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Electroanalysis of Sodium Alizarin Sulfonate at Surfactant Modified Carbon Nanotube Paste Electrode: A Cyclic Voltammetric Study

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Abstract

The electroanalysis of Sodium Alizarin Sulfonate (SAS) was carried by cyclic voltammetric method at carbon nanotube paste electrode modified by the surfactant Sodium Dodecyl Sulfate (SDS) in the presence of 0.2 M Phosphate buffer solution (PBS) with the pH 6.5. The cyclic voltammogram produced an irreversible oxidative peak at 0.794 V, which corresponded to the oxidation of SAS. The effect of concentration of surfactant, pH and scan rate was also studied. The results acknowledge that the modified electrode displayed excellent catalytic property with promising sensitivity and selectivity towards the oxidation of SAS. This modified electrode was used for the simultaneous determination of SAS with Tartrazine (TZ). Under optimized conditions, the cyclic voltammetric peak currents corresponds to the oxidation of the SAS increased linearly with the concentration of SAS and the detection limit was obtained to be 5.90×10^{-7} M and limit of quantification was 19.69×10^{-7} M. Due to excellent detection limit, high sensitivity, selectivity, high reproducible property along with ease of preparation and regeneration of the surface of the electrode make this electrode very advisable for the determination of SAS.

1. Introduction

The derivatives of Alizarin comprise an intriguing clan of Anthraquinone dyes and employed for the determination of molecules, metal ions and in textile industry [1-3]. Among them, (SAS) with molecular formula $C_{14}H_7NaO_7S$ (Figure 1) is widely employed in the textile industry as their broad range of colour shades (Yellow to Purple) and ease of application. Its usage involving the study of bone growth, bone marrow, calcium deposits in the vascular system, tissue engineering and gene expression. Its fused aromatic ring structures are the main reasons for its implicit non-biodegradable character and chemical stability. The presence of the sulfonate group in the molecule leads to extended reactivity in this molecule. Due to the extensive usage of this dye in dying industries produces numerous environmental problems. Identification of these dyes along with the quantification and removal from textile wastewaters is a challenging and expensive process [4-11].

The surfactant SDS is a kind of amphiphilic molecule with hydrophilic head on one side which is compatible with water and long hydrophobic tail compatible on the other side [12-16]. Surfactant has been extensively used in the electrochemical process owing to its ability to enhance the characteristics of the electrode/solution interface. Because of the adsorption of surfactant at the interface and aggregation into a supramolecular structure, it reinforces the properties of the electrode surface, enhances the reaction rate, as well as it enhances the peak current [17-19]. The drop-coating method of fabrication enriched with two main advantages: the modifier covers the entire surface of the electrode and minimum utilization of the modifier. Hence, this fabrication approach gets preference over other methods of fabrication [20-25].

Carbon nanotubes based electrochemical sensors depicts an excellent and compelling substitute for the analysis of various dyes. Because of the explicit features of CNTs, comprises of high thermal and chemical stability and unique mechanical properties made it widely adopted for the construction of electrodes [26-33]. CNT fabricated electrodes have been witnessed to have admirable electroanalytical characteristics such as high sensitivities, wide potential range, low detection limit and resistance to surface fouling [34-39].

In the present work, we portray the fabrication of new electrode containing BCNTP modified with surfactant SDS and scrutinize its efficiency for the electrocatalytic determination of SAS in an aqueous buffer solution. This modified electrode was also used for the simultaneous determination of SAS and TZ.

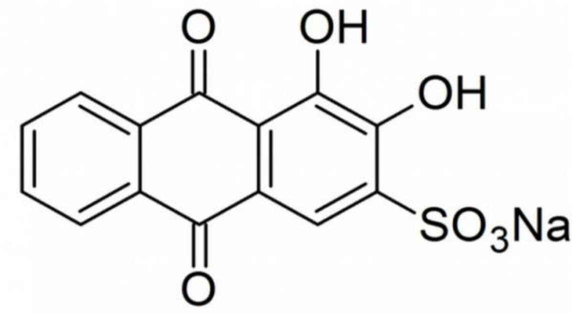

Figure 1: Structure of Sodium Alizarin Sulfonate.

2. Material and Methods

2.1. Apparatus and Chemicals

The electrochemical analysis was performed with an electrochemical workstation of model CHI-6038E (CHInstruments, USA). It includes a three-electrode system with SDSMCNTPE as working electrode, Platinum electrode as an auxiliary electrode and calomel electrode as reference electrode used to get the electrochemical data. FESEM micrographs were obtained from DST PURSE Lab, Mangalore University.

