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Full Paper

Surfactant Immobilized Electrochemical Sensor for the Detection of Indigotine

Chenthattil Raril,¹ Jamballi G. Manjunatha,^{1*} Lingappa Nanjundaswamy,² Gurumallappa Siddaraju,³ Doddarasinakere K. Ravishankar,⁴ Santosh Fattepur⁵ and Eshwarappa Niranjana⁶

¹*Department of Chemistry, FMKMC College, Madikeri, Mangalore University Constituent College, Karnataka, India*

²*UGC - Human Resource Development Centre, University of Mysore, Manasagangotri, Mysore-570 006, Karnataka, India*

³*Department of Chemistry, JSS College for women Chamarajanagar, Karnataka, India*

⁴*Department of Chemistry, Sri. Mahadeshwara govt. First Grade College, Collegial, Chamarajanagar, Karnataka, India*

⁵*School of Pharmacy, Management and science university, Malaysia*

⁶*Department of Engineering Chemistry, S. J. M Institute of technology, Chitradurga, Karnataka, India*

*Corresponding Author, Tel.: +91-08272228334

E-Mail: manju1853@gmail.com

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Abstract- A highly sensitive electrochemical sensor for Indigotine (IG) detection was fabricated at a carbon paste electrode (CPE) modified with TX-100 surfactant. The electrochemical behavior of IG was studied at TX-100 modified carbon paste electrode (TX-100MCPE). The effect of different pH values, scan rate and effect of concentration was also studied using cyclic voltammetry. It was noticed that under optimized condition (pH 6.5) a well-defined redox peak with the higher current response was obtained for IG at TX-100MCPE compare to bare carbon paste electrode (BCPE). The modified electrode exhibited an excellent electrochemical activity towards the oxidation of IG. The electrochemical response of IG is linearly observed in the range of 1.5×10^{-6} M to 2×10^{-5} M, with the detection

limit and limit of quantification of 16×10^{-8} M and 5.3×10^{-7} M. The modified electrode showed good sensitivity ($0.085 \mu\text{A}/\mu\text{M}$) and stability and was employed for the determination of IG in the real sample.

Keywords- Carbon paste electrode, TX-100, Indigotine, Electrochemical determination

1. INTRODUCTION

Indigotine (IG) is a purplish – blue powder synthetic aromatic heterocyclic compound used as a dye in cosmetic and food industries [1], and as a redox indicator [2]. The recent study shows that IG causes a potential risk to human health and can cause permanent injury to the cornea; diarrhea and excess intake of IG can cause tumors [3-4]. So it is essential to develop a new method with high sensitivity, simplicity, and efficiency for the detection of IG. Over the past decades, many analytical methods have been employed like Spectrophotometry [5] thin layer chromatography [6], High-performance liquid chromatography, Electroanalytical method [7-12] have been used for the determination of IG. Compare to all these methods electrochemical methods have received good interest because of their low cost, good sensitivity, rapidity etc.

In recent years chemically modified electrodes become most popular among the scientist because of their potential application in various analyses [13-17]. Modification of carbon paste with different modifier has reported in recent years. TX-100 which is a non-ionic surfactant contains an aromatic hydrophobic group and hydrophilic polyethylene oxide chain. The application of TX-100 has widely reported [18-21] and has introduced to improve the detection limit of some biologically active molecule.

Cyclic Voltammetric (CV) [22] is an electrochemical method and has found to be very sensitive for the determination of electroactive species (organic molecules, drugs, biological fluids etc.) and without any limitation; CV can be applied to all electrochemical reaction. With the help of this method, it is very easy to find out the potential at which the type of reaction occurs.

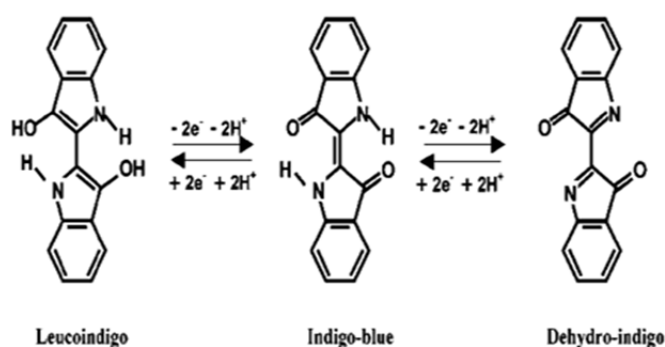


Fig. 1. Scheme of oxidation mechanism of IG

There are many literatures has reported for the determination of azodyes [23-31], but no literature was reported on the voltammetric method for the determination of IG at TX-100MCPE. In this paper, we report that the development of a TX-100MCPE by immobilization technique and studied the behavior of IG towards the modified electrode by the voltammetric method. It has been observed that modified electrode showed good sensitivity and selectivity towards the determination of IG at low-level concentration. The oxidation mechanism was shown in Fig. 1.

