INTRODUCTION

Resorcinol (RS) is used to treat some diseases such as acne, seborrheic dermatitis, eczema, psoriasis, and other skin illness. RS also used to remove unwanted skin. RS is an m-dihydroxybenzene. Benzene is one of the molecules to increase the risk of cancer and other disorders. Benzene contains a harmful things and low degradability in nature, they are considered as environmental pollutants [1,2]. Therefore, it is needed to prepare a simple and fastest analytical method for the detection and determination of RS. Many people proposed many analytical methods to determine RS such as electrochemical [3,4], flow injection chemiluminescence [5], High-performance liquid chromatography [6], fluorescence [7], surface plasmon resonance [8], and spectrophotometric [9]. The redox mechanism of RS was shown in Scheme 1 [4].

Scheme 1: The scheme of oxidation of resorcinol -2H+

Electrochemical detection is a best substitute for the detection of many compounds in pharmaceutical and biological samples [10-15]. However, the detection is sometimes suppressed because it presents limitations of selectivity due to the obstruction from the species which are electroactive at same potentials to the analyte of interest [16]. In these circumstances, a many types of carbon materials such as carbon nanotubes (CNT) and graphite carbon electrodes have been investigated in electroanalysis to get good results in sensitivity, selectivity, and stability of the electrode. The development of sensitive and selective voltammetric sensors has become widely popular, due in part to their simplicity, rapidity, precision, and availability of the basic equipment in laboratory and field uses. The electrocatalytic property of electrode usually relies on the electron transfer at the electrode/electrolyte interface, surface area, and electrical conductivity of the electrode material. Carbon-based materials such as CNT and graphite having large surface area [17], speedy electron transfer, and very good electrical conductivity [18,19] have great use in chemical, biological sensors [10,14,16,20], fuel cell [21], and supercapacitors [22]. However, graphite suffers restrictions due to restacking which can be obviated by combine functional groups such as oxygen, nitrogen [23], and preparing hybrid materials with other nanomaterials such as CNT [24], metal [25], and metal oxides [26]. The common strategies followed to obtain graphite /CNT hybrid material are through simple mixing in mortar with silicone oil [27].

Surfactants have been used extensively in the field of electroanalytical chemistry for many works. Surfactants have been utilized in electrochemistry to enhance the property of the electrode solution interface [10] and also enhance the detection limits of some molecules. The fast literature showed that the electrochemical effect of these compounds was increased in the presence of trace surfactants [11,28-31].

In this work, the electrochemical behavior of RS was analyzed at Sodium dodecyl sulfate (SDS) SDSMCNTGMPE. The reaction mechanisms of RS molecule were examined by cyclic voltammetry (CV) and differential voltammetry (DPV) with different parameters like varying scan rates at different pH values in phosphate buffer solutions (PBS). Carbon electrodes are having tendency to surface fouling problem, the rate and
extent of passivation of SDSMCNTGMPE were examined by scanning several continuous cycles with CV and analyzing the surface by variable pressure scanning electron microscopy (VPSEM). The results were compared to the oxidation of these compounds at carbon electrodes. To the best of our scientific knowledge, there is no voltammetric sensor based on modified CNT-graphite mixture paste electrode for voltammetric determination of RS.

EXPERIMENTAL

Reagents
Silicone oil and SDS were purchased from Nice Chemicals, India. RS purchased from Himedia, India. RS was prepared 25×10^{-3} M stock solution by dissolving in double distilled water. Other chemicals were of analytical grade and used without further purification. SDS was prepared 25×10^{-3} M stock solutions by dissolving in double distilled water. An entire analysis, the supporting electrolyte used was pH 7 (0.2 M PBS). Spectroscopically, pure multiwall CNTs were obtained from Sigma-Aldrich, India.

Apparatus
Electrochemical analysis (EA) was carried out with a model-201 (EA-201 ChemiLink system, Mumbai, India) in a normal three-electrode system. The working electrode was a SDSMCNTGMPE and bare CNT-graphite mixture paste electrode (BCNTGMPE), having cavity of 3 mm diameter. The counter electrode was a bright platinum wire with saturated calomel electrode as reference electrode completing the circuit.

Preparation of the electrochemical sensor electrodes
The BCNTGMPE was prepared by mixing in a mortar CNT, graphite, and silicone oil in ratio 35.0% w/w CNTs, 35.0% w/w graphite, and 30.0% w/w silicone oil. The paste was then packed into the cavity of a homemade electrode and smoothed out on a tissue paper. SDS modified carbon paste electrode (SDSMCNTGMPE) was prepared by immobilizing 20 μL of SDS surfactant on the surface of the BCNTGMPE for 5 min [10,11].