Analytical grade multiwalled carbon nanotubes (external diameter 30-50 nm and length 10-30 μm) were purchased from Sisco Research Laboratory Pvt. Ltd. Maharashtra, SAS, and TZ were procured from Molychem, Mumbai, India. Silicone oil was purchased from Nice Chemicals, Kerala, India. All reagents were used without further purification. Na_2HPO_4 and NaH_2PO_4 were obtained from Sigma-Aldrich. The phosphate buffer solution was used to prepare different pH solutions and was used as supporting electrolyte. Double distilled water was utilized for the preparation of all aqueous solutions.

2.2. Preparation of BCNTPE

The homogeneous carbon nanotube paste was prepared by grinding 60% carbon nanotubes and 40% silicone oil using mortar and pestle. The prepared paste was then packed into the cavity (internal diameter 3 mm) of working electrode and the surface of the electrode was smoothened on the tissue paper.

2.3. Preparation of SDSMCNTPE

The SDSMCNTPE was prepared by the immobilization of 10 μl SDS solution on the surface of the BCNTPE. After immobilization of the surfactant, the surface of the electrode was rinsed with distilled water. The copper wire was connected to the end of the tube to provide the electrical contact between the electrode and the electrolyte.

3. Results and discussion

3.1 Surface morphology of BCNTPE and SDSMCNTPE

The surface morphology of bare (BCNTPE), as well as the current modified electrode (SDSMCNTPE), was analyzed by widely used FESEM images. Irregularly structured nano-sized tubes were observed on the exterior of the BCNTPE (Fig. 2a), whereas on the superficial of SDSMCNTPE (Fig. 2b), the deposition of surfactant molecules was observed. These adsorbed surfactant molecules influenced to enhance the electrocatalytic activity of the electrode.

3.2 Electrocatalytic response of SAS

The electrochemical activity of SDSMCNTPE was checked by studying the cyclic voltammograms obtained in the absence and presence of 2×10^{-4}mol/L SAS in 0.2 M PBS of pH 6.5 in the potential window 0.4 to 1.1 V, and the graph obtained as shown in Figure 3. No characteristic peak was observed in the absence of SAS (curve b). When 2×10^{-4}mol/L SAS was added to the electrolyte solution a characteristic oxidation peak was obtained at 0.794 V with I_{pa}=53.26 μA (curve a).

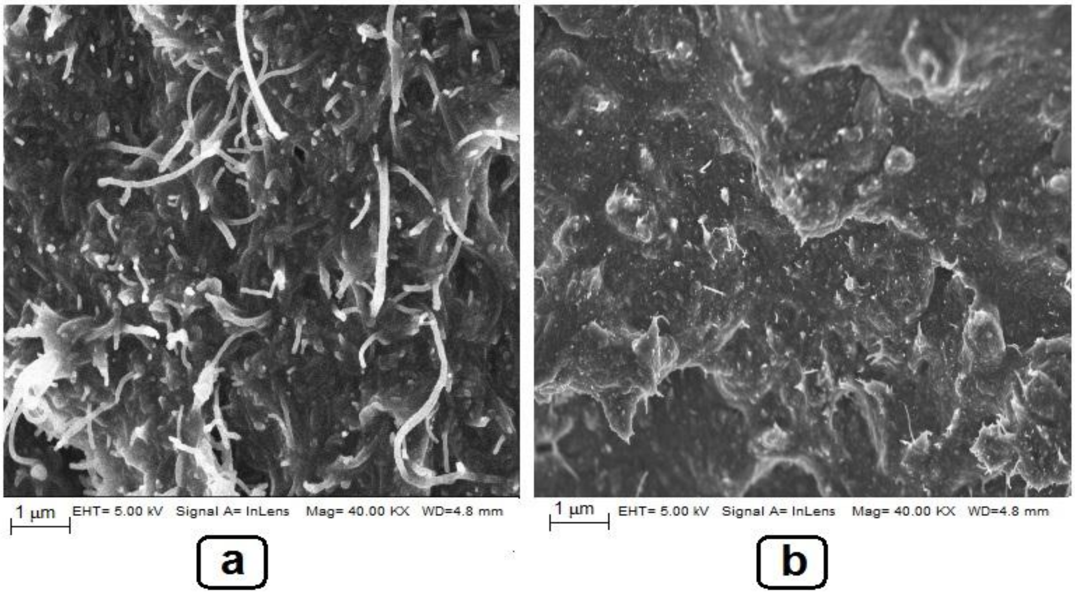

Figure 2: FESEM images of (a) BCNTPE (b) SDSMCNTPE.

