

*Full Paper*

## **Fabrication, Characterization and Development of a Modified Poly(Bromocresol Purple/Multiwalled Carbon Nanotubes) Carbon Paste Electrode for the Determination of Sulfanilic acid**

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**Abstract-** A sensitive electrochemical sensor was assembled by the electropolymerization of bromocresol purple on the surface of multiwalled carbon nanotubes modified carbon paste electrode i.e., poly(BC/MWCNTs)CPE. The surface network of the newly constructed electrochemical sensor was recorded by scanning electron microscope. The developed sensor has demonstrated improved electrocatalytic activity towards sulfanilic acid detection in presence of 0.1 M phosphate buffer solution at pH 7.5. The experimental parameters including the effect of scan rate, buffer pH and analyte concentration were optimized systematically. A linear relationship was found between the peak currents and analyte concentrations with limit of detection and limit of quantification values  $0.98 \times 10^{-7}$  M and  $3.2 \times 10^{-7}$  M respectively, which are significantly lower than the reported methods. The kinetic parameters such as reaction rate constant ( $ks$ ), charge transfer coefficient ( $\alpha$ ), total number of electrons transferred ( $n$ ) were evaluated and found to be 0.269, 3.27 and 2.0 respectively. The results deduced that the modified poly(BC/MWCNTs)CPE provides high sensitivity, good stability, excellent catalytic activity and better reproducibility along with lower limit of detection for the analysis of sulfanilic acid.

**Keywords-** Bromocresol purple, Cyclic voltammetry, Differential pulse voltammetry, Multiwalled carbon nanotubes, Scanning electron microscope, Sulfanilic acid

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## 1. INTRODUCTION

Sulfanilic acid (4-Aminobenzene-1-sulfonic acid) is an off-white crystalline solid and hydrophilic aromatic amine which finds applications in the industries for the preparation of dyes and sulpha drugs [1,2]. Sulpha drugs are pharmaceutical products that are mainly used as antibacterial agents, which includes sulfonamides and erythromycins etc. Although sulfanilic acid drugs have great chemotherapeutic activities, sulfanilic acid exhibits higher toxicity [3]. Further, sulfanilic acid has lot of importance in its diazotized form, which is useful to measure bilirubin content in human blood serum by the reaction of unconjugated and conjugated bilirubin pigments of serum to form azo-bilirubin [4]. Moreover, it is used for the detection of drugs and their decomposition products in pharmaceuticals [5]. The properties of sulfanilic acid made it as a good catalyst when it is doped with certain polymeric materials and the experiments showed that the doping increases the conductivity of polymer [6,7]. Sulfanilic acid has been found to be very effective reagent in the detection and determination of lanthanides and some transition metals [8,9]. Besides the advantages of sulfanilic acid, the hazardous properties cause serious damage to the environment. Sulfanilic acid is the metabolite of azo dyes that can affect the aquatic life when it is released into the water streams. Hence, it is necessary to detect and determine sulfanilic acid in wastewater before going to release into the aquatic environment.

There are few high performance liquid chromatography, spectrophotometry and capillary electrophoresis methods reported for the investigation of sulfanilic acid [10,11]. Although great success has been achieved, many of the methods reported with above techniques have one or more drawbacks that includes costly instrumentation, laborious sample pretreatment methods and lengthy analysis time. Besides the above said methods, electrochemical methods have provided higher selectivity, sensitivity and reliable analysis for the electroactive species including pesticides, drugs, dyes and various types of pollutants [12-14]. Electroanalytical techniques provide various advantages including low cost, higher selectivity and sensitivity, wide potential ranges, surface renewal and easy handling [15-18]. However, the use of conventional glassy carbon electrode (GCE) and bare carbon paste electrode (CPE) provides poor sensitivity and low stability. Therefore, surface modification of conventional electrodes is necessary to improve their analytical performance. Several studies have been conducted for the electrode surface modification using variety of nanomaterials like carbon nanotubes, gold nanoparticles, silver nanoparticles, palladium nanoparticles, and different bio-molecules like proteins, enzymes and conducting polymers [19-21].

Multiwalled carbon nanotubes (MWCNTs) were found as preferred choice for the electrode surface modification after their discovery in 1991 [22]. These MWCNTs provide unique benefits such as high aspect ratio, high chemical stability, outstanding mechanical strength, high porosity, significant current carrying capacity and good electronic properties from metallic to semiconducting [23,24]. They possess higher hydrophobic surface with  $\pi$ - $\pi$

conjugative structure. Hence, MWCNTs interact with aromatic molecules through the  $\pi$ - $\pi$  electronic interactions to result new structures [25,26]. Electropolymerization is a good technique that is used to deposit certain polymers on the surface of electrodes. The use of conducting polymers in electrode surface modification provides several benefits such as reduced overvoltage, hastened electrode processes (i.e., electron transfer), and reduced surface fouling than the bare electrodes [27].

