSD) of 0.96% for ten consecutive

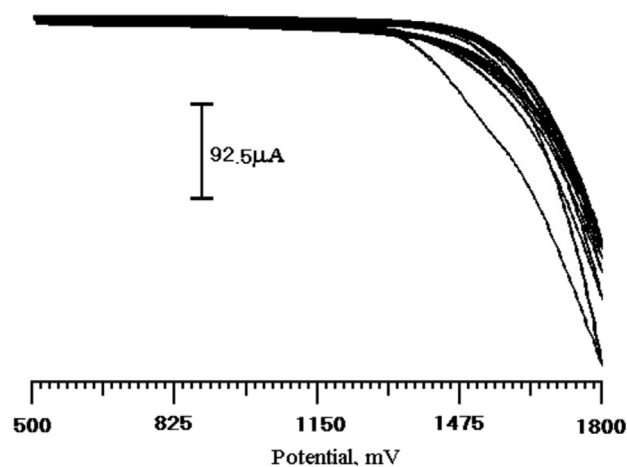


Fig. 1 – Continuous 10 cyclic voltammograms for the electrochemical polymerization of 1×10^{-3} M glycine on a CPE in 0.2 M PBS (5.7 pH) at the scan rate 100 mV/s.

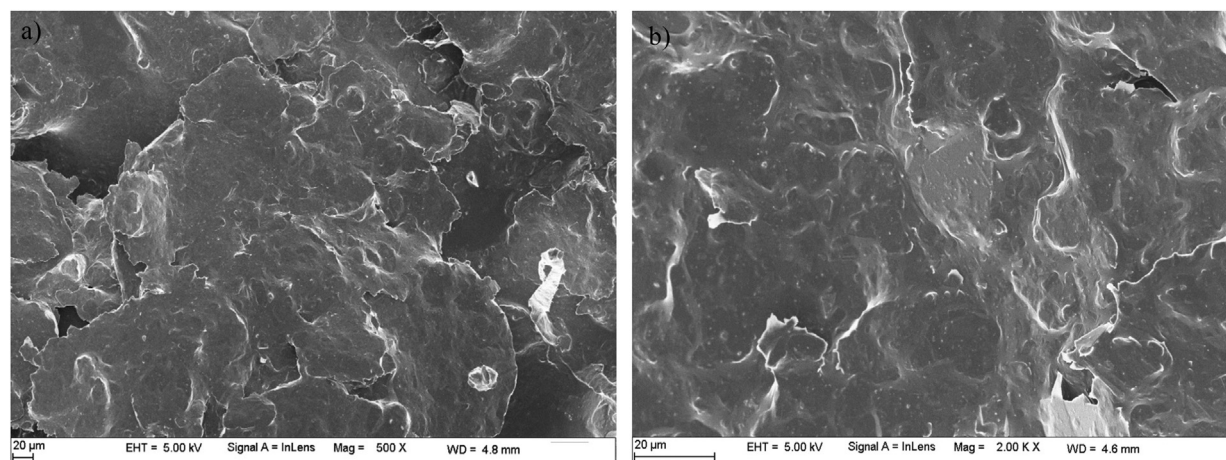


Fig. 2 – FESEM images of (a) BCPE (b) PGMCPPE.

determinations of the 1×10^{-4} M IC solution were obtained. These small values indicate that the PGMCPPE is not subject to surface fouling by the oxidation products. The proposed modified electrode has a further attraction of good long-term stability. This was tested by measuring the decrease in voltammetric current during repetitive CV measurements of IC solution with the PGMCPPE stored in air for 20 days. When the electrode was stored in the atmosphere for 20 days, the oxidation peak current of IC were reduced less than 4.2%.

3.4. Electrochemical behaviors of IC

Electrooxidation of IC at the PGMCPPE with PBS at pH 6.5 in the presence (dashed line) and absence (solid line) of IC is characterized by CV which is an electrochemical measuring technique used for electrochemical analysis or for the determination of the kinetics and mechanism of electrode reactions (Fig. 3). Within the potential window from 150 to 600 mV, there is no observable redox peaks for a PGMCPPE. However, upon addition of 1×10^{-4} mol/L IC, a well-defined and sensitive redox peaks appears at 436 mV and 358 mV.

