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Determination Of Nitrite And Sulphite By Using Pedot Polymer Based Sensor

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Abstract:

Electro polymerization is versatile method for producing electrically conducting polymers because of its simplicity and reproducibility. To determine the Nitrite and Sulphite by using PEDOT polymer based sensor in micro level. PEDOT, LiClO₄, β -Cd chemicals are used in this polymerization and then cyclic Voltammetry, Square wave Voltammetry, Impedance Spectroscopy methods are used in this work. 10 μ M of Nitrite and Sulphite are determined by using electrochemical polymerization.

Keywords: Poly(3,4-ethylene dioxythiophene)- PEDOT, LiClO₄, β -Cd, Sodium Nitrite, Sodium Sulphite

1. Introduction:

Sensor is defined as a device which receives energy from one system and transmits it to another, like physical variable into signal variable. Broadly defined, the sensor is a device which capable of being activated by energizing input from one or more transmission media and in turn generating a related signals to one or more transmission systems.

A **Biosensor** is an analytical device, used for the detection of an analyte that combines a biological component with a physiochemical detector. Biosensor [1,2] can generally be classified as electrochemical electrodes that obtain an electrical signal from an analyte through chemical reactions. However biosensors are different from traditional electrodes, as biologically active materials are used as modifiers to achieve selectivity, specificity and catalytic activity. Due to their sensitivity and specificity, the application of biosensors to nitrite detection has attracted much attention. A number of excellent reviews have been compiles over the past decade.

The oxidation and reduction of **conducting polymers** are associated with volumetric changes [3]. The volume changes of conducting polymers are induced by charge compensating ions and solvent molecules flowing in and out of the polymers during the reduction and oxidation processes [4,5]. Poly(3,4-ethylenedioxythiophene) (**PEDOT**) is highly promising conducting polymer owing to its extraordinary electrical properties and transparency to visible-light at its doping state [6,7].

Nitrite and sulphite have been widely used in industrial and agricultural production and ubiquitous in food, water, biology and the environment. Nitrite been widely used in meat curing [8], food preservation [9,10], dyes, bleaches, fertilizers as well as for medicinal purposes[11]. Nitrite can also be converted to potent vasodilator nitric oxide [12], which is relevant in numerous physiological processes [13]. However,

the nitrile is also a toxic inorganic contaminant that is hazardous to the health of humans and other organisms. Methemoglobinemia or “blue baby syndrome” [14], carcinogenic nitrosamines [15], gastric cancer (GC) [16], spontaneous intrauterine growth restrictions [17], abortions [18], and birth defects of the central nervous system [19] have been associated with high nitrite concentrations. Nitrites can also cause damage to aquaculture through its toxicity to aquatic animals, including fish and crustaceans. As nitrite can oxidize hemoglobin to methemoglobin, which is not capable of carrying oxygen, the latter can reach toxic concentrations in a high-density aquaculture system in contaminated waters.

This work was organized by the electric signal from dissolved nitrite and sulphite, with voltametric, potentiometric, impedimetric and scanning electron microscopy methods included. Electrochemical detection techniques have been investigated for in situ quantitative analysis and real-time monitoring of environmental parameters.

1. Materials and Methods:

2.1 Reagents:

> Poly(3,4-ethylenedioxythiophene)- (PEDOT), Lithium perchlorate- (LiClO_4), β

(beta)- cyclodextrin, $-\beta\text{-Cd}$, these chemicals were purchased from Sigma Aldrich.

> 0.01M Potassium chloride (electrolyte solution) is purchased from Sigma Aldrich.

> 0.01M Phosphate buffer saline (PBS)- 0.01M Sodium phosphate dibasic (from Vetec) and 0.01 M sodium phosphate monobasic monohydrate (from Sigma Aldrich)

> Sodium nitrite and Sodium sulphite were purchased from Merck chemical company.

2.2 Instrumentation:

Cyclic voltammetric measurements were carried out using CH analyser. A electro chemical cell with conventional three electrode system was employed in all measurements, A glassy carbon electrode (GCE - area = 3mm diameter) and a platinum electrode were used as working and counter electrodes, respectively. A saturated silver- silver chloride electrode was used as reference electrode, Before each experiment the surface of GCE was polished with alumina powder followed by thorough rinsing with double distilled water. **Square wave voltammetry (SWV)** is a form of linear potential sweep voltammetry which has found numerous applications in various fields, including within medicinal and various sensing communities. Electro chemical **impedance spectroscopy (EIS)** a tool or testing the kinetic barrier of the electrode interface, has been employed to investigate the impedance changes of the electrode surfaces in the modified process.