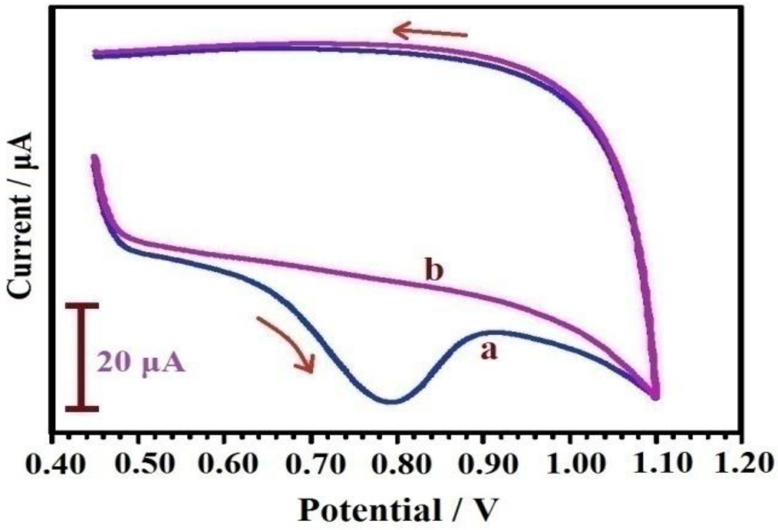

Figure 3: Typical cyclic voltammograms of SDSMCNTPE with 2×10^{-4} M SAS in pH 6.5 PBS (curve a) and without containing 2×10^{-4} M SAS at pH 6.5 PBS (curve b).

3.3 Electrocatalytic response of SAS at SDSMCNTPE

The electrocatalytic behavior of SAS (2×10^{-4}mol/L) was investigated at BCNTPE and SDSMCNTPE using CV technique. The investigations were carried out in 0.2 M PBS of pH 6.5 as supporting electrolyte at a sweep rate 0.1 V/s. As can be seen from the Figure 4 the BCNTPE (curve b) does not show response towards the SAS dye. However, under identical conditions, a distinct oxidation peak with high sensitivity was detected at SDSMCNTPE (curve a) at 0.794 V with I_{pa}=53.26 µA and during the reverse scan no characteristic peak response was observed. This behavior confirms the irreversible nature of the electrode process. As expected, SDSMCNTPE showed a better response compared to that of BCNTPE due to the high surface area render by the modified electrode.

3.4 Effect of scan rate on SDSMCNTPE

Cyclic voltammograms recorded for SAS in 0.2 M phosphate buffer solution of pH 6.5 at different scan rates depicted in Figure 5a. This observation was considered to scrutinize the kinetics of the electrode process and to validate the mass transfer process takes place in the electrochemical process is either adsorption controlled or diffusion controlled. The study of the effect of scan rate on the I_{pa} reveals that I_{pa} increased linearly with scan rate ranges from 0.05 to 0.20 V/s with correlation coefficient 0.999 (Figure 5b). This study suggested that the mass transfer process involved at the electrode surface is adsorption controlled [40, 41]. This activity was further validated by consider the slope from the graph of log I_{pa} vs. log ν (Figure 5c) and it was obtained to be 0.85, which is nearly equal to the speculative value 1.0. This confirms the adsorption controlled behaviour of the electrode [42].

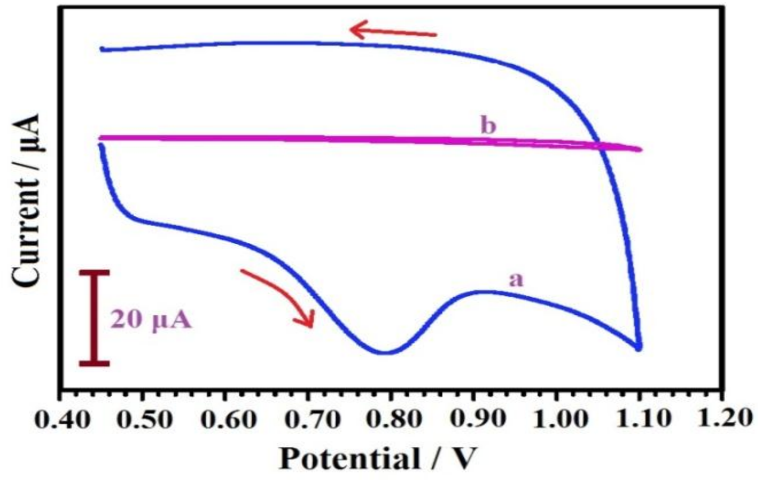

Figure 4. Cyclic voltammograms of 2×10^{-4} M SAS at the BCNTPE (curve b) and the SDSMCNTPE (curve a) in 0.2 M PBS (pH 6.5).