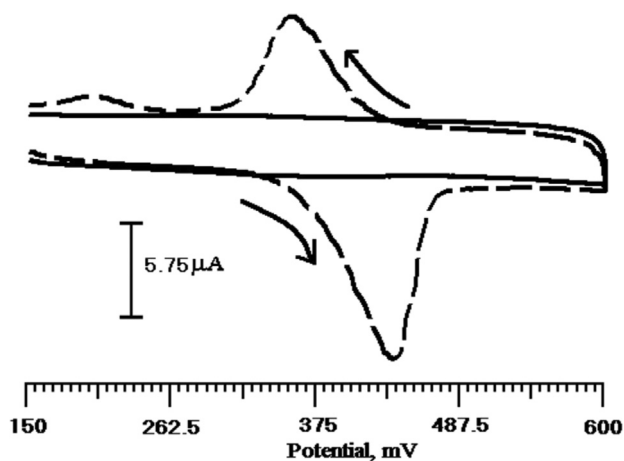


Fig. 3 – A typical cyclic voltammograms of PGMCPPE with IC (1×10^{-4} M) (dashed line) in pH 6.5. PBS without 1×10^{-4} M IC (solid line) at pH 6.5 PBS.

This parameter indicates, the electrode response was proportional to the oxidation of the electroactive species produced. Above results shows that the PGMCPPE, which increase the electroactive surface area of the electrode, increases the electrocatalytic activity for IC oxidation and reduction of the IC. Oxidation and reduction mechanism explained in Fig. 4 [34].

3.5. Electrochemical behavior of IC at PGMCPPE

Fig. 5 shows the CVs of IC in pH 6.5 PBS at BCPE and PGMCPPE. As can be seen, at BCPE, IC shows a sluggish and much small CV peak response. Quasi-reversible voltammogram was observed for IC at BCPE (dashed line) with cathodic peak current (I_{pc}) and anodic peak current (I_{pa}). The cathodic peak potential and (E_{pc}) and anodic peak potential (E_{pa}) were located at 0.435 V and 0.355 V respectively. The potential difference of two reversible peaks was found to be 0.080 V. On modification with poly (glycine) the voltammogram has shown enhancement in both I_{pc} and I_{pa} (solid line). The E_{pa} and E_{pc} were found at 0.436 V and 0.358 V and potential difference was 0.078.

Further, substantial increases in peak current were also observed due to the improvements in the reversibility of the electron transfer processes and the larger real surface area of the film. This suggests an efficient oxidation reaction of IC at PGMCPPE.

3.6. Electrocatalytic oxidation of IC by DPV

Fig. 6 depicts the DPV responses from the electrochemical oxidation of 1×10^{-4} M IC at PGMCPPE (dashed line) and BCPE (solid line). As can be seen, the anodic peak potential for the oxidation of IC at PGMCPPE is about 407 mV and at the BCPE peak potential is about 433 mV for IC. From these results it is concluded that the best electrocatalytic effect for IC oxidation is observed at PGMCPPE. The results are shown that the peak potential of IC oxidation at PGMCPPE shifted by about 26 mV toward the negative values compared with BCPE and there is a dramatic enhancement of the anodic peak current at PGMCPPE. In the other words, the data obtained clearly show that the PGMCPPE definitely improve the characteristics of IC oxidation.