3. Results and discussion:

3.1 Preparation of PEDOT:

The electrochemical polymerization of the PEDOT was carried out by cyclic voltametric (CV) technique in aqueous solution containing 0.01M PEDOT, 0.1M LiClO_4 and 0.025M β -Cyclodextrine. The polymerization was carried between -0.2 and 0.95 V at a scan rate 50m V/s for different cycles, for example 1,3 and 6 cycles, to control thickness of the film. 3 cycles of deposition was the suitable thickness cycle for the to detect the nitrite and sulphite. After polymerization, the electrode was washed with double distilled water and the electro chemically treated using CV in 0.1 M phosphate buffer solution until a stable background was obtained. So the working electrode is either an unmodified GCE or PEDOT film modified GCE.

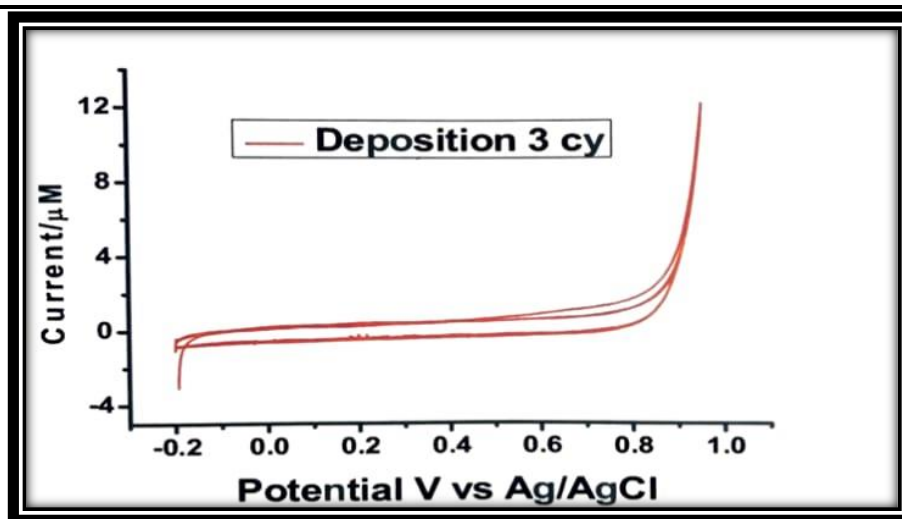


Fig 1: Cyclic voltammogram of the electro polymerization process of GCE in 0.01M of PEDOT containing 0.1M LiClO₄ in the range of -0.2 and 0.95V for 3 cycles at 0.05 V/s.

3.2 Optimization of anodic switching potential on the performance of the sensor:

The PEDOT- film was prepared at different polymerization potential ranges in cyclic voltammetry between -0.2 to 1.00V to 1.45V. It could be noticed when the anodic switching potential of polymerization was increased from 0.1V to 1.4V, the oxidation potential of the nitrite and sulphite decreased. High catalytic current for the sulphite and nitrite at polymer prepared at 0.1V must be due to high catalytic by property of PEDOT-film on GCE. The reverse trend observed in peak current at polymer film damage film prepared at higher switching potentials. Moreover, by increasing the oxidation potential of the monomer, the thickness of the polymer id being increased the oxidation and so the capacitive background current is also increased, which causes lower signal to noise ratio in the detection limit of the voltametric measurements.

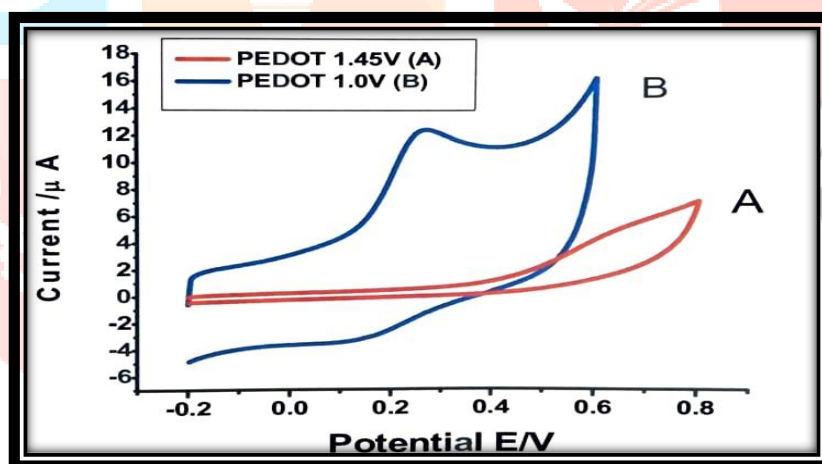


Fig:2 CVs of the sulphite at PEDOT prepared at different switching potentials (A)1.45V and (B)1.0V