Electrochemical measurements procedure
Electrochemical depictions of the electrodes were performed in 0.2 M phosphate buffer (pH 7.0) through CV and DPV in the potential range from 0 to 100 mV all electrochemical measurements were carried out at room temperature. RS stock solution was added as per the requirement. The electrochemical cell contained a SDSMCNTGMPE or BCNTGMPE as a working electrode, a Pt wire counter electrode, and Ag/AgCl (3 M KCl) reference electrode.

RESULTS AND DISCUSSION

Surface analysis by VPSEM studies
VPSEM is a powerful technology to offer a general view of the electrode surface. Compared the VPSEM images of BCNTGMPE (Fig. 1a) and SDSMCNTGMPE. (Fig. 1b), the mixture of CNT, graphite, and silicone oil was clearly observed. When the SDS was electrodeposited on the electrode surface, the deposition of SDS with some large group of molecules on observed with VPSEM. This indicated that the SDS film was successfully fabricated.

Stability and reproducibility
The SDSMCNTGMPE sensor had a good stability and the peak current only decreased <4% after the electrode for 25 days. Tested the reproducibility of the modified electrode, five SDSMCNTGMPE were prepared for the detection of RS. The relative standard deviation (RSD) of peak currents for RS (n=5) was calculated as 4.67%, values indicating that the reproducibility of the proposed electrode was good. The modified electrode shows good stability, reproducibility, and repeatability.

The electrochemical behavior of the SDSMCNTGMPE and BCNTGMPE toward potassium ferrocyanide
The electrochemical behavior of the SDSMCNTGMPE toward potassium ferrocyanide was also examined by CV. Fig. 2 shows cyclic voltammograms of BCNTGMPE and SDSMCNTGMPE, containing 1 M KCl and 1 mM potassium ferrocyanide. The SDSMCNTGMPE exhibited a characteristic increase of the peak for ferrocyanide represents the successful modification. Higher peak currents (Ipa=26.6 μA, Ipc=24 μA; ∆Ep=40 mV) when compared with those at the BCNTGMPE (Ipa=11.6 μA, Ipc=7.4 μA; ∆Ep=128 mV) were found. This can be responsible to the higher electrochemical activity of surfactant which gives the increase of the active area of the electrode. The presence of the electrodeposited SDS surfactant impacts the slight shifts of the anodic peak potential to less positive side, giving rise to a smaller peak-to-peak separation (∆Ep=40 mV). This more than two-fold increase in both the anodic and cathodic peak currents can be attributed to the electrocatalytic effect of the surfactant.

Electrochemistry of RS at SDSMCNTGMPE
The voltammetric behavior of RS at SDSMCNTGMPE was investigated with CV. Fig. 3 shows the CVs at the SDSMCNTGMPE in 0.2 M PBS at pH 7.0 in the absence (blank) and presence of 1 mM of RS at a scan rate of 100 mV/s. The CVs on SDSMCNTGMPE with RS shows broader oxidation peak with the peak potential at 542 mV. For SDSMCNTGMPE absence RS no significant peak appeared (solid line) and the current enhancement after the addition of RS is completely evident (dashed line). Above results show that the SDSMCNTGMPE improves the electrocatalytic activity for RS oxidation. In the present electrochemical approach, the electrode effect was directly proportional to the oxidation of the electroactive species produced.

Electrochemical study of RS at SDSMCNTGMPE by CV and DPV
The electrochemical behavior of 1 mM RS in 0.2 M PBS (pH 7.0) at the BCNTGMPE and the SDSMCNTGMPE were studied by CV. As shown in Fig. 4, the CVs obtained at the BCNTGMPE display an irreversible oxidation peak with very small peak current 18.5 μA. In contrast, the CVs of RS at the SDSMCNTGMPE (dashed line) show well-defined peak in potential range between 0 and 100 mV, with the greatly enhanced peak current 50.5 μA. The appearance of the irreversible peak indicates that SDSMCNTGMPE film can significantly accelerate the oxidation reaction process. It is worth noting that the peak currents obtained at SDSMCNTGMPE present the higher values in comparison with those obtained at the BCNTGMPE, about 2.7 times as large as that recorded at SDSMCNTGMPE. The enhanced results show that SDSMCNTGMPE exhibit good conductivity and excellent catalytic activity toward the oxidation of RS.