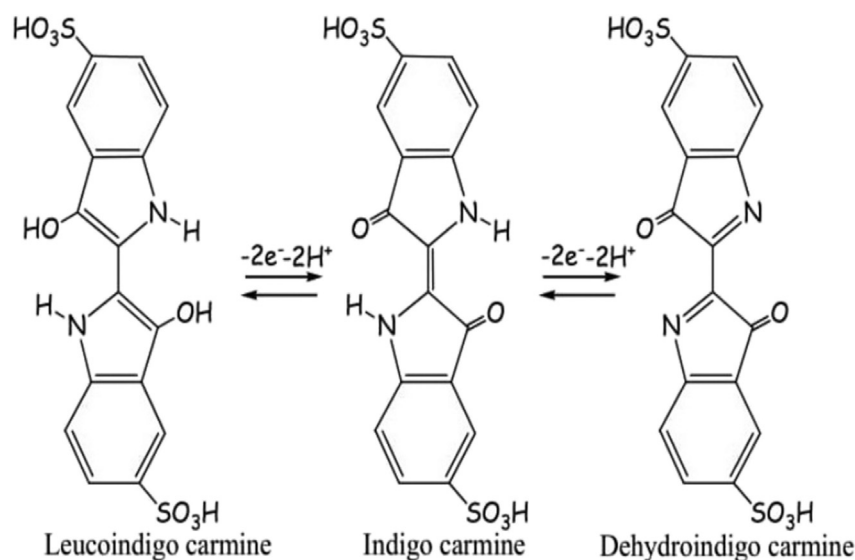
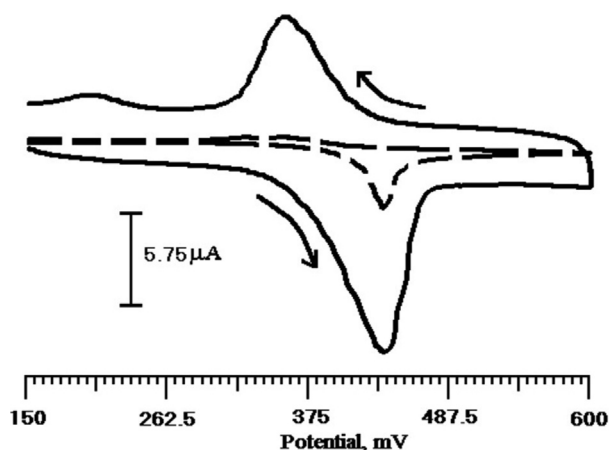
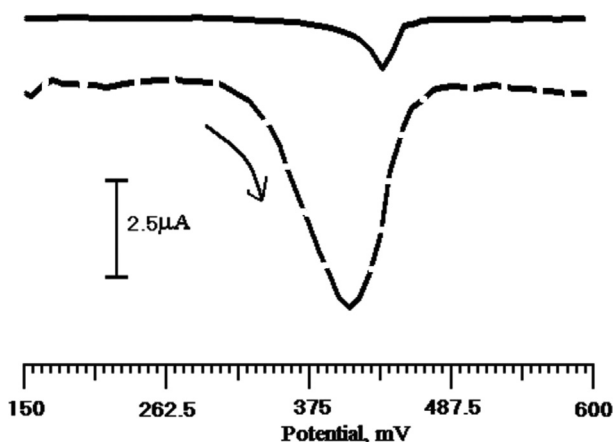


Fig. 4 – The scheme of oxidation of IC.

Fig. 5 – (a) Cyclic voltammograms of IC (1×10^{-4} M) in 0.2 M phosphate buffer solution of pH 6.5 at BCPE (dashed line) and PGMCPPE (solid line).Fig. 6 – DPVs of a solution containing IC (1×10^{-4} M) in 0.2 M PBS (pH 6.5) at the BCPE (solid line), the PGMCPPE (dashed line).

3.7. The effect of scan rate on the electrochemical response of IC

The effect of scan rate on the electrochemical response of 1×10^{-4} mol/L IC was also investigated in the range from 100 to 400 mV s^{-1} and the results were shown in Fig. 7a. It can be seen that with the increase of the scan rate, the redox peak current increased gradually along with the slight shift of redox potential. The relationship of redox peak currents with the scan rates was constructed and the results showed the redox peak currents were proportional to the scan rate in the range from 100 to 400 mV s^{-1} , which indicated the electron transfer reaction of IC on the PGMCPPE was adsorption controlled process in the solution [35]. The electrochemical parameters of the IC on the PGMCPPE were further calculated. From Fig. 7b, it can be seen that the redox peak potentials were also moved with the increase of the scan rate and the peak-to-peak separation increased. A linear relationship between the peak current with the scan rate was established and straight line were got with linear regression equation as $I_{pa} (\text{mA}) = 3.145 + 0.10844 V (\text{mV s}^{-1})$ ($R = 0.99912$) [29].

