Electrochemical Sensor for the Determination of Alizarin Red-S at Non-ionic Surfactant Modified Carbon Nanotube Paste Electrode

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The cyclic voltammetric (CV) behavior of Alizarin red-S (ARS), an anthraquinone dye, was examined by utilizing TX-100 modified carbon nanotube paste electrode (TX-100MCNTPE). The surfactant utilized is TX-100 which shows a good electrocatalytic activity towards ARS. Distinctive parameters like pH, scan rate, and detection limit were studied in the potential range of 0.4-1.0 V using 0.2 M phosphate buffer solution (PBS) as supporting electrolyte. Based on the results, ARS shows well characterized irreversible oxidation peak in the solution of pH 6.5 at a scan rate of 0.1 V s\textsuperscript{-1}. Scan rate studies reveal that the entire process is adsorption controlled. Oxidation peak current rises linearly with the increase in the concentration of ARS. Two linear ranges are observed in the array of 2 \times 10^{-6} to 10 \times 10^{-6} M and 15 \times 10^{-6} to 35 \times 10^{-6} M. First linear range was assigned to a limit of detection (LOD) 1 \times 10^{-6} M and limit of quantification (LOQ) 3 \times 10^{-6} M. The fabricated sensor can be productively employed for the simultaneous determination of ARS and Tartrazine (TZ). The superior electrocatalytic activity was shown by resultant TX-100MCNTPE in contrast to BCNTPE in the oxidation of ARS.

Keywords: Cyclic voltammetry, Carbon nanotube paste electrode, TX-100, Alizarin red-S, Tartrazine

INTRODUCTION

Dyes are widely utilized in the textile industry to color the fabric. However, all dyes used will not be fixed in the fabric. Relatively 30% of the unfixed dye goes into the effluent, which has a high potential for sulllying the ground water and drinking water [1,2]. Since these dyes are lethal and carcinogenic, there is a prerequisite to identify them in the effluent water [3]. Of all the analytical techniques, the electroanalytical technique is found to be more proficient and advantageous [4-6]. Several kinds of synthetic dyes are commercially accessible. Among these dyes, anthraquinone dyes are generally utilized because they form a covalent bond with the hydroxyl group and amino group of the fiber [7]. These dyes are accessible in a broad scope of hues, and their application is correspondingly simple. ARS is a water-soluble orange powder with a molecular formula C\textsubscript{14}H\textsubscript{8}O\textsubscript{4}SO\textsubscript{3}Na [8]. The natural source of alizarin is found in madder plant, and it is a mordant vegetable dye [9]. Recently, some techniques have been developed to synthesize this dye chemically. It is used for dyeing cotton and silk fabric.

ARS is also used as a staining agent in biological research since it can stain free calcium and certain compounds into red or light purple color. Since ARS has a thermodynamic stability towards the biological and photocatalytic oxidation, it is not easy to remove ARS by casual waste water treatments like coagulation and precipitation [10]. People having skin allergies are more susceptible to its toxicity [11]. Its acute hazardous nature leads to irritation of eyes and lungs. It also causes dermatitis. Structure of ARS is shown in Fig. 1 [12].

Carbon nanotubes (CNT) are widely used in electrochemical sensors for voltammetric studies. Because of their novel structural, chemical, mechanical and electronic behavior, they are highly preferred sensors. CNTs
have high thermal stability, high tensile strength, and high elasticity [13-16]. Their precise electronic properties suggest the fact that CNTs can promote electron transfer reactions by improving the sensitivity. To enhance the stability and responsiveness of CNTs, they are modified by using suitable surfactants. These modified electrodes have superior electroanalytical properties like a wide potential window, low detection limit, excellent sensitivity, and resistance to surface fouling [17,18].

