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Fabrication of the Tartrazine Voltammetric Sensor based on Surfactant Modified Carbon Paste Electrode

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ABSTRACT

In this paper, TX-100 modified carbon paste electrode (TX-100MCPE) was fabricated for the resolution of tartrazine (TZ). The modified electrode showed magnificent electrocatalytic activity towards TZ. Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) was used to characterize the electrochemical properties of modified electrodes. CV studies point out that the oxidation of TZ at the modified electrode surface was irreversible, adsorption controlled, and reaction which involves one electron transfer. The effects of different experimental parameters like pH, Scan rate, Concentration on the voltammetric response of TZ were investigated. After optimizing the experimental parameter, the oxidation peak current of TZ was linear to its concentration in the range of 6×10^{-6} to 1×10^{-4} M, and the detection limit was 11.14×10^{-7} M. The modified electrode was found to be, inexpensive, provide good stability and reproducibility.

Keywords: *Tartrazine, Carbon paste electrode, TX-100, cyclic voltammetry, Differential pulse voltammetry*

INTRODUCTION

Color is a major assign when it comes to food choices. Food colorants are added to food to enhance its appealing, and its applicability. TZ is an orange-colored, water soluble, Synthetic azodye widely used in food products, drugs, and pharmaceuticals. Synthetic azodyes with aromatic structures were harmful to human health [1]. TZ can cause diarrhea, anxiety, allergies and even cancer if they overly ingest [2-3]. It became an analytical challenge because of increasing the legal restriction.

There are many methods have been used for the resolution of TZ such as spectrophotometry [4] high-performance liquid chromatography [5] and capillary electrophoresis [6] and electrochemical techniques [6-9].

The Electrochemical methods traditionally have found broad applications in sample analysis due to the short analysis time, low power consumption and inexpensive equipment. CV is the most widely used electroanalytical technique for the qualitative information about electrochemical reactions.

Carbon electrodes are widely used in electroanalysis due to their wide potential window, chemical inertness, low cost and suitability for various sensing detection applications [10-20]. Among these carbon electrodes, carbon paste electrode (CPE) was widely used because due to the low cost, obtaining a new reproducible surface, etc. There for over the past decades, CPEs containing various modifiers was widely used and applied in the resolution of different analytes [21-23]. CPEs can provide a suitable electrode substrate for preparation of modified electrode.

There are a number methods reported for the resolution of TZ using various modified electrodes includes poly (p-amino benzene sulfonic acid)/Zinc oxide nanoparticle [24] Multiwalled carbon nanotube modified pyrolytic graphite electrode [25], nanogold modified carbon paste electrode [26], etc.

The surfactant has been widely used in chemistry. Due to its distinct structure and being surface active, surfactants are used in the electrochemical investigation. The modification of electrode by surfactant increases the electron transfer rate and also improves the detection limit. In this study, an electrochemical sensor was developed based on TX-100 surfactant modified with carbon paste electrode for the resolution of TZ.

The electrochemical behavior of TZ was studied by using CV and DPV. The oxidation mechanism of TZ was irreversible, and one electron reaction on TX-100MCPE was shown in Figure.1 [27].

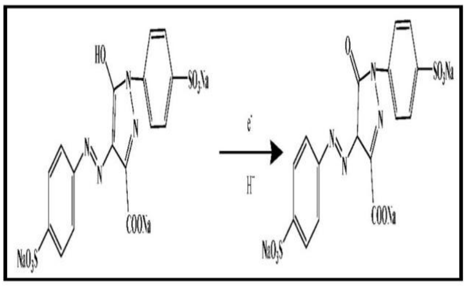


Fig1. *Scheme of oxidation mechanism of TZ*

EXPERIMENTAL CHEMICALS AND REAGENTS

TX-100, Graphite, Silicone oil, TZ were obtained from nice chemicals Pvt. Ltd. TX-100 stock solution (25×10^{-3} M) was prepared by using distilled water. TZ was analytical grade and used without further purification. TZ stock solution (25×10^{-4} M) was prepared by dissolving in distilled water. Phosphate buffer solution (PBS) was prepared by mixing disodium phosphate (0.1 M) and monosodium phosphate (0.1 M). Distilled water was used throughout the preparation of solutions.

INSTRUMENTATION

CV and DPV were obtained using CHI-6038 electrochemical analyzer in conjugation with a conventional three-electrode system and a personal computer for data storage and processing. The bare and TX-100MCPE used as the working electrode, saturated calomel electrode (SCE) as a reference electrode and a platinum wire as the auxiliary electrode. All the experiments carried out at room temperature.