2. EXPERIMENTAL

2.1. Apparatus and Chemicals

A potentiostat (EA-201 electroanalyser, Mumbai, India) was used to carry out the electrochemical experiment. A conventional three - electrode set up with the saturated calomel electrode (SCE), Pt wire, TX-100MCPE were used as reference, auxiliary and working electrode. All the solutions were prepared with distilled water. Graphite, silicone oil, purchased from Nice Chemicals, India. IG (25×10^{-5}) obtained from Molychem India Pvt. Ltd. Phosphate buffer solution (0.2 M) was prepared by mixing the suitable amount of 0.2 M monosodium phosphate and 0.2 M disodium phosphate. All the experiments are carried out under room temperature ($25 \pm 1^\circ\text{C}$).

2.2. Development of the electrodes

Carbon paste was prepared by hand mixing of graphite powder and silicone oil at the ratio of 70/30 (w/w) in an agate mortar and pestle for homogeneous mixture and was packed into the cavity of Teflon tube (3 mm diameter). The electric contact was provided by a copper wire connected paste in the inner hole of the tube. The TX-100MCPE prepared by immobilizing 10 μL of TX-100 on the surface of the carbon paste electrode for 5 minutes and is washed with distilled water.

3. RESULTS AND DISCUSSION

3.1. Morphological studies

Surface morphology of BCPE and TX-100MCPE was studied using variable pressure scanning electron microscopy (VPSEM). Fig. 2 shows the VPSEM image of BCPE (a) and TX-100MCPE (b). The surface of BCPE shows irregular arrangements of graphite whereas the TX-100MCPE shows that the uniform surface which displays that the surface of the BCPE was mostly covered with surfactant TX-100. This shows that the CPE was successfully modified with TX-100.

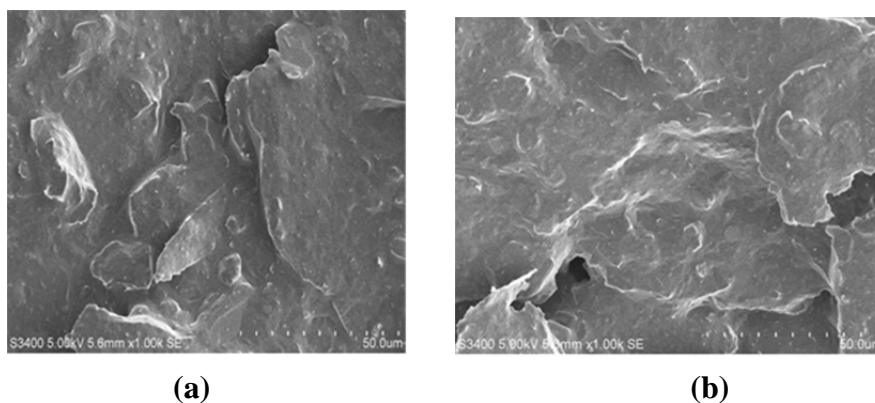


Fig. 2. VPSEM image of (a) BCPE and (b) TX-100MCPE

3.2. Electrochemistry of IG at TX-100MCPE

Fig. 3 shows the CVs of blank solution (solid line) and in the presence (dashed line) of 1×10^{-5} M IG at TX-100MCPE in the potential range from 0–800 mV at the scan rate of 100 mV/s in 0.2 M PBS (pH 6.5). There is no redox peak was observed for the blank solution. But a well-defined redox peak of IG was observed at the peak potential of 363 mV (E_{pa}) and 325 mV (E_{pc}) upon the addition of IG (1×10^{-5} M) with the redox peak current ($I_{pa}=3.51 \mu\text{A}$ and $I_{pc}=2.64 \mu\text{A}$). The behavior makes clear that good electrochemical response of IG at TX-100MCPE.