Surfactants have the capacity to enhance the property of electrode at the electrode and solution interface by increasing the detection efficiency. A surfactant is an amphiphilic linear molecule which has a hydrophilic group at one end, and a hydrophobic group at the other end and these molecules will be spontaneously absorbed in the interface of the electrode [19-21]. TX-100 is a non-ionic surfactant forming a monolayer with a hydrophobic group directed towards the electrodes outer surface. The prevailing electrostatic interaction between the analyte and TX-100 leads to the adsorption of the analyte on the electrode surface, and hence, TX-100MCNTPE exhibits enhanced behavior in sensitivity and detection limit [22].

In this paper, electrochemical behavior of ARS, belonging to the family of anthraquinone dye, is studied in 0.2 M phosphate buffer, at pH 6.5, using surfactant-modified carbon nanotube paste electrode in the potential range of 0.4-1.0 V at a scan rate of 0.1 V s⁻¹. The present work shows a novelty in comparison to the previous works, where the LOD and LOQ are not mentioned [9]. The TX-100MCNTPE offers low detection limit, high sensitivity, and good repeatability and reproducibility in contrast with previously reported data for ARS determination. The modified electrochemical sensor displays an enhanced resolution towards the simultaneous determination of ARS in the presence of TZ.

**EXPERIMENTAL**

**Apparatus**

Cyclic voltammetry was performed using model CHI6038E [CH-Instrument from USA]. The experiment was carried out using a conventional electrochemical cell consisting of three electrodes: TX-100MCNTPE as a working electrode, platinum wire as an auxiliary electrode, and Calomel electrode as a reference electrode.

**Fabrication of TX-100MCNTPE**

TX-100MCNTPE was prepared by taking 60% CNT powder and 40% Silicone oil, which was finely ground for 20 min into the homogeneous mixture by using a mortar and pestle. The paste is then packed into a Teflon tube of 3 mm diameter. The surface is smoothened by rubbing the tube on a soft weighing paper to get a BCNTPE. 25 × 10⁻³ M TX-100 was prepared by using distilled water. Carbon nanotube electrode was immobilised by adding 10 µl of surfactant TX-100 on BCNTPE for 5 min.

**Reagents and Chemicals**

Multi-walled carbon nanotube (MWCNT) of dimension 30-50 nm and length of 10-30 µm was obtained from Sisco research laboratories, Maharashtra. Silicone oil, Tartrazine

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**Fig. 1. Structure of ARS.**
and TX-100 surfactant were purchased from Nice Chemicals, India. ARS was purchased from Molychem. Analytical grade chemicals were used without any purification process. ARS and TZ stock solutions were prepared by dissolving ARS and TZ in double distilled water, respectively. PBS of strength 0.2 M was prepared by mixing a suitable amount of 0.2 M monosodium dihydrogen phosphate and 0.2 M disodium hydrogen phosphate.

RESULTS AND DISCUSSION

Surface Morphology

FESEM is a powerful technology to offer a general view
of the electrode surface morphology. The CNTs, BCNTPE, and TX-100MCNTPE were characterized by FESEM. Image of CNTs (Fig. 2a) shows that the nanotubes are entangled like spaghetti. Image (Fig. 2b) of BCNTPE shows irregular arrangement. When the electrode surface is modified by TX-100, a spongy like appearance (Fig. 2c) is formed which indicates the deposition of TX-100 film on the surface of BCNTPE enhancing the surface morphology for the adsorption-controlled mechanism.

**Effect of pH**

Effect of pH was studied in the pH range of 6-8 using 0.2 M PBS as a supporting electrolyte at a scan rate of 0.1 V s\(^{-1}\). From the CV response (Fig. 3a) obtained, it was clear that the peak potential of ARS is reliant on pH and peak potential shifts to the less positive side due to the hindrance of oxidation at lower proton concentration. The plot of \(I_{pa}\) vs. pH (Fig. 3b) reveals that anodic peak current increases with the increase of pH reaching an optimum
value at 6.5 and a gradual decrease was observed after that [23-25]. From the CV pH, 6.5 is recorded as the optimum pH, since it shows enhanced sensitivity and reliable shape of voltammogram due to the effective interaction between the TX-100MCNTPE and ARS. At pH 6.5 faster transfer of electrons take place. A linear relationship was observed for the plot (Fig. 3c) $E_{pa}$ vs. pH with a correlation coefficient of 0.9903.