FABRICATION OF BCPE AND TX-100MCPE

The bare carbon paste electrode (BCPE) was made by mixing 70% graphite powder and 30% silicone oil in an agate mortar and pestle for about 15 min to get a homogeneous carbon paste. Prepared paste was packed into the hole of a teflon tube (3 mm in diameter), and the surface of the electrode was made to uniform with the help of a tissue paper. TX-100MCPE was prepared by immobilizing 10 µL of TX-100 on the surface of the electrode for 5 min.

RESULT AND DISCUSSION

Determination of Electrochemical Surface Area

The surface area can be calculated by using the Randles-Sevcik equation which is related to the peak current with the square root of scan rate. For irreversible reaction, $I_p=2.69\times10^5 n(\alpha n)^{1/2}AD^{1/2}Cv^{1/2}$, Where I_p is the peak current (A), n is the number of electrons, A is the electroactive area (cm^2), D is the diffusion coefficient (cm^2/s), C is the concentration of the electroactive species (mol/cm^3), and $v^{1/2}$ is the square root of scan rate (V/s).

Diffusion coefficient was obtained from the slope of I_{pa} Vs. $v^{1/2}$ (Data not shown). The surface area of the electrode is calculated using the Randles equation and acquired as 0.042 cm^2.

Electrochemical Response of TZ at TX-100MCPE

Figure.2 shows the CVs of the blank solution in 0.1 M PBS, pH 6.0. It was noticed that there was no anodic peak for the blank solution (b), but a large, intense peak (E_{pa}=0.921 V, I_{pa}=29.48 µA) was noticed in the presence of TZ (1×10^{-4} M) (a), gives the clear authentication of the well electrocatalytic effect of TZ at TX-100MCPE.

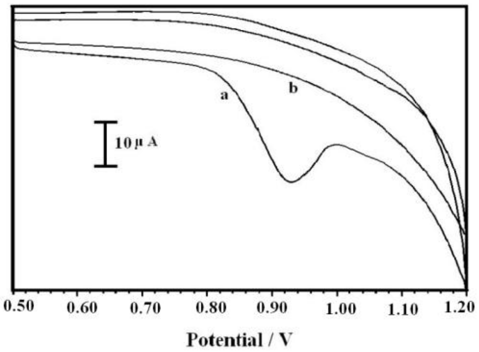


Fig2. *Cyclic voltammogram of TZ in the presence (a) and in the absence (b) of TZ (1×10^{-4} M) in 0.1 M PBS, pH 6.0 at the scan rate of 0.1 V*

The cyclic voltammogram for TZ in 0.1 M PBS at pH 6.0 at 0.1 V/s scan rate investigated in the potential window from 0.50 to 1.2 V. Figure. 3 show the cyclic voltammogram of TZ at BCPE (a) and TX-100MCPE (b).

At BCPE, a weak oxidation peak was observed at about 0.903 V with a low current response. However, the oxidation current of TZ (E_{pa}=0.921 V, I_{pa}=29.48 µA) at TX-100MCPE was higher than that of BCPE.

TZ exhibit only oxidation peak and no reduction peak were observed in reverse scan suggests that electrochemical reaction is a totally irreversible process. The oxidation of TZ molecules which shows more current response compared to BCPE due to the increase in surface area of the modified electrode which is rich in electroactive groups.

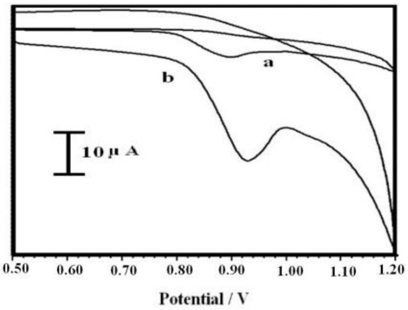


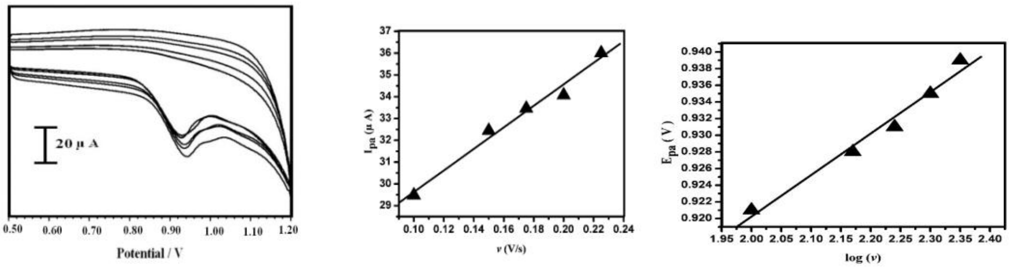
Fig3. *Cyclic voltammogram of TZ (1×10^{-4} M) in 0.1 M PBS, pH 6.0 at BCPE (solid line) and TX-100MCPE (dashed line).*