Further, CPEs are generally preferable for the surface modification over GCEs owing to their selectivity in the analysis of organic and inorganic compounds. Also, the electrode cleaning process of CPE is simple and does not affect the performance significantly, whereas GCE needs careful cleaning between each measurement. Although, sulfanilic acid has been reported as surface modifier in the electrochemical detection of several analytes [28,29], no study has been reported its electrochemical behaviour by cyclic voltammetry. Therefore, the present study aimed to design a modified sensor by electropolymerizing bromocresol purple on MWCNTs CPE for the voltammetric determination of sulfanilic acid. The use of poly(BC/MWCNTs)CPE enhanced the electron transfer reactions by its extraordinary properties such as large surface area,  $\pi$ - $\pi$  conjugated bonds, increased active sites and superior conductivity [30,31]. The sensor has offered high specificity and optimum response for the detection of sulfanilic acid at the corporal pH conditions that made it possible to employ this method for the detection of sulfanilic acid concentrations in various samples.

## 2. EXPERIMENTAL

### 2.1. Chemicals and reagents

All chemicals and reagents received were in analytical grade and used as such. Millipore water was utilized in all the experiments including for the preparation of stock and standard solutions. Sulfanilic acid, sulfuric acid ( $\text{H}_2\text{SO}_4$ ), nitric acid ( $\text{HNO}_3$ ), sodium dihydrogen phosphate ( $\text{NaH}_2\text{PO}_4$ ) and disodium hydrogen phosphate ( $\text{Na}_2\text{HPO}_4$ ) were supplied by Hi-Media Laboratories Pvt. Ltd., Mumbai. Fine graphite powder and silicon oil were provided by Merck and Sigma-Aldrich Laboratories Pvt. Limited, Mumbai. Bromocresol purple was procured from Fine Laboratories Pvt. Limited, Mumbai.

### 2.2. Instrumentation

All cyclic voltammetry (CV) and differential pulse voltammetry (DPV) measurements were performed on CH Instruments Potentiostat Model CHI610D (USA) consisting a conventional three electrode cell, an Ag/AgCl (Saturated KCl) as a reference electrode and a platinum wire as a counter electrode. A bare CPE (2.0 mm i.d.) and modified poly(BC/MWCNTs)CPE were utilized as working electrodes. The pH measurements were conducted on Elico Li 120 pH meter. The surface morphology of the constructed new electrode

was analysed by scanning electron microscope (Carl Zeiss EVO MA 15). Sonics sonicator-XI was used to sonicate the MWCNTs mixture. All electrochemical studies were accomplished at room temperature ( $25\pm 1.0$  °C).

### 2.3. Preparation of bare and MWCNTs modified CPE

The bare CPE was processed by mixing the graphite powder with silicone oil at 70:30 (w/w) ratio. Then, the mixture was taken in agate mortar and grinded with pestle for 30 min to get the homogenous paste. The resulted homogenous paste was compacted into the cave of CPE. For the modification of CPE with MWCNTs, it was acidified with a mixture of  $\text{HNO}_3\text{-H}_2\text{SO}_4$  by adding 10 mg of untreated MWCNTs with excess amount of concentrated  $\text{HNO}_3\text{-H}_2\text{SO}_4$  (wt. 68%, v/v 1:1). The mixture was sonicated for about 4.0 h at the room temperature followed by its filtration and washing with double distilled water. The treated MWCNTs were completely dried under an infrared lamp. Afterwards, the MWCNTs/MCPE was formed in a similar way by mixing the graphite powder, treated MWCNTs and silicone oil in the ratio of 70:25:5 (w/w/w). Then the resulted homogenous paste was compressed into the cave of CPE. The quantity of MWCNTs was optimized for the best result [32].