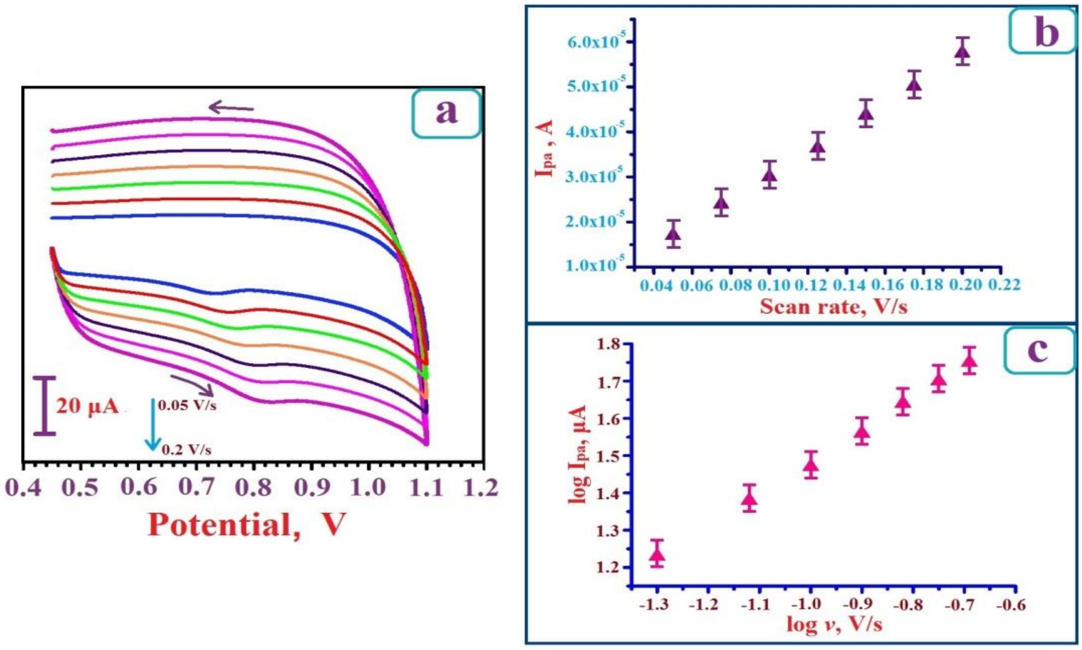

Figure 5: a) Cyclic voltammograms of 1×10^{-4} M SAS at the SDSMCNTPE in pH 6.5 PBS at various scan rates, from 0.05-0.2 V/s. b)The plot of the anodic peak current of SAS as a function of scan rate. c) The plot of log I_{pa} against log ν.

3.5 Effect of pH

Figure 6a shows the effect of solution pH on peak potential as well as oxidation peak current for SAS at SDSMCNTPE in 0.2 M PBS over the pH range from 6.0 to 8.0. It was observed that the oxidation peak current was increased from pH 6.0–6.5 and then I_{pa} was decreased as the pH of the supporting electrolyte increased (Figure 6b). From the CV obtained, it is evident that the electrode exhibits superior sensitivity with enhanced current response at pH 6.5, because of the higher rate of electron transfer at this particular pH. Hence, the PBS of pH 6.5 was chosen as the supporting electrolyte for the investigation of further parameters.

The relationship between pH and E_{pa} (Figure 6c) shows that as the values of pH increases, the anodic peak potentials move towards the negative region. The linearity was observed between the pH of the electrolyte solution and the anodic peak potential in the pH range of 6.0–8.0. The linear regression equation was given by E_{pa} (V)=1.50-0.11 pH (R=0.993).