**Electrochemical Behavior of ARS at TX-100MCNTPE**

To illuminate the captivating properties of TX-100MCNTPE in the electrochemical oxidation of ARS under different conditions, the CV was compared. Figure 4a demonstrates the cyclic voltammogram in the absence of ARS and presence of ARS ($1 \times 10^{-3}$ M) with 0.2 M PBS in the potential range of 0.4-1.0 V at a scan rate of 0.1 V s$^{-1}$. Oxidation peak was not observed in the absence of ARS but under identical condition in the presence of ARS, a well-defined peak is observed at a potential of 0.762 V. The peak was characterized with an enlargement in oxidation peak current of 27.76 $\mu$A. Hence, the fact is clear that ARS shows enhanced electrochemical behavior with TX-100MCNTPE. Figure 4b shows that at BCNTPE oxidation of ARS has been reduced sensitivity. However, the voltammogram obtained for TX-100MCNTPE in the same condition was with high peak current due to enhancement in surface area. In the case of reverse scanning, reduction peak is not observed, suggesting that the electrode reaction is an irreversible process. The oxidation mechanism is explained in Fig. 4c.

**Effect of Scan Rate on the Determination of ARS by TX-100MCNTPE**

The interaction between the surface of TX-100MCNTPE and the target analyte was considered by taking ARS of $1 \times 10^{-4}$ M stock solution with 0.2 M PBS. Cyclic voltammetric behavior of ARS was studied by varying the scan rate from 0.050 V s$^{-1}$ to 0.250 V s$^{-1}$. Based on the experimental results, the oxidation peak current increases with the increase in scan rate (Fig. 5a). This correlation provides useful information about the type of mechanism taking place. The oxidation peak current of $1 \times 10^{-4}$ M ARS was measured. A plot (Fig. 5b) of anodic current $I_{pa}$ vs. scan rate ($v$) shows a linear correlation with a linear regression equation $I_{pa} (\mu A) = 2.98 + 73.95 \times v (V/s^3)$ and $R = 0.9884$, indicating that the electron transfer reaction is adsorption controlled. Concerning electrochemical oxidation, the anodic peak potential shifts towards the more positive side, giving us a clear idea about the irreversible electrochemical process on the electrode surface [26,27].

**Effect of ARS Concentration**

The concentration of ARS was varied from $2 \times 10^{-6}$ M to $1.3 \times 10^{-4}$ M. Based on the electrochemical response, shown in Figure 6a, the peak current increases with the increase in the concentration of the analyte. The plot of anodic peak current vs. concentration of analyte shows two linear relations (Fig. 6b) in the range $2 \times 10^{-6}$-10 $\times 10^{-6}$ M and $15 \times 10^{-6}$-35 $\times 10^{-6}$ M. Slight deviation in linearity was observed for higher concentration due to the deposition of ARS oxidation product on the electrode surface. First linear range was considered for the linear regression equation $I_{pa} (A) = 1.46 \times 10^{-5} + 0.755 C$ (M) and correlation coefficient of 0.9910, and the second linear range for the linear regression equation $I_{pa} (A) = 2.01 \times 10^{-5} + 0.132 C$ (M) with a correlation coefficient of 0.9884. The LOD and LOQ values calculated by the equation 3S/N, and 10S/N (S is the standard deviation, and N is the slope) were found to be $1 \times 10^{-6}$ M and $3 \times 10^{-6}$ M respectively [28,29].