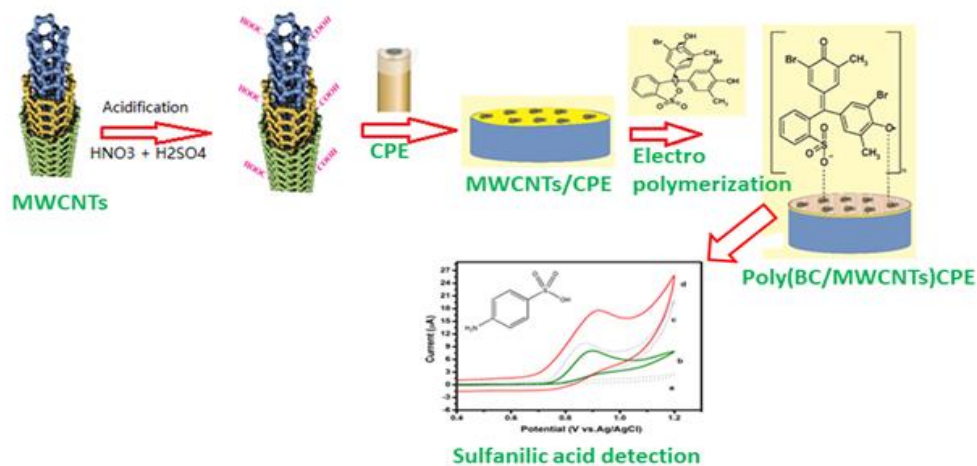
### 2.4. Preparation of poly(BC)CPE

The modified CPE with bromocresol purple was prepared by the electropolymerization of bromocresol purple on the surface of CPE in 0.1 M phosphate buffer solution at pH 7.5 containing 1.0 mM of bromocresol purple. The reaction was conducted with CV sweeps in the potential range between 0.4 V to 1.3 V at the scan rate of  $50 \text{ mVs}^{-1}$ . The complete polymerization process was conducted in 20 cycles. After the polymerization process, the electrode surface was thoroughly cleansed with double distilled water.

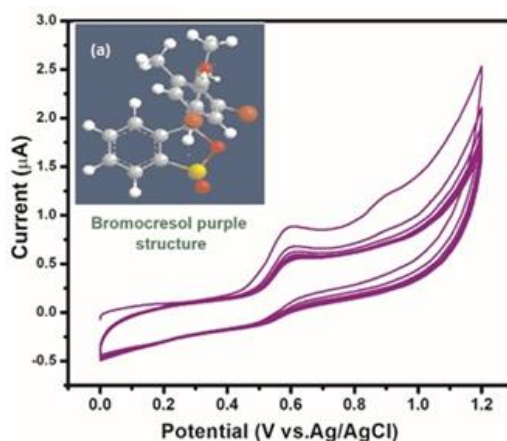
### 2.5. Preparation of working electrode poly(BC/MWCNTs)CPE

Electropolymerization of bromocresol purple at modified MWCNTs/CPE was carried out by taking previous method suggested by *O. Gilbert et.al* [33]. The preparation of working electrode was based on the CV method in aqueous solution containing 1.0 mM of bromocresol purple and phosphate buffer solution of pH 7.5. Electropolymerization was accomplished by employing the potential between 0.4 V to 1.3 V at the scan rate of  $50 \text{ mVs}^{-1}$  for 20 cycles using CV to form polymer layer on the surface of electrode. The schematic representation for the formation of modified poly(BC/MWCNTs)CPE is presented in Fig. 1. The electropolymerization reaction mechanism was illustrated in few steps which includes the deprotonation of bromocresol purple followed by the addition polymerization between MWCNTs modified carbon paste electrode and bromocresol purple. The electrode was comprehensively cleansed with distilled water after the electropolymerization and employed for the

electrochemical analysis. The electrochemical polymerization of bromocresol purple on the surface of MWCNTs/CPE for 20 cycles of cyclic voltammograms at scan rate of  $50 \text{ mV s}^{-1}$  and  $0.1 \text{ M}$  phosphate buffer solution of pH 7.5 is presented in Fig. 2.



**Fig. 1.** Schematic representation for the electrochemical polymerization of bromocresol purple at modified MWCNTs/CPE

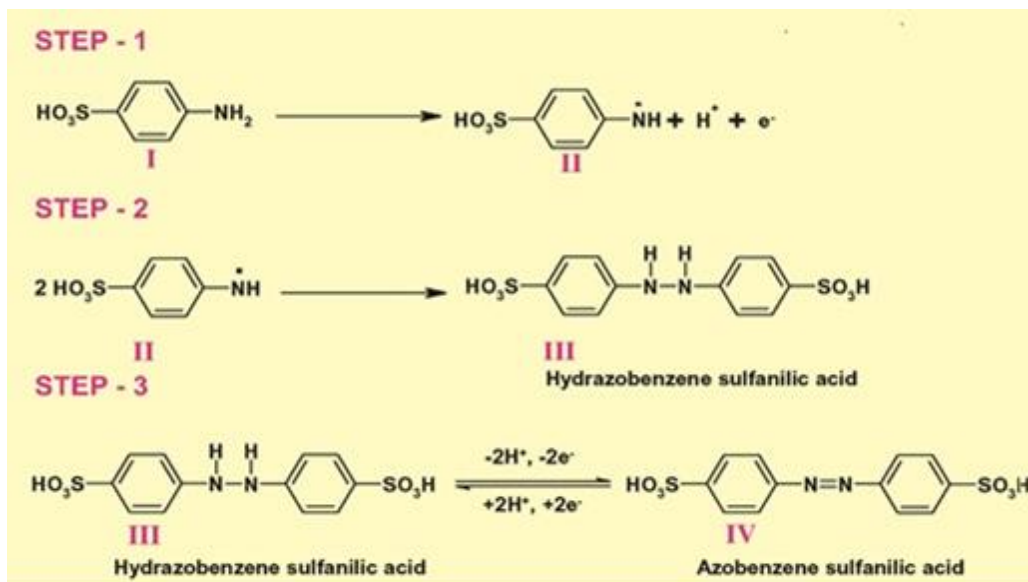


**Fig. 2.** Continuous 20 cycles of cyclic voltammograms for the electrochemical polymerization of bromocresol purple onto the surface of MWCNTs/CPE (Scan rate  $50 \text{ mV s}^{-1}$  and  $0.1 \text{ M}$  phosphate buffer solution of pH =7.5) [Inset (a) structure of bromocresol purple]