3.3 Electrochemical impedance spectroscopy (EIS) of PEDOT modified GCE:

EIS is an efficient tool to examine the electrical properties of the materials and to monitor the changes associated with interfacial properties and thereby to understand the chemical transformation and processes associated with the conductive electrode surface. The EIS experiments were performed in a background solution of 5 mM Fe (CN)₆^{3-/4-} containing 0.1M KCl as the supporting electrode using the frequency range between 100mHz and 10 kHz at the applied AC voltage 100mV. EIS of polymer modified electrodes prepared at different switching potentials such as at 1.45V(black), 1.0V(red)and (C) Bare GCE (blue). These films are modified GCEs represented as Nyquist plots (Z_{im} vs Z_{re}). Due to the over oxidation of PEDOT modified film at 1.45V, resistance of the film increases and it's become unable to detect the nitrite and sulphite. Whereas the PEDOT modified film (at 1.0V)/GCE (curve b, Fig.9) exhibit to semicircular attributed to high conductivity of PEDOT modified film whereas EIS of PEDOT modified film (at 1.45V) (curve c, Fig 8) exhibits large semicircle with R_{ct} 25000Ω indicating that the resistance has been greatly increased due to poor conductivity of over oxidized PEDOT.

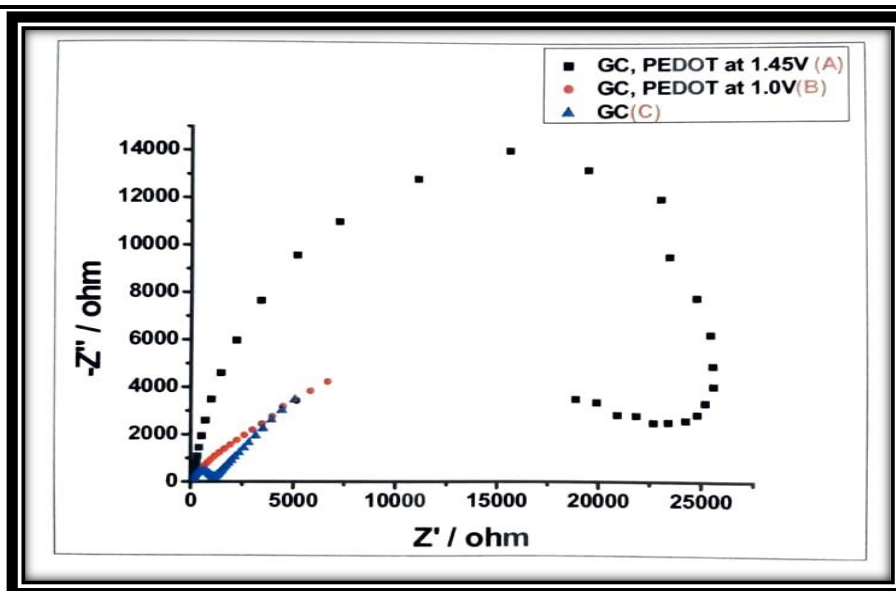


Fig: 3 EIS of polymer electrode prepared at different switching potentials modified electrode: PEDOT at 1.45V (A), (B) PEDOT at 1.0V (red), (C) Bare GCE (blue). These films are tested in 0.1M KCl containing 5mM Fe (CN)₆^{3-/4-}.

3.4 Effect of scan rate:

Cyclic voltammogram of different scan rates on the peak currents at the PEDOT modified electrode was recorded in Fig.10. The oxidation peak currents for sulphite increased with increasing the sweep rates, while their oxidation peak potential gradually shifted to positive values, suggesting the electron transfer was quasi-reversible. Plots of the anodic peak currents intensified linearly as the scanning rate increased from 10 to 200mV s⁻¹, which displayed the electrode reactions of Sulphite was adsorption-controlled processes, according to the following equations: $I_{pa} (\mu A) = -28.00 + 5.48v (Vs^{-1})$ and $I_{pc} (\mu A) = 655.93 + 10.43v (Vs^{-1})$ with the correlation coefficients (R²) of 0.9575 and 0.9946, respectively. This result was well consistent with other previous studies [20].