3.8. Supporting electrolyte and pH

The IC has different electrochemical behaviors in different electrolytes. The effects of some electrolytes on peak currents of IC were studied. The results show that IC has the best electrochemical responses in PBS. When the measurements were performed in this electrolyte, the largest peak current, the lowest background current and the best shape of peak were obtained. We studied the electrochemical behavior of IC in 0.2 M PBS with various pHs (5.5–8.0) at the surface of PGMCPPE using cyclic voltammetry for determination of IC (Fig. 8a). This study showed that the electrocatalytic peak current and peak potential depended on the solution pH. It can be seen that the anodic peak current of IC reach a maximum value at pH 6.5 and then decrease gradually with increasing of pH (Fig. 8b). Therefore, pH 6.5 was taken as the

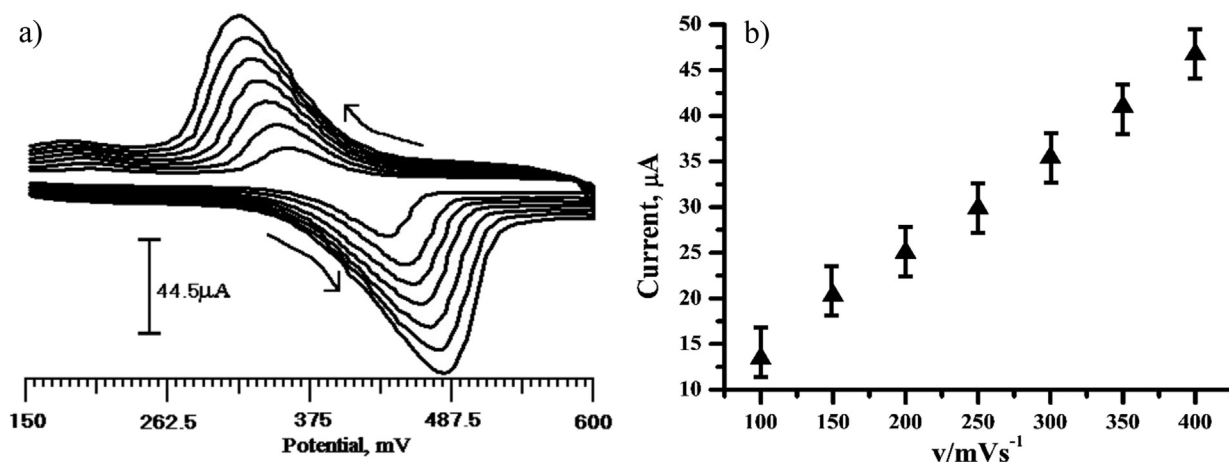


Fig. 7 – (a) Cyclic voltammograms of IC (1×10^{-4} M) at the PGMCPe in pH 6.5 PBS at various scan rates. From: 100, 150, 200, 250, 300, 350 and 400 mV/s. (b) Plot of the peak current of IC as a function of the scan rate.

optimum pH for the determination of IC. Also, the anodic peak potential of IC at the surface of this modified electrode shifts to less positive values with increasing pH of the buffered solution. As shown in Fig. 8c, a linear shift of the reduction peak potential (E_{pc}) towards negative potential with an increase in

pH indicated that protons are directly involved in the oxidation of IC, and that it obeys the following equation: E_{pc} (mV) = $-61.02 \text{ pH} + 759.276$ ($r = 0.997$). A slope of 61 mV per pH, this behavior was obeyed the Nernst equation for equal number of electron and proton transfer reaction [31].