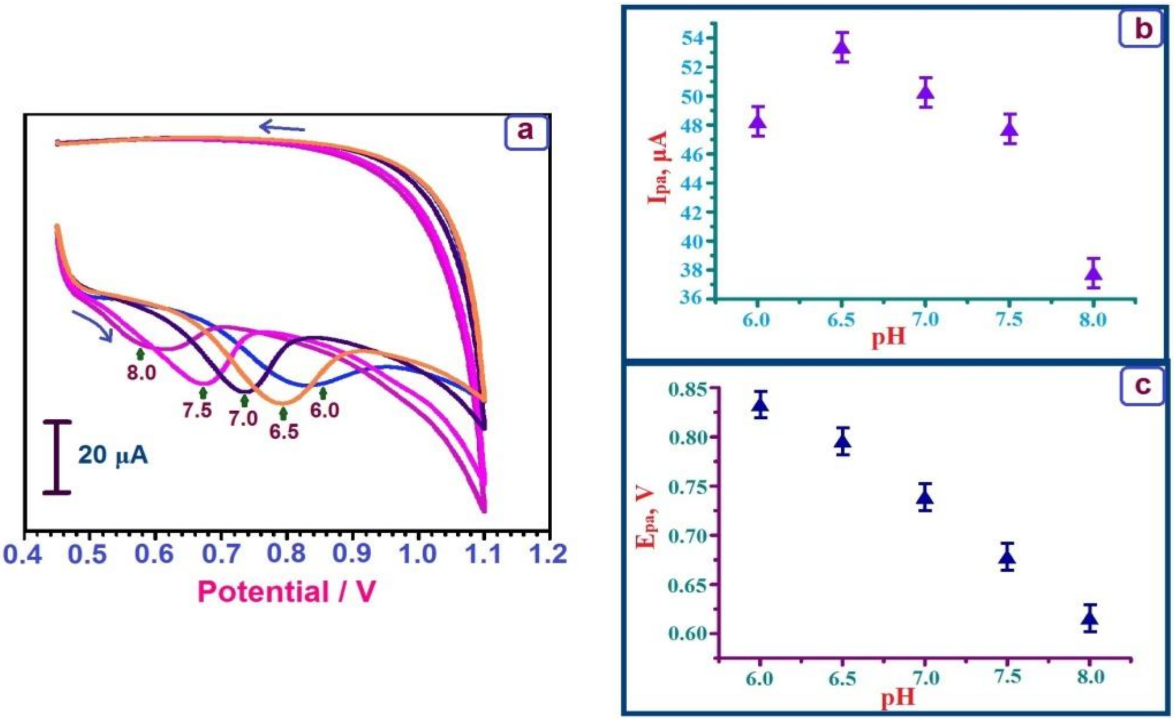

Figure 6: a) Cyclic voltammograms obtained at the SDSMCNTPE in 0.2 M PBS in pH values, 6–8 containing 2×10^{-4} M SAS. b) Graph of anodic peak current vs. pH (6.0–8.0) of 2×10^{-4} M SAS at the SDSMCNTPE. c) Graph of E_{pa} vs. pH for SAS.

3.6 Simultaneous determination of SAS and TZ at SDSMCNTPE

The dyes SAS and TZ can co-occur in the textile effluent water coming from the industries which causes health effects to aquatic organisms as well as for human beings, its detection and elimination was played an important role. So, SAS and TZ were determined simultaneously under optimized condition using CV technique. The studies were carried out in the potential window 0.4–1.1 V in 0.2 M PBS (pH 6.5). The cyclic voltammogram (Figure 7) displayed well-separated peaks at 0.818 V and 0.946 V corresponding to the oxidation of 3×10^{-4} M SAS, 1×10^{-4} M TZ at SDSMCNTPE (curve a).

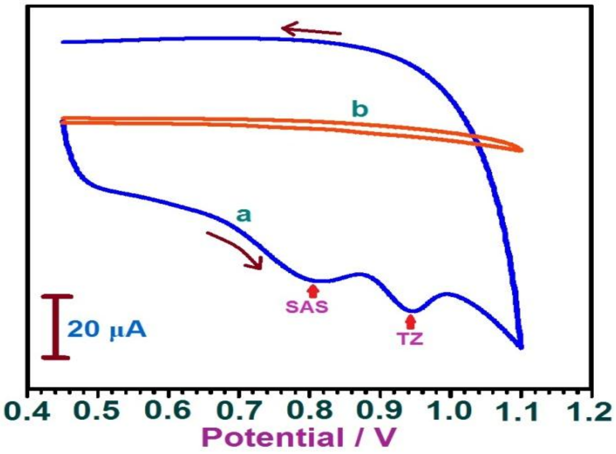

Figure 7: Simultaneous determination of3×10^{-4} M SAS and 1×10^{-4} M TZ at BCNTPE (curve b) and SDSMCNTPE (curve a).