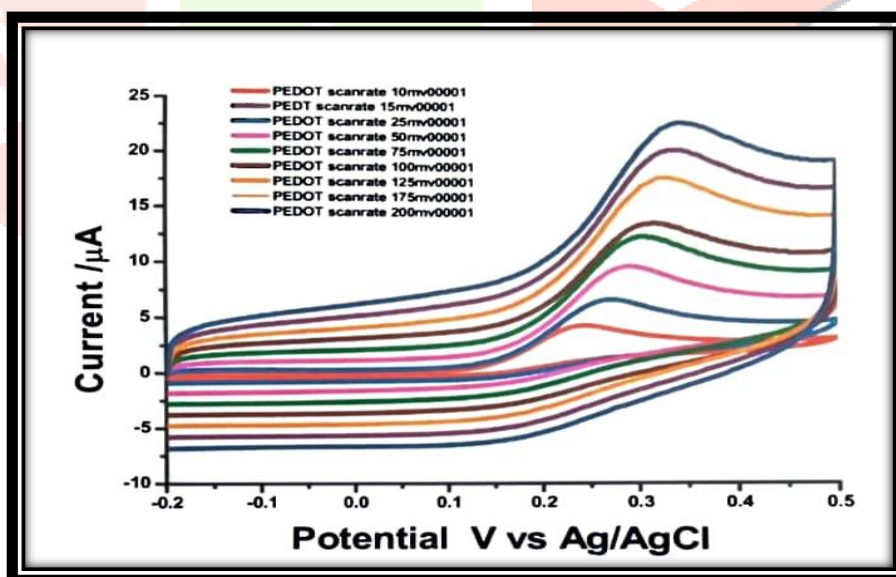


Fig: 4. Cyclic voltammogram for Electrocatalytic oxidation of sulphite(40μM) in PEDOT modified electrode at different scan rate (from bottom to top):10, 15, 25, 50,75,100,125, 175, 200mV

3.5 SWV of nitrite on modified PEDOT modified electrode:

As per the earlier reports [21], it is well known that the PEDOT film has high catalytic power for nitrite. With this idea, we have selected the PEDOT film to coat on GCE mainly for the catalytic oxidation of nitrite using PEDOT film coated GCE. The SWVs were carried for the bare GCE and PEDOT modified electrode for the 10μM of nitrite. The anodic peak current of nitrite was observed three times higher. When electrode were modified with Ppy film, the oxidation peak current of sulphite and nitrite increased drastically. The results obtained can be attributed to the electrostatic attraction between the oxidized PEDOT film and nitrite at the electrode surface/solution interface.

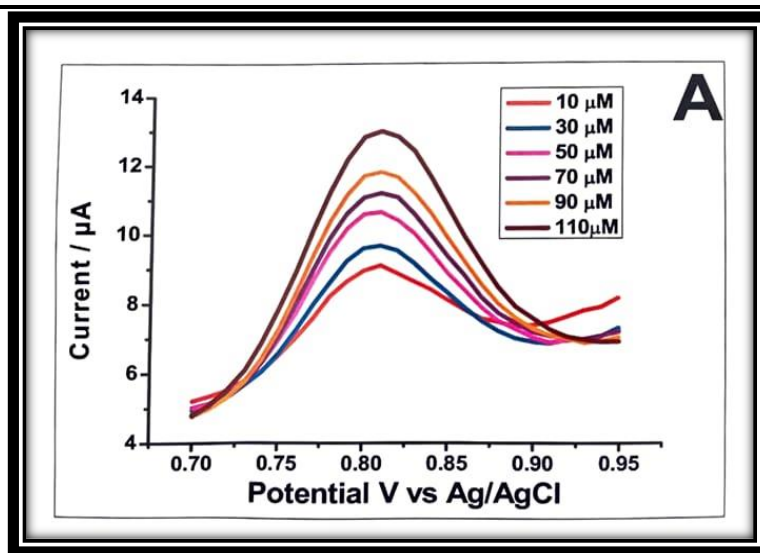
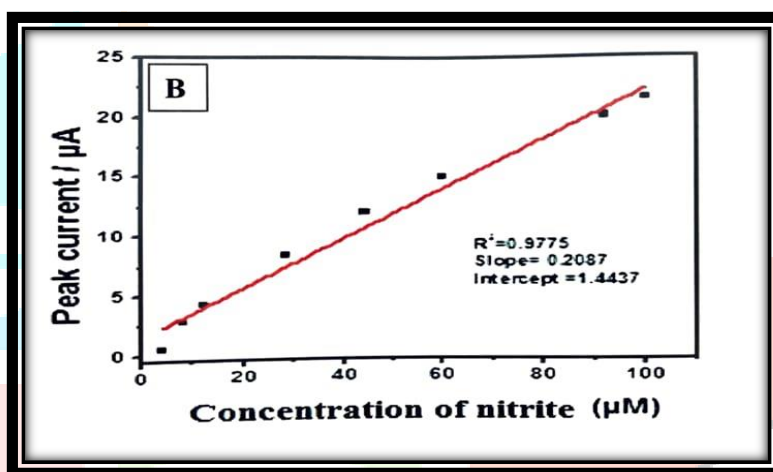