The Effect of Scan Rate and pH on Electrochemical Response of TZ at TX-100MCPE

Cyclic voltammogram of (1×10^{-4} M) TZ on TX-100MCPE at different potential scan rate was shown in Figure. 4a in the range from 0.1-0.225 V/s. in 0.1 M PBS (pH 6.0). With the increase of the scan rate, the oxidation peak current also increased gradually, indicating the direct electron transfer between TZ and TX-100MCPE surface. The anodic peak current (I_{pa}) of TZ was proportional to scan rate (v) with a linear regression equation I_{pa} (μA) = 24.69 + 49.40 v (V/s) with the correlation coefficient of 0.99 (Figure.4b), shows that the TZ oxidation was adsorption controlled. The relation between Peak potential (E_{pa}) and log (v) explained in the following equation,

$$E_{pa} = \frac{b}{2}(\log v) + k$$

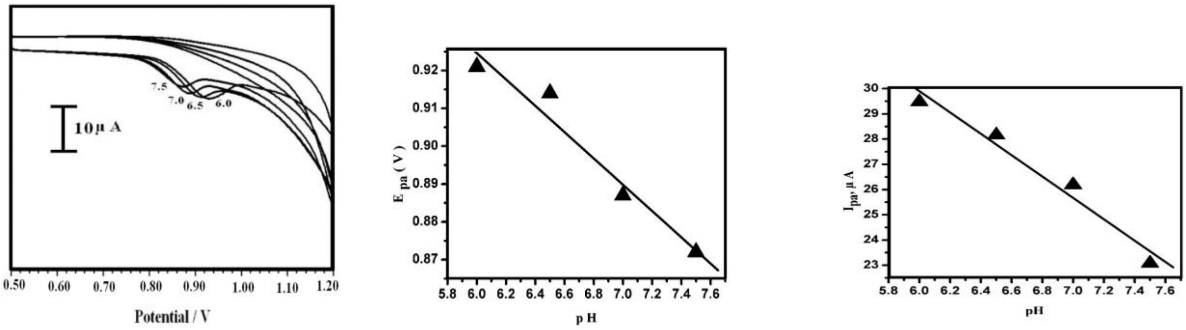
Here, v is the scan rate, b is the Tafel slope, and K is the constant value. From the graph, E_{pa} Vs. log (v) (Figure.4c) slope is 49.84. Therefore the Tafel slope becomes 99.68. By considering α as 0.5 for the irreversible reaction, the number of electrons involved in the oxidation reaction of TZ was calculated as 1.1 ~=1. The result was by following with the mechanism that was explained in Figure.1



a) **b)** **c)**

Fig4. *(a) Cyclic voltammogram of TZ (1×10^{-4} M) at TX-100MCPE in pH 6.0 at various scan rates. From 0.1 to 0.225 V/s. (b) anodic peak current (I_{pa}) Vs scan rate (v). (c) E_{pa} Vs log (v).*

Figure. 5a shows the effect of pH on the electrochemical response of the TX-100MCPE on 1×10^{-4} M TZ over the pH range of 6.0 to 7.5 in a 0.1 M PBS solution. As the pH increases from 6.0 to 7.5, the anodic peak potential shifted towards the positive value and a well-defined peak, with high current response was obtained at pH 6.0. Thus, a solution of pH 6.0 was taken for the electrochemical resolution of TZ. The anodic peak potential of TZ shifted from 0.921 V to 0.872 V with respect to the pH from 6.0 to 7.5. The potential diagram was constructed by plotting anodic peak potential E_{pa} Vs. pH (Figure.5b), and the relation between peak current and pH was shown in the Figure. 5c.



a) **b)** **c)**

Fig5. *(a) Cyclic voltammogram at TX-100MCPE in 0.1 M PBS in different pH values from 6.0 to 7.5 containing TZ (1×10^{-4} M) (b) Plot of anodic peak potential (E_{pa}) Vs. pH at TX-100MCPE (c) anodic peak current (I_{pa}) Vs. pH for TZ.*