Electrochemical determination of RS was performed by employing the DPV response at BCNTGMPE and SDSMCNTGMPE in 0.2 M PBS (pH 7.0) solution containing 1 mM RS. As shown in Fig. 5, at the BCNTGMPE, the electrooxidation of RS presents very small peak current so that the determination of the RS at BCNTGMPE is very difficult. In contrast, at
the SDSMCNTGMPE well-defined oxidation peak and peak current were observed at 544 mV, 7.8 μA, respectively, with higher (approximately 2.6 times) oxidation peak current appeared.

**Effect of scan rate**
The effect of the scan rate on the electrochemical reactions of RS was studied by CV at the SDSMCNTGMPE. The results are exhibiting an increase in the redox peak currents with an increase in the scan rate (100-500 mV/s), as revealed in Fig 6a. The peak currents versus scan rate (ν) are plotted in Fig 6b. The graph displays a linear relationship between the scan rates and peak currents. In the scan rate from 100 to 500 mV/s, the anodic peak currents usually proportional to the scan rate. The linear regression equation for the SDSMCNTGMPE is Ipa (μA) = 36.97 + 0.1349 V (mV/s) with the correlation coefficient equal to 0.9907. The regression equation indicates the SDSMCNTGMPE reaction process was adsorption-controlled [32-34].

**Influence of pH**
The influence of pH on the oxidation peak current of RS at the SDSMCNTGMPE was examined by recording CV in PBS (pH 5.5-8) shows in Fig 7A. The study of the influence of pH on the anodic peak current was also introduced out to determine the pH value for the maximum evidence. The height of the peak reached a highest and the shape of the curve is good in PBS at pH 7.0 than other buffers shows Fig. 7B. This supporting electrolyte was chosen with respect to good peak for the detection of RS. The effect of pH on the anodic potential and anodic peak current was analyzed over a pH range 5.5-8 in the solution containing 1 mM RS using CV. The E° of RS decreased with respect to increasing pH. From the plot of Epa versus pH, the slope of 0.094 was obtained, corresponding to the following equation: Epa (mV)=1244.97-94.514 pH (R^2=0.998) shows in Fig. 7C.

**Calibration plot and detection limit**
The quantitative determination of RS at SDSMCNTGMPE is carried out by CV technique under the optimized conditions. CV was carried out in the potential range of 0 to 1000 mV for the addition different concentrations of RS (20-1000 μM) in 0.2 M, PBS (pH 7.0). Obviously, the anodic current of RS has been obtained nearly at the potential of 544 mV increased as the concentration of RS increased, attributed to the electrooxidation of RS at the modified electrode. A calibration plot was made between the concentrations of RS and peak currents Fig. 8. The linear range of RS concentration was from 20 to 1000 μM and the regression equations were Ipa (A)=7.6894×10^-4+0.05424 C (R^2=0.9937), the detection limit was 5.8×10^-5 and limit of quantification 19×10^-5 (S/N=3). The result was compared with other literature [3,4,35,36] (Table 1). The proposed electrode shows good comparable electroanalytical values with the previous reports revealing the ability of the SDSMCNTGMPE toward sensitive determination of RS.
Determination of RS in commercial sample

To verify the reliability of the method for analysis of RS in commercial sample, this SDSMCNTGMPE was applied to determine RS in RS injection, with required amounts of the diluted commercial sample being shifted into the cell for the determination using CV.

The injections of RS were analyzed by the standard addition method. The injection sample was used after suitable dilution; it contains 4 g/100 mL RS. The mixtures were diluted to achieve different known standard 100, 200, and 300 μM concentrations of RS. The sample solutions were analyzed by CV using the SDSMCNTGMPE.

Each experiment was repeated out at least 5 times and the results are presented in Table 2. The recoveries ranged from 98.5% to 101.1%. The results are receivable, showing that our recommended method could be efficiently used for the determination of RS in commercial samples.

CONCLUSIONS

In this paperwork, we have prepared and characterized a SDSMCNTGMPE. SDSMCNTGMPE surface was probed by VPSEM, DPV, and CV techniques. The high sensitivity and low detection limit together with the ease of preparation and good repeatability and better stability
the SDSMCNTGMPE are the applications of the proposed electrode. Table shows some parameters such as detection limit and linear range for analysis of RS by the proposed electrode in contrasting with some other electrochemical procedure.

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