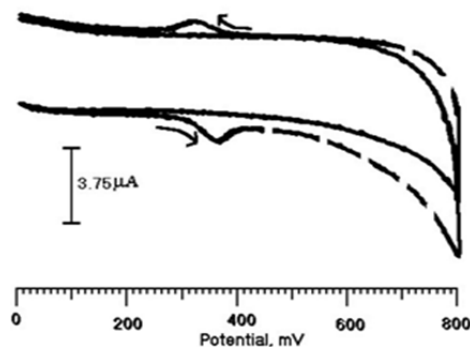


Fig. 3. Cyclic voltammogram of TX-100MCPE with IG (1×10^{-5} M) (dashed line) and without IG (solid line) in 0.2 M PBS, pH 6.5

3.3. Electrochemical behavior of IG at BCPE and TX-100MCPE

The electrochemical behavior of 1×10^{-5} M IG in 0.2 M PBS (pH 6.5) at the BCPE (solid line) and TX-100MCPE (dashed line) at the scan rate of 100 mV/s as shown in Fig. 4. The corresponding peak potential of 383 mV (oxidation peak potential, E_{pa}) with a Peak current (I_{pa}) of $1.36 \mu\text{A}$, and 346 mV (reduction peak potential, E_{pc}) with a peak current (I_{pc}) of $0.56 \mu\text{A}$ and the potential difference was found to be 37 mV for BCPE. For TX-100MCPE, peak potential was observed at 363 mV (E_{pa}) with the I_{pa} value of $3.51 \mu\text{A}$ and 325 mV (E_{pc}) with

the I_{pc} value of $2.64 \mu\text{A}$ and the potential difference was observed as 38 mV . Compare to BCPE E_{pa} shifted to more negative confirms that electrocatalytic ability of TX-100MCPE. It was observed that, at TX-100MCPE there was an increased peak current because of due to the improvement in the reversibility of the electron transfer process.

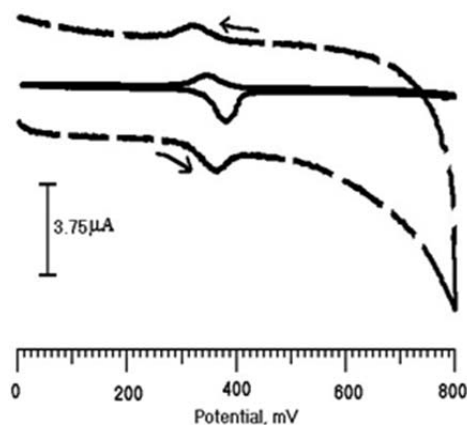


Fig. 4. Cyclic voltammogram of IG ($1 \times 10^{-5} \text{ M}$) in 0.2 M PBS of pH 6.5 at BCPE (solid line) and TX-100MCPE (dashed line)

3.4. Effect of scan rate and pH

The effect of scan rate on the oxidation of IG was examined by using CV by ranging sweep rate from $100\text{--}300 \text{ mV/s}$ containing $1 \times 10^{-5} \text{ M}$ IG in 0.2 M PBS (pH 6.5) in order to investigate the kinetics of electrode reaction and was shown in Fig. 5a. With the increase of scan rate, the anodic peak current was increased. It can be seen that a good linearity was observed between peak current and the scan rate with a regression equation $I_{pa} = -1.344 + 0.04823 \nu$ (Fig. 5b) with a coefficient of correlation of 0.99992 in the range from $100\text{--}300 \text{ mV/s}$. The result shows that the adsorption - controlled process on the surface of TX-100MCPE. Anodic peak potential was shifted to more positive side as the increase of scan rate (ν) and having a linear relation with $\log(\nu)$ with a regression equation of $E_{pa} (\text{mV}) = 58.343 \log(\nu) (\text{mVs}^{-1}) + 247.27$ (Fig. 5c). The relationship between E_{pa} and $\log \nu$ defined by the following equation:

$$E_{pa} = K + [2.3 RT / (1-\alpha) n F] \log(\nu) \quad [32]$$

Where α is the charge transfer coefficient, and was calculated from Tafel equation, as follows, $E_p = b/2 \log(\nu) + K$, where ν is the scan rate, b is the Tafel slope, K is a constant value. The slope of the E_{pa} Vs. $\log \nu$ was 58.34. Therefore the Tafel slope will become 116.68. The charge transfer coefficient was calculated and obtained as 0.74, and the number

of electrons involved in the oxidation reaction has calculated and is $2.02 \sim 2.0$. The result was in accordance with the mechanism that has explained in Fig. 1.