Calibration Plot for TZ

CV is a sensitive electrochemical technique and used to find out the detection limit of TZ. Calibration plot for the resolution of TZ at the TX-100MCPE in pH 6.0 PBS with the scan rate of 0.1 V/s was shown in Figure. 6. The anodic peak current response of TZ is directly proportional to the TZ concentration over a range of 6×10^{-6} to 1×10^{-4} M. The linear regression equation was I_{pa} / A = 1.06×10^{-5} + 0.11 C (M) with a correlation coefficient of 0.992. The detection limit (DL = $3S_b$ / m, where S_b is the standard deviation of the blank response and m is the slope of the calibration plot) and limit of quantification was found to 11.14×10^{-7} M and 3.7×10^{-6} M. The proposed electrode exhibited a lower detection limit and the comparison of the detection limit with other modified electrodes was tabulated in Table.1 [28-32]

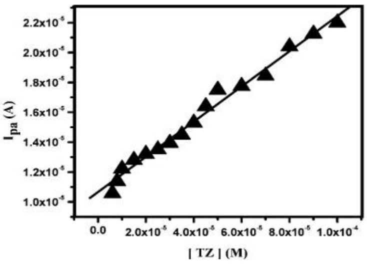


Fig6. *Calibration plot for the determination of TZ at the TX-100MCPE in pH 6.0 PBS with the scan rate 0.1 V/s.*

Table1. *Comparison of the detection limit with different electrodes.*

Electrode	Detection limit (M)	Technique	Reference
Carbon nanotubes/GCE	1.88×10^{-7}	DPV	[28]
Acetylene black/GCE	1.87×10^{-7}	DPV	[29]
GCE/MIPF	2.7×10^{-8}	DPV	[30]
SPCE	7.0×10^{-8}	AdSV	[31]
HMDE/CPB	3.3×10^{-6}	AdSV	[32]
TX-100MCPE	11.14×10^{-7}	CV	Present work

GCE: Glassy carbon electrode, MIPF: Molecularly imprinted polymer film, SPCE: Screen Printed Carbon Electrode, AdSV: Adsorptive Stripping Voltammetry, HMDE: Hanging mercury drop electrode, CPB: cetyl pyridinium bromide.

Electro catalytic Oxidation of TZ by DPV at BCPE and TX-100MCPE

DPV gives better sensitivity compared to CV. Figure. 7 depicts the DPV response of TZ (1×10^{-4} M) at BCPE and TX-100MCPE in 0.1 M PBS (pH 6.0) in the potential range of 0.5 to 1.2 V, with the amplitude 0.05 V and Pulse width of 0.5 sec. The anodic peak potential for the oxidation of TZ at TX-100MCPE was found to be 0.873 V. The oxidation current appears for TX-100MCPE was 3.3 higher than the current response obtained for TZ at the BCPE. From this, it is concluded that TX-100MCPE enhances the characteristics of TZ oxidation.

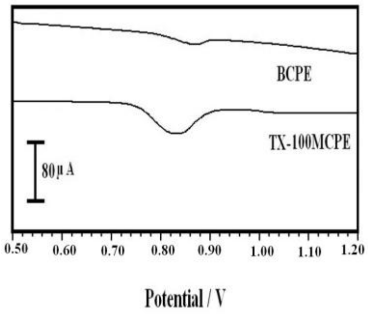


Fig7. *DPV of a solution containing TZ (1×10^{-4} M) in 0.1 M PBS at the BCPE and TX-100MCPE.*

Reproducibility and Stability

Reproducibility was studied for the 5 successive renewal of TX-100MCPE for 1×10^{-4} M TZ in 0.1 M PBS, pH 6.0. It was observed that the relative standard deviation (RSD) of 4.3%. Shows that the modified electrode having acceptable reproducibility. The stability of the TX-100MCPE was evaluated by measuring peak current of TZ after the continuous scanning of 30 cycles in 0.1 M PBS, 6.0 pH. The percentage of degradation of TZ at TX-100MCPE was calculated using the following equation

$$\%Degradation = \frac{I_{pn}}{I_{p1}}$$

Here, the I_{pn} is the nth anodic peak current and I_{p1} is the first anodic peak current. The percentage of degradation was found to be 0.6 %, which shows that the developed modified electrode was stable.

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CONCLUSION

This work demonstrates the development of TX-100MCPE by immobilization technique. Voltammetric behavior of TZ was investigated by CV in 0.1 M PBS (pH 6.0). The modified carbon paste electrode is effective towards the resolution of TZ. Oxidation of TZ found to be irreversible with adsorption controlled. TX-100MCPE exhibited excellent electrocatalytic activity. The sensor was characterized by rapid response and low detection limit (11.14×10^{-7} M) with satisfactory stability, reproducibility.

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