## 2.6. Analytical procedure

The modified poly(BC/MWCNTs)CPE was placed in phosphate buffer solution of pH 7.5 consist of  $1.0 \text{ mM}$  sulfanilic acid solution. The electrolytic solution was stirred thoroughly and recorded the CV and DPV measurements between  $0.4 \text{ V}$  to  $1.3 \text{ V}$  at the scan rate of  $50 \text{ mV s}^{-1}$ . When a potential range applied to the electrode, the sulfanilic acid present in solution gets oxidized to form azobenzene sulfanilic acid as shown in Fig. 3. In the first step, sulfanilic acid

(I) first oxidized to free radicals (II). Then free radicals (II) formed in the first step combined rapidly to form hydrazobenzene sulfanilic acid (III). In the final step, the hydrazobenzene sulfanilic acid (III) oxidized to form azobenzene sulfanilic acid (IV).



**Fig. 3.** Proposed electrochemical oxidation mechanism of sulfanilic acid at the fabricated poly(BC/MWCNTs)CPE electrode

## 2.7. Determination of sulfanilic acid in dye samples.

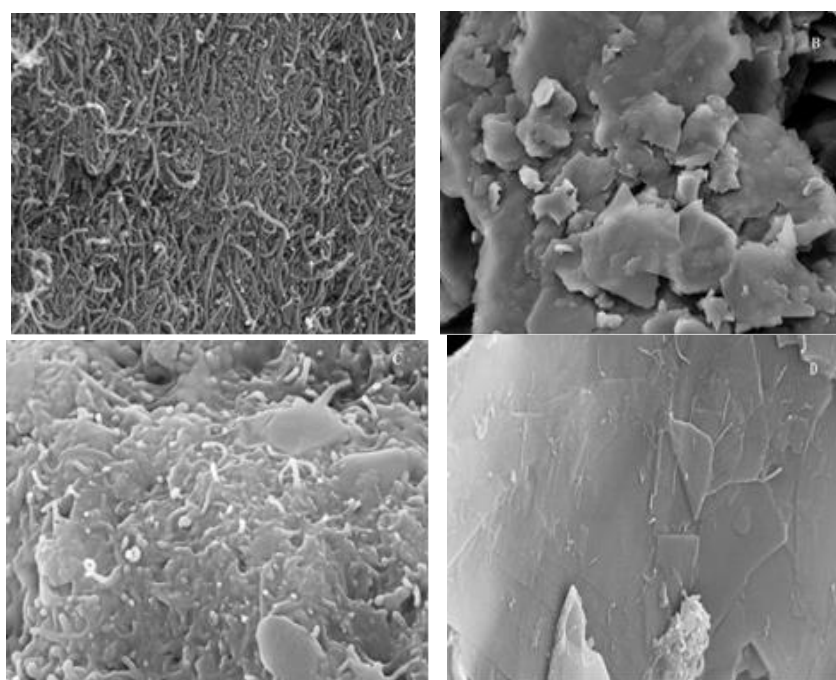
Dye samples were diluted using 0.1 M phosphate buffer solution (pH=7.5) without any pretreatment and subjected for the analysis. 25 mL of the diluted solution was added each time with measured volumes of sulfanilic acid solution with known concentrations to attain different spiked concentrations of sulfanilic acid. This solution was analyzed by DPV at the modified poly(BC/MWCNTs)CPE and the experiments were conducted three times.

## 3. RESULTS AND DISCUSSION

### 3.1. Characterization

The morphology of different surface modified electrodes was determined by scanning electron microscopy analysis. In fact, the electrochemical determinations highly depend on the surface morphology of the developed electrode. The changes in the morphology of different electrodes was shown in Fig. 4. The SEM images of MWCNTs were taken by using 1.0 mg of MWCNTs suspended in 5.0 mL of ethanol using sonication. A drop of the sonicated solution was dispersed on the glass surface and it was taken into the instrument to get the images. From the Fig. 4 (a), the SEM image of MWCNTs shows that the ratio of MWCNTs are very eventual

without any modification (higher than 75%) at 200 nm diameter. They exist as bundles of transverse size. The surface of the bare CPE in Fig. 4 (b) was erratically arranged with the flakes of graphite with 2.0  $\mu\text{M}$  diameter. From the Fig. 4 (c), it was noticed that the half flaky structures confirmed the surface modification of bare CPE with MWCNTs and it was the natural accompanying of the amorphous carbon with catalytic particles of MWCNTs. Finally, Fig. 4 (d) confirms the molecules of poly-bromocresol purple were coated on the surface of MWCNTs/MCPE to make a thin film which shows the catalytic activity towards the sulfanilic acid. The polymerization of bromocresol at this electrode provided uniform and smooth surface indicating the polymer growth on this electrode.