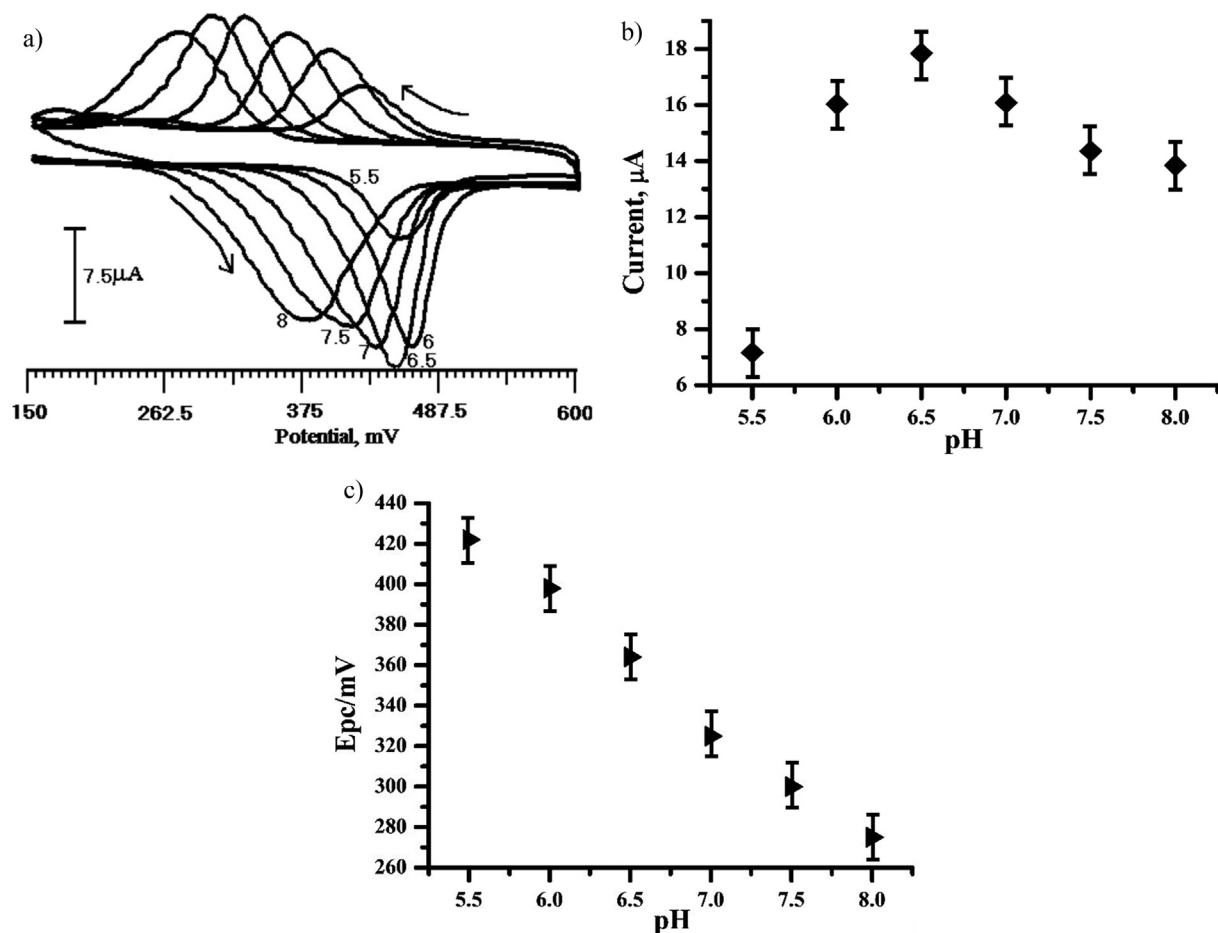


Fig. 8 – (a) Cyclic voltammograms obtained at the PGMCPe in 0.2 M PBS in pH values, (a) 5.5 (b) 6 (c) 6.5 (d) 7 (e) 7.5 (f) 8 containing IC (1×10^{-4} M). (b) Plot of anodic peak current vs. pH (5.5–8.0) of IC (1×10^{-4} M) at the PGMCPe. (c) Plot of E_{pc} vs pH for IC.