**Repeatability, Reproducibility and Stability**

Repeatability, reproducibility, and stability are the parameters to evaluate the sensing performance of the modified electrode under the optimum condition. The electrode capability for the generation of a stable, reproducible surface was examined by CV data which show a well characterized reproducible peak. The calculated RSD for repeatability and reproducibility comprised at 3.6% (n = 4) and 3.9% (n = 3), respectively [30]. In addition, stability was tested where CV was recorded after running 40 cycles successively. The peak potential remained unaltered, and the current signal showed less decline relative to the initial response. Percentage degradation was calculated using the formula [31]:

$$\text{Percentage of degradation} = \frac{I_{p1}}{I_{p0}} \times 100$$
Fig. 4. (a) Cyclic voltammogram of $1 \times 10^{-4}$ M ARS in 0.2 M PBS buffer of pH 6.5 at TX-100MCNTPE (Curve a) and without ARS (curve b) at a scan rate of 0.1 V s$^{-1}$. (b) Cyclic voltammogram of $1 \times 10^{-4}$ M ARS in 0.2 M PBS buffer of pH 6.5 at TX-100 MCNTPE (curve a) and BCNTPE (curve b) at a scan rate of 0.1 V s$^{-1}$. (c) Oxidation mechanism of ARS.
where $I_{pa}$ is the peak current in the $n^{th}$ cycle, and $I_{p1}$ is the peak current in the first cycle. 90% of the initial current was retained even after running 40 cycles indicating excellent stability. These factors show that there is no fouling of the electrode surface, and TX-100MCNTPE shows good sensitivity.

Electrochemical Behaviour of ARS and TZ Using TX-100MCNTPE

TX-100MCNTPE was employed for the study of simultaneous identification of ARS ($2 \times 10^{-4}$ M) and TZ ($2 \times 10^{-4}$ M) under optimized conditions of pH 6.5 in 0.2 M PBS. It was performed by simultaneously changing the concentration of ARS and TZ. The voltammetric results in

Fig. 5. (a) Cyclic voltammogram of ARS ($1 \times 10^{-4}$ M) in 0.2 MPBS at diverse scan rates from 0.05 V s$^{-1}$ to 0.250 V s$^{-1}$. (b) Plot of $I_{pa}$ vs. scan rate.

Fig. 6. (a) Cyclic Voltammogram of ARS at different concentrations ($2 \times 10^{-6}$ M to $35 \times 10^{-4}$ M). (b) Calibration plot for the determination of ARS at the TX-100MCNTPE in 0.2 M PBS of pH 6.5.
Fig. 7 shows isolated oxidation peaks with a peak separation of 0.190 V. Well resolved oxidation peaks were obtained at the potentials of 0.750 V and 0.940 V with an enhanced current response corresponding to oxidation of ARS and TZ indicating that simultaneous identification of these compound is feasible at TX-100MCNTPE. BCNTPE shows poor sensitivity for the simultaneous identification of ARS and TZ.

Real Sample Analysis

To evaluate the applicability of TX-100MCNTPE for the real sample analysis, the effluent water containing ARS sample used for dying fabric in the textile industry was procured. A standard addition method of the ARS solution in 0.2 M PBS with pH 6.5, and the electrocatalytic activity were studied by recording the CV. The reliability of TX-100MCNTPE was evaluated by comparing the data of the commercially available sample with the textile sample. Excellent recoveries of the sample evince the promising applicability of this method for determination of ARS in textile water samples. The recovery determination is in the range of 98-102.5%. The results are tabulated in Table 1.
showing admirable regularity and selectivity of TX-100MCNTPE [32].

CONCLUSIONS

This work portrays the fabrication of TX-100MCNTPE for sensitive determination of ARS using CV. TX-100MCNTPE demonstrates common electrocatalytic activity for the oxidation of ARS at an optimum pH of 6.5 in 0.2 M PBS. The LOD and LOQ were found to be $1 \times 10^{-6}$ M and $3 \times 10^{-6}$ M, respectively. The TX-100MCNTPE provides good repeatability, reproducibility, and stability. The electrode process is found to be adsorption controlled. The concentration and pH effects were observed to be linear in room temperature. The recovery results obtained in the real sample analysis demonstrates that the proposed method can be used for the electrochemical sensing of ARS in the effluent water emerging from the textile industry, and that fabricated sensor can be convincingly used for simultaneous determination of ARS and TZ.

REFERENCES


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