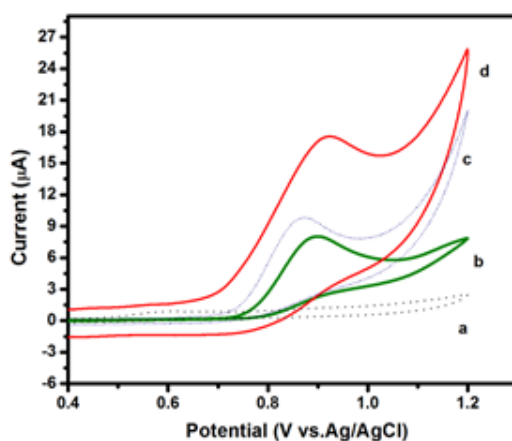


**Fig. 4.** SEM images of (a) MWCNTs; (b) bare CPE; (c) MWCNTs/MCPE and (d) poly(BC/MWCNTs)CPE

### 3.2. Voltammetric investigation of SA at fabricated electrodes

The electrochemical performance of 1.0 mM sulfanilic acid in PBS of pH 7.5 at bare CPE, poly(BC)/CPE, MWCNTs/CPE and poly(BC/MWCNTs)CPE was examined by CV and DPV techniques. The cyclic voltammograms derived for sulfanilic acid using different electrodes are presented in Fig 5. From Fig. 5, it was observed that, in the forward scan from 0.4 V to 1.3 V, the oxidation peak was detected at the potential of 0.9051 V and it was basically formed due to the oxidation of sulfanilic acid. At bare CPE, sulfanilic acid has showed very poor current response of  $1.032 \times 10^{-6}$  A (Fig. 5 (a)). By the modification of CPE, the enhanced current response was observed when compared to the bare CPE. From the Fig. 5 (b) and Fig. 4 (c), it is evident that the enhanced current response of sulfanilic acid was due to the electropolymerization of CPE with bromocresol Purple and modification with MWCNTs

respectively. The enhanced current response of sulfanilic acid by the electropolymerization of CPE with bromocresol purple and by the modification of CPE with MWCNTs shows  $8.052 \times 10^{-5}$  A and  $9.010 \times 10^{-5}$  A respectively. The enhanced current response of sulfanilic acid by the modification with MWCNTs was due to the vicinity of hexagonal sheets in the MWCNTs structure. These hexagonal groups might have transferred the electrons and increased the conducting nature of the electrode. The topmost current response of sulfanilic acid i.e.,  $1.731 \times 10^{-4}$  A was mainly due to the modification of MWCNTs/CPE with poly bromocresol purple and it was shown in Fig. 5 (d). Hence, poly(BC/MWCNTs)CPE was selected as the working electrode throughout the experiment.



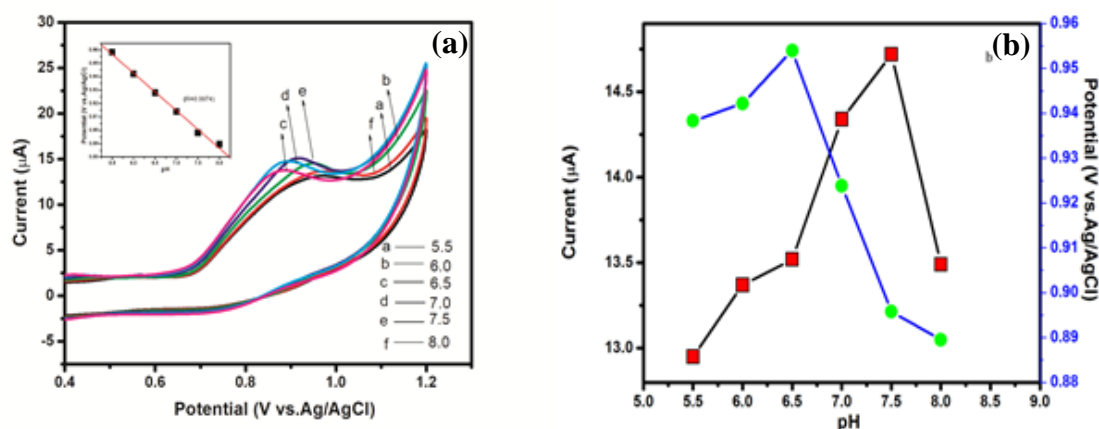
**Fig. 5.** Cyclic voltammograms for the electrochemical response of sulfanilic acid at different electrodes in 0.1 M PBS (pH=7.5) (a) bare CPE, (b) poly(BC)/CPE, (c) MWCNTs/CPE, and (d) Poly(BC/MWCNTs)CPE