The electrochemical response of IG was studied in 0.2 M PBS with different pH (6.0-8.0) values at the TX-100MCPE containing 1×10^{-5} M of IG at the scan rate of 100 mV/s, and cyclic voltammogram was shown in Fig. 6a. It was observed that anodic peak potential was shifted towards negative potential (381 mV to 273 mV) with increase of pH from 6.0 to 8.0. The optimum current response was observed when the pH reached 6.5, and was taken for whole experiment.

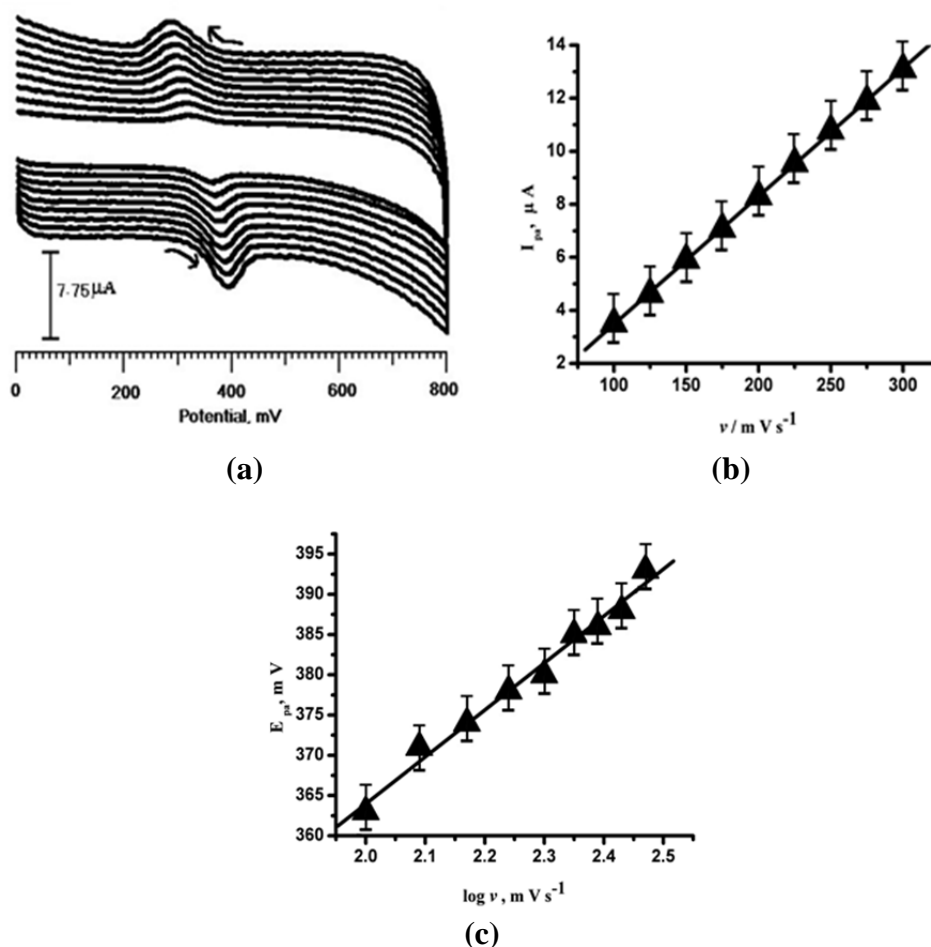


Fig. 5. (a) Cyclic voltammogram of IG (1×10^{-5} M) at TX-100 MCPE in pH 6.5 at various scan rates (100, 125, 150, 175, 200, 225, 250, 275, 300 mV/s); (b) anodic peak current (I_{pa}) Vs scan rate; (c) E_{pa} Vs $\log v$

The relationship between E_{pa} Vs. pH expressed as follows: $E_{pa} = 715.8 - 55.4 \text{ pH}$ ($R = 0.99284$) (Fig. 6b) and the relation between I_{pa} Vs. pH was shown in Fig. 6c.

The slope of 55.4 mV/ pH is close to the theoretical value 59 mV/ pH shows that the number of proton and electrons involved in the reaction of IG are equal. As the IG oxidation is two –electron process, the number of protons involved is also predicted to be two.