Fig 5. (A) SWV profiles at PEDOT modified electrode in 0.1M PBS for different concentrations of nitrite from 10 μ M to 110 μ M.



(B). The linear relationship between SWV peak current and nitrite concentrations.

3.6 SWV of sulphite at modified PEDOT modified electrode:

As per the earlier reports [21], it is well known that the PEDOT film has high catalytic power for nitrite. With this idea, we have selected the PEDOT film to coat on GCE mainly to the catalytic oxidation of nitrite using PEDOT film coated GCE. The SWVs were peak current of nitrite was observed three times higher at modified GCE than that of unmodified GCE and there is no change in peak potential. The results obtained can be attributed to the electrostatic attraction between the oxidized PEDOT film and sulphite (exists as acerbate anions at pH=7) that resulted in preconcentration of these anions at the electrode surface/solution interface.

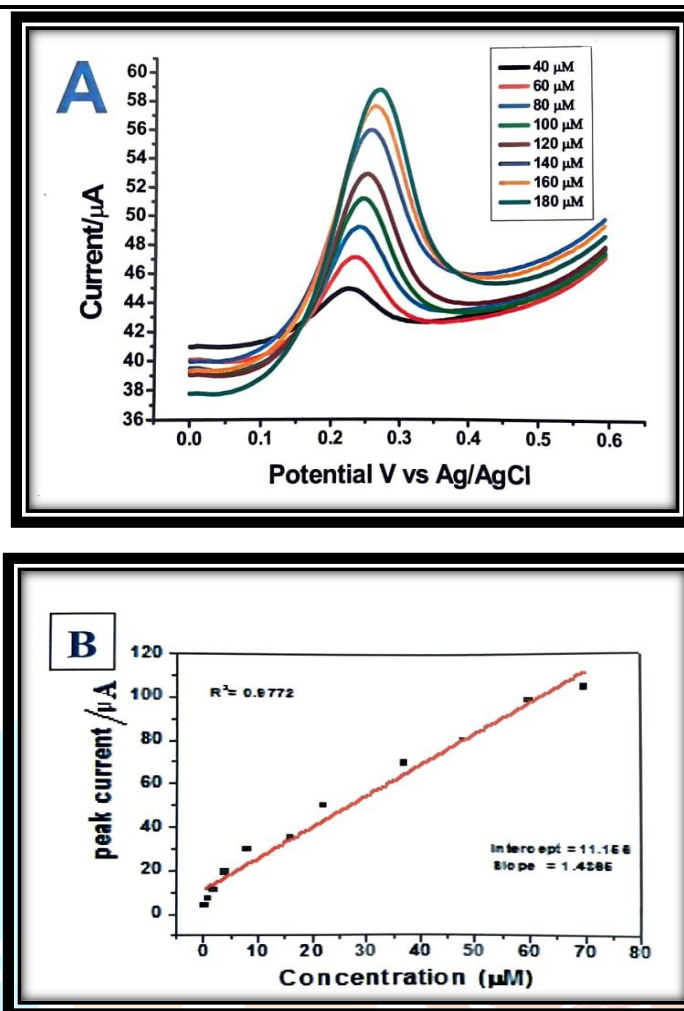


Fig 6. SWV profile at PEDOT modified electrode in 0.1 M PBS for (A) different concentration of sulphite from 40 μM to 180 μM . (B) The relationship between SWV peak currents and sulphite concentrations.