### 3.3. Optimization of pH

To measure the influence of pH on peak currents, the CV response was examined for 1.0 mM sulfanilic acid at the modified poly(BC/MWCNTs)CPE over the pH range between 5.5 - 8.0. Fig. 6 (a) clearly indicated that, increasing the buffer pH from 5.5 to 8.0 increase the oxidation peak current of sulfanilic acid and obtained the maximum value at pH 7.5. Thereafter, the oxidation peak current of sulfanilic acid started to decrease with increasing pH. Thus, pH 7.5 was considered as the optimum value for all subsequent analytical experiments. Also, Fig. 6(a) indicated a shift in anodic peak potential towards the negative value owing to the direct involvement of protons in the rate determining step of sulfanilic acid oxidation. In addition, a well-established linear relationship (Inset of Fig. 6 (a)) was found between solution pH and anodic peak potential in accordance with the linear regression equation  $E_p$  (V) =  $-0.02805 + 1.1194$  pH, ( $R=0.9972$ ). The obtained slope of this equation was 0.028 mV/pH that is almost similar to the theoretical value of 30 mV/pH, which confirms the involvement of protons in the oxidation of sulfanilic acid at poly(BC/MWCNTs)CPE [34-36]. Hence, assuming a Nernstian behavior, the sulfanilic acid oxidation at poly(BC/MWCNTs)/CPE



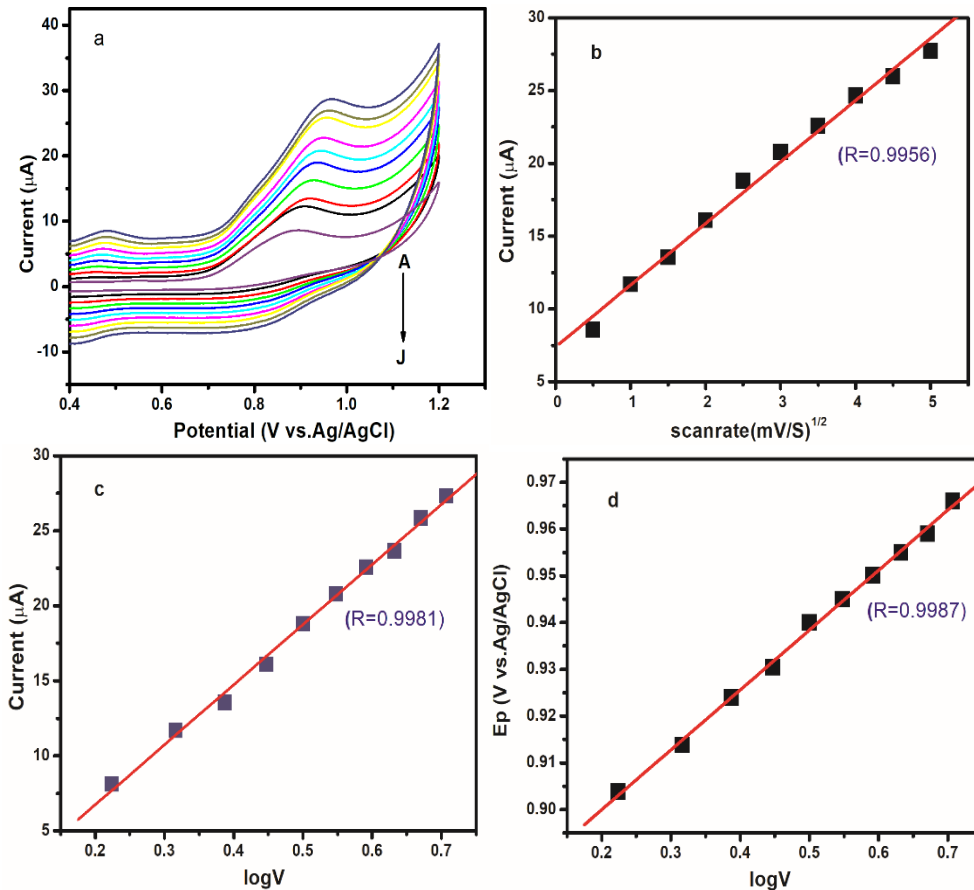
complements a two-electron/one proton process [37]. The pH effect on the oxidation peak currents were also showed in Fig. 6 (b). It is a plot between oxidation peak current and pH of phosphate buffer solution ranging between 5.5-8.0. From the plot, it is noticed that the solution pH has significant effect over the peak currents. After the optimum level, the peak current was declined with any increment in pH of the buffer solution. So, PBS with pH 7.5 was chosen for all experimental investigations.