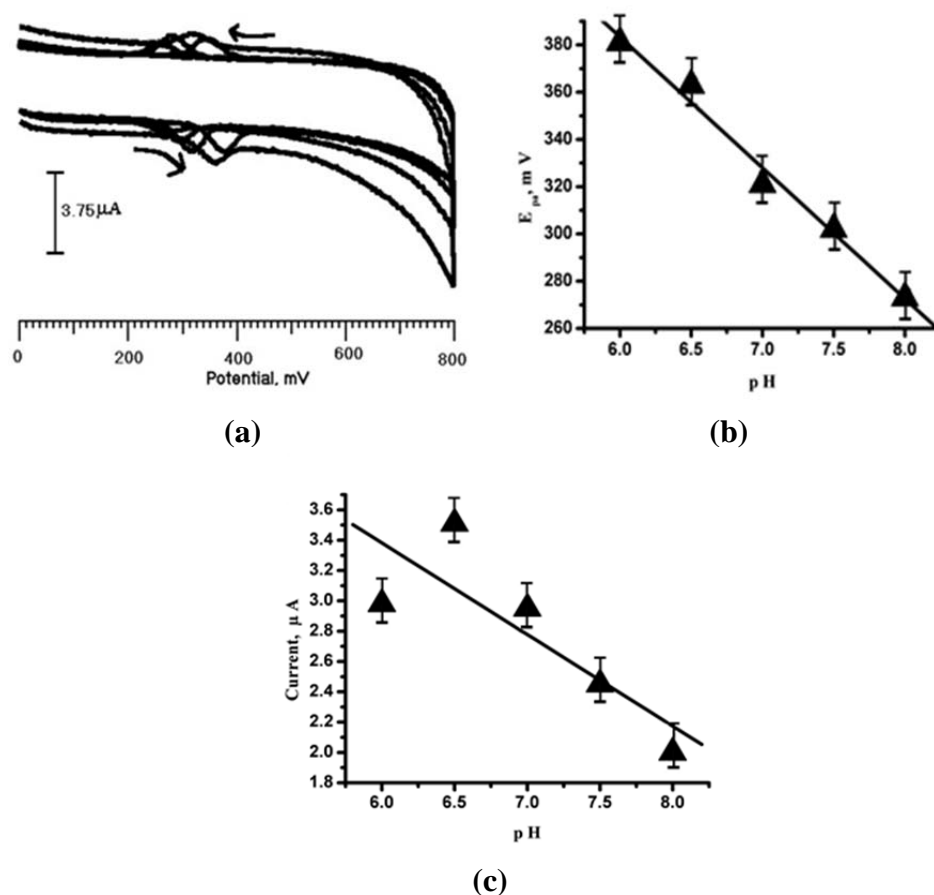


Fig. 6. (a) Cyclic voltammogram at TX-100MCPE in 0.2 M PBS in different pH values (a) 6.0 (b) 6.5 (c) 7.0 (d) 7.5 (e) 8.0 containing IG (1×10^{-5} M); (b) Plot of anodic peak potential (E_{pa}) Vs pH at TX-100MCPE; (c) anodic peak current (I_{pa}) Vs pH for IG.

3.5. Effect of concentration of IG and detection limit

The effect of various concentration of IG at TX-100MCPE was shown in Fig. 7 and was observed that current response was linearly increased with the increase of IG concentration in the range from 1.5×10^{-6} M to 2×10^{-5} M range with the slope value of 0.089 ($\mu\text{A}/\mu\text{M}$). The graph between concentration and anodic peak current was drawn and was proportional with the regression equation of $I_{pa} = 1.79 \times 10^{-6} + 0.08956 C$ ($R = 0.99034$). The detection limit and limit of quantification were found at the value of 16×10^{-8} M and 5.3×10^{-7} M. The detection limit and limit of quantification was calculated by using following equation, $\text{LOD} = 3S/M$ and $\text{LOQ} = 10S/M$, Where S is the standard deviation and M is the slopes obtained from the calibration plot. The detection limit obtained with different modified electrodes for the determination of IG was compared and listed in Table.1 [33-36].

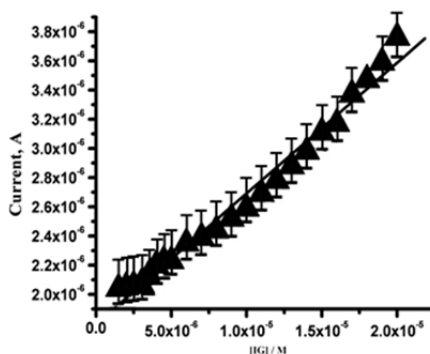


Fig.7. Effect of concentration of IG on TX-100MCPE at 0.2 M PBS having pH 6.5 PBS with the scan rate 100 mV/s

Table. 1 Comparison of the proposed electrode with other electrodes for the determination of IG