3.9. Calibration curve

Cyclic voltammetry was used to investigate the current response of IC at the carbon paste electrode in the concentration range from 2×10^{-6} to 6×10^{-5} M. It is found that the oxidation peak current increase linearly with the increase of IC concentration, moreover, the oxidation peaks shift gradually towards more positive potential. The calibration curve for the IC is established using the proposed voltammetric procedure after its accumulation on the surface of the electrode (Fig. 9). The two linearity is observed in the concentration range from 2×10^{-6} to 1×10^{-5} M and 1.5×10^{-5} M to 6×10^{-5} M with a limit of detection 11×10^{-8} M and limit of quantification 3.6×10^{-7} M ($S/N = 3$) [29]. Variation of peak current (I_p) with the concentration of IC gives a straight line following the equation: $I_p = 2.27 \times 10^{-7} + 0.1645C$ ($r = 0.999$). The detection compared with other reported electrodes [36–39], the PGMCPPE had some advantages, such as low detection limits, long linear ranges and wide peak separations (Table 1).

3.10. Application of PGMCPPE to the detection of IC in real sample

In order to illustrate the applicability of the sensor for real sample analysis, indigo carmine (Indigotindisulfonate) injection was selected as the real sample to investigate the reliability of the proposed method using the standard addition method. Indigo carmine was purchased from a medical store.

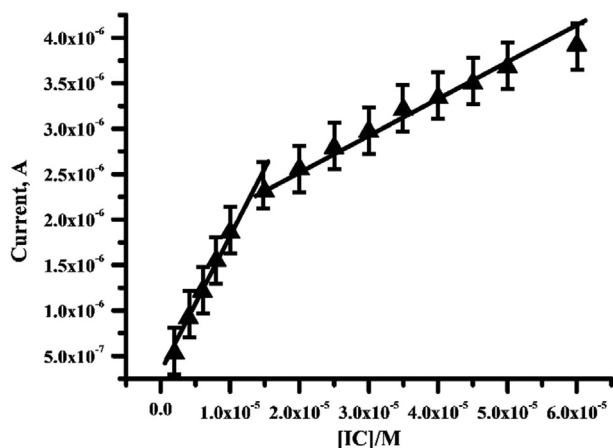


Fig. 9 – Calibration plot for the determination of IC at the PGMCPPE in pH 6.5 PBS with the scan rate 100 mV/s.

Table 1 – The comparison of PGMCPPE with some other methods for the determination of IC.

Methods	Linear range (mol/L)	Detection limits (mol/L)	Reference
Resonance Rayleigh scattering	2×10^{-6} – 32×10^{-6}	2.4×10^{-8}	[36]
Spectrophotometric	1.7×10^{-6} – 39×10^{-6}	2.5×10^{-8}	[37]
LC-APCI-MS	2.1×10^{-7} – 21×10^{-7}	6.2×10^{-8}	[38]
SERRS	1×10^{-8} – 1×10^{-5}	1.9×10^{-5}	[39]
Cyclic voltammetry	2×10^{-6} – 6×10^{-5}	11×10^{-8}	This work

Prior to measurements, samples were diluted with 0.2 M PBS without any pre-treatment process. The recovery were in the range of 98.25–105.15% with a relative standard derivation (RSD, $n = 5$) of less than 3.8%, indicating the applicability and reliability of the proposed method.

4. Conclusions

A simple PGMCPPE was used in combination with the CV and DPV technique to develop a novel and alternative electroanalytical method for IC determination through the oxidation of the IC compound. The proposed approach showed excellent performance and great potential for application in control procedures. IC was successfully determined with a limit of detection 11×10^{-8} M and limit of quantification 3.6×10^{-7} M which is comparable to those obtained using carbon electrodes. This low detection limit indicates that the proposed electroanalytical method is attractive and also suitable for trace analysis. In addition, due to the simplicity of the preparation procedures, fast routine determination can be achieved by this method.

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