3.7 Simultaneous determination of nitrite and sulphite on PEDOT modified electrode:

To test the practical application of PEDOT modified electrode, the SWV was carried out in an electrolyte containing nitrites and sulphites at physiological pH [22]. Two well resolved independent anodic peaks are observed for nitrites and sulphites at 0.25mV and 0.7mV, respectively at PEDOT modified electrode whereas at are GCE no peak is obtained. The anodic peak separation between sulphite and nitrite is 4.5Mv.

The SWVs that were obtained PEDOT modified electrode at the during the simultaneous change of concentrations of the sulphites and nitrites. They demonstrated that the calibration curves for sulphites and nitrites were linear for a wide range of concentration from 20 μM to 160 μM , and 60 μM to 300 μM respectively. Since SWV has much higher current sensitivity and selectivity than CV does, then it was used to estimate the linear range, detection limit and simultaneous determination of sulphites and nitrites under the optimized experimental conditions. As is shown in Fig 13. SWVs for the oxidation current of different concentrations of sulphites and nitrites were increased at the PEDOT modified electrode with the increase of concentration. An increase in the peak current of nitrite is observed with increasing of sulphite concentration and the voltametric peak of nitrite is almost unchanged during the oxidation of sulphite.

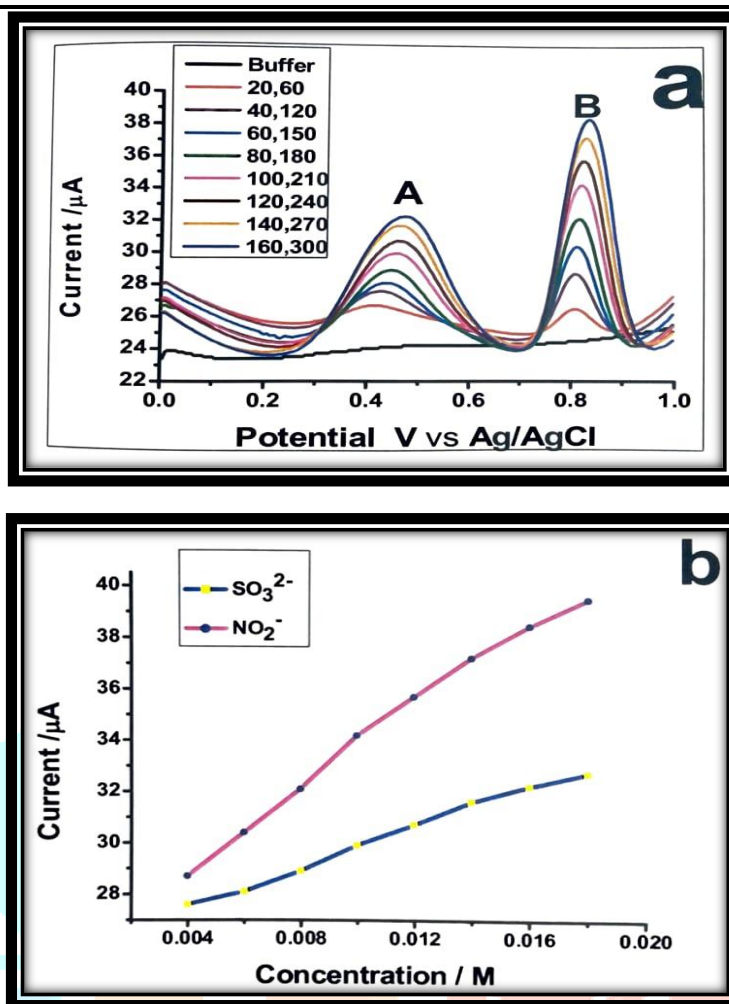


Fig 7 (a) SWV profiles at PEDOT modified electrode in 0.1M PBS containing different concentrations of sulphites and nitrites, from bottom to up the concentrations from (A) 20 to 16 μM concentration of sulphites, (B) 60 to 300 μM of nitrites. (b). The linear relationship between SWV peak current and sulphites and nitrite concentration.

Conclusion:

Electrochemical sensors and biosensors, which are simple, in expensive and easily miniaturized, have been investigated for many years to improve their selectivity and sensitivity. The PEDOT based sensor was developed and applied for the determination of sulphite and nitrite ions in aqueous medium. The PEDOT modified electrode can resolve the oxidation peaks of sulphite and nitrite ions. Low detection point is 10 μM of sulphites and nitrites.

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