**Fig. 6.** (a) Cyclic voltammograms achieved at poly(BC/MWCNTs)CPE in 0.1 M PBS of pH ranges from 5.5 to 8.0. Inset expresses the relationship of  $E_{pa}$  with pH (5.5–8.0); (b) A plot of sulfanilic acid oxidation peak current vs. PBS solution pH (5.5–8.0) and formal potential vs. PBS solution pH (5.5–8.0) at scan rate  $50 \text{ mV s}^{-1}$

### 3.4. Effect of scan rate

The scan rate effect on the peak currents was determined by the electrocatalytic oxidation of sulfanilic acid at poly(BC/MWCNTs)CPE over the range between  $50\text{--}500 \text{ mVs}^{-1}$ . The scan rate effect on the peak currents were plotted Fig. 7. It is observed that the anodic peak currents were increased in accordance with the square root of scan rates following the linear regression equation  $I \text{ (mA)} = 4.0032 \times 10^{-4} + 1.2701 \times 10^{-4} V^{1/2} \text{ (mV}^{1/2} \text{ s}^{-1/2})$  ( $R^2 = 0.9981$ ). This points out that electrocatalytic oxidation of sulfanilic acid at poly(BC/MWCNTs)CPE is a diffusion-controlled process [38]. In addition, the anodic peak potential ( $E_{pa}$ ) presents a linear relationship with  $\log v$  and the regression equation can be expressed as  $E_{pa} = 0.12812 \log v + 0.8743$  ( $R^2 = 0.9987$ ), which indicates the oxidation of sulfanilic acid at poly(BC/MWCNTs)CPE is irreversible.



**Fig. 7.** (a) Cyclic voltammograms for 25 mM sulfanilic acid in 0.1 M PBS (pH=7.5) on the poly(BC/MWCNTs)CPE at the scan rates of 50, 100, 150, 200, 250, 300, 350, 400, 450 and 500 mV s<sup>-1</sup>; (b) The plot of I<sub>pa</sub> vs scan rate; (c) The linear plot for current vs log v, and (d) The linearity plot of peak potentials with log v

For a complete irreversible electrode reaction, the data can be utilized to find the rate determining step, which can be obtained from the following Laviron’s equation [39].

$$E_p = E_o - m [0.78 + \ln (D_{1/2} / K_s) + (m/2) (\ln m)] + m / 2 \ln v \tag{1}$$

Since  $m=RT/(1-\alpha)nF$ , the equation is written as follows

$$\log k_s = \alpha \log (1-\alpha) + (1-\alpha) \log \alpha - \log (RT/nFv) \alpha (1-\alpha) nF\Delta E_p / 2.3RT \tag{2}$$

Where n denotes the number of electrons participated in rate-determining step,  $\alpha$  denotes electron transfer coefficient,  $k_s$  denotes reaction rate constant, R denotes gas constant, F denotes Faraday constant, and T denotes absolute temperature.

$$E_{pa} = E^\circ - RT \frac{RT}{(1-\alpha)nF} \ln \frac{RTk_s}{(1-\alpha)nF} + \frac{RT}{(1-\alpha)nF} \ln \vartheta \tag{3}$$

$$\log k_s = \alpha \log (1-\alpha) + (1-\alpha) \log \alpha - \log (RT/nFv) \alpha (1-\alpha) nF\Delta E_p / 2.3RT \tag{4}$$

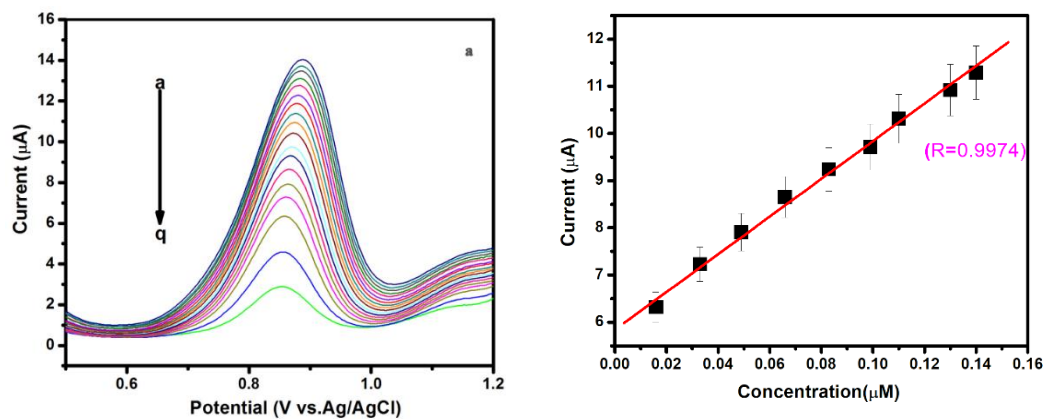
### 3.5. Analytical performance

The DPVs of sulfanilic acid at the poly(BC/MWCNTs)CPE was represented in Fig 8. From the Fig 8 (a) and (b), it is found that the anodic oxidation peak currents and sulfanilic acid concentration were proportional within the dynamic range between  $1.665 \times 10^{-7}$  to  $1.336 \times 10^{-5}$  and the linear dynamic range was found to be  $0.0165 \times 10^{-7}$  -  $0.149 \times 10^{-6}$  as calculated from the following linear regression equation:  $I_{pa} (\mu A) = 39.12789C (\mu mol L^{-1}) + 5.90$  ( $R^2 = 0.9974$ ). The LOD and LOQ concentrations were determined using the following equations.

$$LOD = \frac{3S}{M} \quad (5)$$

$$LOQ = \frac{10S}{M} \quad (6)$$

Where, S denotes the standard deviation, and M denotes the slope of calibration plot. The LOD and LOQ values were found to be  $0.98 \times 10^{-7}$  M and  $3.2 \times 10^{-7}$  M respectively. The fabricated poly(BC/MWCNTs)CPE demonstrated higher sensitivity, broad linearity range and easy fabrication of the modified electrode.