The SDSMCNTPE was capable of distinguishing the oxidation peaks of SAS and TZ with compelling enhancement in the peak current values. Whereas, at BCNTPE no oxidation peak was detected for SAS and TZ (curve b).

3.7 Repeatability, reproducibility and stability of SDSMCNTPE

The surface of the electrode has to be renewed after every use by the ejection of carbon nanotube paste from the cavity of the electrode and reinstate it with a new paste. So, the study of repeatability, reproducibility, and stability of the modified electrode is very important. The repeatability of the current modified electrode was examined using five successive measurements taken at the same electrode, and the relative standard deviation (RSD) was obtained to be 5%. The stability of the electrode was examined by evaluating the I_{pa} value after scanning for 40 cycles in PBS (pH 6.5). The percentage degradation of the SDSMCNTPE was determined by substituting the anodic peak current values corresponding to the first scan (I_{p1}) and the n^{th} scan (I_{pn}) in the following expression,

$$\%\text{Degradation} = \frac{\text{Ipn}}{\text{Ip1}} \times 100$$

and it was obtained to be less than 8%, signifies the excellent stability of the modified electrode. The reproducibility of the electrode was also evaluated by extract the data from five successive renewals of the modified electrode, and it shows good reproducibility towards the determination of SAS.

3.8 Calibration plot for SAS

Figure 8 depicts the data recorded for the different concentration of SAS at SDSMCNTPE. The peak current corresponds to the oxidation of SAS increased linearly with the increase in the concentration of SAS. From the data, we observed the presence of two calibration curves which corresponds to two concentration ranges of SAS. The calibration equation corresponds to the first linearity is I_{pa} (A)=$2.976\times10^{-5}+0.114$ with R=0.983 for the concentration range from 2×10^{-6} to 3.5×10^{-5} M. Likewise, the calibration equation corresponds to the second linearity is I_{pa} (A)=$2.966\times10^{-5}+0.196$ with R=0.992 for the concentration range from 4×10^{-5} to 8×10^{-5} M. The second linearity range was considered for the calculation of limit of detection (LOD) and limit of quantification (LOQ) and it was evaluated as 5.90×10^{-7} M and 19.69×10^{-7} M respectively. This values were calculated using the equations,

$$\text{LOD}=3s/m\ ;\ \text{LOQ}=10s/m$$

here, s represents the standard deviation of the blank assessments and m denotes the slope of the calibration plot.

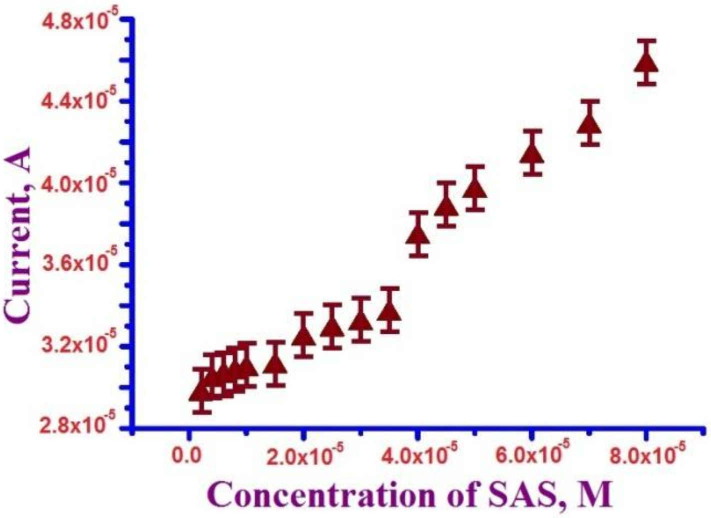

Figure 8: Calibration plot for the determination of SAS at the SDSMCNTPE in pH 6.5 PBS with the scan rate 0.1 V/s.

Conclusion

In the present study, the adsorption of SDS at carbon nanotube paste electrode was scrutinized by cyclic voltammetry technique, which might be able to explain the enhancement effects of surfactant in electroanalytical chemistry for SAS. Scan rate studies revealed that the electrochemical process proceeded through adsorption controlled step. The modified electrode was suggested for the simultaneous determination of small fragments of SAS, and TZ. This fabricated sensor exhibited high sensitivity, stability, reproducibility and repeatability towards the determination of SAS. The current developed sensor exhibits antifouling properties and the regeneration of the electrode is easy and less time consuming.

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