Electrodes	Method	Linear range(M)	Detection limit(M)	Ref.
PGMCPE	CV	2×10^{-6} - 6×10^{-5}	11×10^{-8}	[28]
NBE/CPE	DPV	1×10^{-6} - 1×10^{-4}	36×10^{-8}	[29]
SPE	CV	5×10^{-7} - 1×10^{-4}	20×10^{-8}	[30]
SPCE	CV	5×10^{-7} - 1×10^{-4}	19×10^{-8}	[31]
TX-100MCPE	CV	1.5×10^{-6} - 2×10^{-5}	16×10^{-8}	This work

PGMCPE: Polyglycine modified carbon paste electrode, (NBE/CPE): 4-(4-nitrophenylazo) N-benzyl,N-ethylaniline carbon paste electrode, SPCE: Screen printed carbon electrode, SPE: Screen printed electrode

3.6. Electrochemical behavior of IG by DPV

DPV which gives good current sensitivity and better quality than CV technique because it will minimize the migration current. Fig. 8 shows the DPV response of IG (1×10^{-5} M) at the BCPE and MCPE in 0.2 M PBS (pH 6.5) in the potential window from 0 to 800 mV at the scan rate of 50 mV/s with pulse amplitude of 20 mV, pulse width of 60 msec and pulse interval of 200 msec. Oxidation peak potential of IG was observed at the peak potential of 356 mV and of BCPE was observed at 364 mV. It was found that there was an increase in the peak current at TX-100 MCPE compare to BCPE. This shows that the MCPE improves the oxidation of IG.

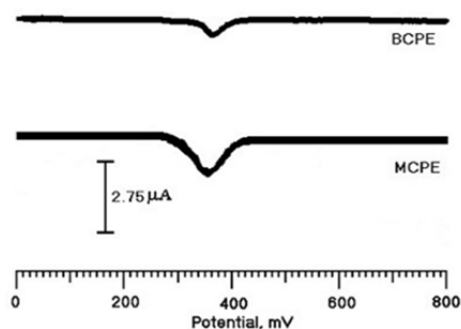


Fig. 8. DPV of a solution containing IG (1×10^{-5} M) in 0.2 M PBS at the BCPE and TX-100 MCPE

3.7. Electrochemical investigation of repeatability and stability

Repeatability and stability of the prepared TX-100MCPE towards IG at the fixed concentration (1×10^{-5} M) was investigated in 0.2 M PBS (pH 6.5) at the scan rate of 100 mV/s by CV. Repeatability of the modified electrode was investigated based on 5 replicates and was observed as 3.6% (RSD), indicating the good repeatability of the modified electrode. Stability of the developed electrode was studied by 40 consecutive cycles (graph not shown), 93% of the initial current signal was retained after 40 cycles, shows the electrode having good stability.

3.8. Determination of IG in real samples

In order to investigate the applicability of the fabricated electrode for the determination of IG in the real sample, candy coated-chocolate was selected, and it was purchased from the local market. The chocolate was grounded into powder, dissolved in water and then further diluted. Standard addition method was used for measuring. It was observed that the recoveries were in the range from 98.9% to 104.6%. Determination of IG in local tap water and laboratory wastewater samples was also performed. However, no analyte can be detected in tap water and laboratory wastewater.

Table 2. Recovery result for IG in water samples

Sample	Detected (μM)	Added (μM)	Found (μM)	Recovery (%)
1	ND	200	198.24	99.12
2	ND	250	251.75	100.70
3	ND	300	295.86	101.39

Then different standard concentration of IG was added 5 ml of water sample. The amount of IG in water sample was determined, and the results are listed in Table 2. The recoveries were in the range from 99.12% to 101.39%. This confirms that the proposed modified electrode can apply for the determination of IG in the chocolate sample and in local water samples with a satisfactory result.

4. CONCLUSION

This work explains the ability of TX-100MCPE for the electrochemical determination of IG. It was observed that there was an enhanced activity of IG towards TX-100MCPE compared to BCPE. Electrocatalytic oxidation of IG at TX-100MCPE occur about 363 mV which is less positive than BCPE. Under optimised condition the peak current was observed in the linear range from 1.5×10^{-6} M to 2×10^{-5} M with the detection limit of 16×10^{-8} M and limit of quantification of 5.3×10^{-7} M. The modified electrode shows good repeatability, stability and good sensitivity with the low detection limit, which makes the modified electrode useful for the quantitative analysis of IG in the real sample with the satisfactory result.

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