**Fig. 8.** (a) DPV collected for poly(BC/MWCNTs)CPE adding  $0.0165 \times 10^{-7}$  to  $0.113 \times 10^{-5}$  sulfanilic acid into 0.1 M PBS (pH=7.5), and (b) Calibration curve for the oxidation peak current vs. concentration of sulfanilic acid

Furthermore, designing the environmentally friendly electrochemical sensor by a simple electropolymerization procedure enable the platform for the electrochemical sensing of the sulfanilic acid.

### 3.6. Comparison of poly(BC/MWCNTs)CPE with other electrodes

To appraise the performance of the developed poly(BC/MWCNTs)CPE, a comparison was made by taking the linear range and detection limit of different MWCNTs based electrodes that were employed for the detection of different analytes and the comparison is shown in Table 1.

From the Table 1, it is concluded that the prepared working electrode poly(BC/MWCNTs)CPE shows good catalytic activity, improved sensitivity and lower detection limits for the analysis of sulfanilic acid. Also, the results showed that the developed poly(BC/MWCNTs)CPE is sensitive than other MWCNTs based electrodes for the detection of analytes [39,42].

**Table 1.** Observation of linearity and detection limits of poly(BC/MWCNTs)CPE with reported MWCNTs electrodes for different analytes

Electrode	Linear range (mol L <sup>-1</sup> )	Detection limit (M)	Ref.
f-MWCNTs/GCE	3.0×10 <sup>-6</sup> to 2.0×10 <sup>-4</sup>	6.0×10 <sup>-7</sup>	[39]
MWCNTs/poly(L-Cys)/GCE	10×10 <sup>-6</sup> to 4.0×10 <sup>-5</sup>	2.8×10 <sup>-6</sup>	[40]
MWCNTs-IL GeI/GCE	1.0×10 <sup>-6</sup> to 1.0×10 <sup>-4</sup>	1.0×10 <sup>-7</sup>	[41]
GC/MWCNTs/Fe-NAZ-CH	7.35×10 <sup>-6</sup> to 8.33×10 <sup>-4</sup>	1.05×10 <sup>-6</sup>	[42]
Poly-BP/MWCNTs/CPE	1.6×10 <sup>-7</sup> to 1.3×10 <sup>-5</sup>	9.8×10 <sup>-8</sup>	Present work

### 3.7. Real sample analysis

The developed poly(BC/MWCNTs)CPE electrode was examined for the analysis of sulfanilic acid in dye samples. The results demonstrated the capability of the newly constructed electrode towards the quantification of sulfanilic acid in dye samples as presented in Table 2. The recoveries were performed by standard addition method to evaluate the accuracy of the modified electrode. The results were found satisfactory within the range between 93%-108% with RSD <6.01%, which indicates the ability of the developed method for the analysis of sulfanilic acid in complex dyes and food additives.

**Table 2.** Determination of sulfanilic acid in real dye samples using poly(BC/MWCNTs)CPE

Sample	Added (mM)	Found (mM) <sup>a</sup>	Recovery (%) <sup>b</sup>	RSD (%) <sup>c</sup>
Dye sample 1	0.1	0.093	93.0	6.019
	0.2	0.189	94.5	2.936
	0.3	0.312	104.0	1.771
Dye sample 2	0.1	0.108	108.0	5.495
	0.2	0.215	107.5	6.014
	0.3	0.291	97.0	3.029

<sup>a</sup> Found (mM)= Mean of the triplicated Injected I<sub>pa</sub> values. Recovery (%)<sup>b</sup>=Found\*100/ Added

## 4. CONCLUSION

A modified electrochemical sensor i.e., poly(BC/MWCNTs)CPE was developed and optimized for the determination of sulfanilic acid in the present study. The optimization of the

study was conducted at various parameters like pH, scan rate and concentration effect. The developed electrochemical sensor has provided relatively lower LOD and LOQ values i.e.,  $0.98 \times 10^{-7}$  M and  $3.2 \times 10^{-7}$  M respectively for the sulfanilic acid. From the results, the kinetic parameters such as the reaction rate constant and charge transfer coefficients were also evaluated. The prepared electrochemical sensor has provided good catalytic activity towards the oxidation of sulfanilic acid. Overall, this study concluded that the developed poly(BC/MWCNTs)CPE has showed good repeatability, reproducibility and stability. Hence, the above modified electrode could be useful for the detection of sulfanilic acid from various pharmaceutical and environmental samples.

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