



Original scientific paper

Screen printed graphite electrode modified with two-dimensional leaf-like zeolitic imidazolate framework-L (Zn) for efficient electrochemical sensing of sulphite

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Abstract

In this paper, we describe the use of a screen-printed graphite electrode modified with a two-dimensional leaf-like zeolitic imidazolate framework-L (Zn), ZIF-L (Zn) for the determination of sulphite. We started by using linear sweep voltammetry to investigate the redox properties of the modified electrode at different scan rates (10 to 400 mV s⁻¹). Next, we evaluated sulphite oxidation at the modified electrode. Using differential pulse voltammetry (DPV), the linear dynamic range of 0.04-900.0 μM and the limit of detection (3s/m) of 0.01 μM were obtained. DPV was also used to quantify sulphite in various real samples using the standard addition method.

Keywords

Differential pulse voltammetry; metal-organic frameworks; electrochemical sensors; chemically modified electrodes; real sample analysis

Introduction

Food safety is a significant concern for consumers worldwide and health organizations. According to the World Health Organization (WHO), over 200 diseases can be transmitted to humans through food, and many people are unknowingly infected with foodborne illnesses. Food additives and

preservatives are substances added to certain foods in small quantities to extend their shelf life. These additives and preservatives are crucial for maintaining the quality, appearance, taste, safety, and flavour of food over time [1]. Sulphite is a key additive in many food products because it effectively prevents enzymatic and non-enzymatic browning during processing and storage. However, sulphite can trigger asthmatic reactions in a small percentage of individuals, and excessive amounts may lead to undesirable off-flavours in food. Furthermore, some sulphite added can diminish due to reversible and irreversible chemical reactions. Therefore, accurately measuring the sulphite levels in foods is often essential [2].

Common analytical methods for detecting sulphite include high-performance liquid chromatography (HPLC)/ultraviolet spectrophotometric, colorimetric, fluorescent, HPLC-DAD-MS/MS, liquid chromatography-tandem mass spectrometry (LC/MS/MS), and LC-ICP-MS [3-9]. However, many of these techniques have drawbacks, such as the need for expensive equipment, lengthy result times, the use of hazardous solvents, and the requirement for highly skilled personnel. In contrast, electrochemical methods offer significant advantages, including simple sample preparation, relatively low instrument costs, rapid detection, and ease of miniaturization. These techniques are robust and versatile analytical tools that deliver high sensitivity and accuracy, a broad linear dynamic range (LDR), and cost-effective instrumentation. Electroanalytical sensors that utilize pulse techniques are particularly prevalent in the analysis of drugs in real samples [10].

Carbon electrodes have become increasingly popular for several reasons. They are easily modified, exhibit low background current, allow for simple renewal, show chemical stability, and are sensitive and cost-effective. These benefits make chemically modified carbon electrodes widely used for detecting a variety of analytes, such as food additives, vitamins, drugs, dyes, and amino acids [11].

One way to enhance the analysis in electroanalytical techniques is through the use of screen-printed carbon electrodes (SPGEs), which offer a simpler alternative to traditional electrochemical cells. SPGEs are relatively inexpensive, easy to manufacture, and suitable for mass production, aligning with green chemistry principles such as the development of safe products. Additionally, SPGEs enable fast analysis with a linear response, high sensitivity, low energy consumption, and effective operation at room temperature. These advantages contribute to their widespread application in various fields. Moreover, when paired with miniaturized potentiostats, SPGEs provide portability, making them ideal for point-of-care (POC) analysis. This technology has already seen commercial and academic applications [12].

Despite these advantages, electrochemical detection of analytes with bare electrodes often faces challenges related to poor sensitivity and reproducibility. Modifying the electrode surface can help reduce overvoltage and enhance the kinetics of various electrode processes [13]. Nanotechnology is a promising field that has shown significant progress and potential across many domains [14]. Recent advances in nanoscience provide new opportunities for electroanalytical techniques by facilitating electron transfer and thus improving sensitivity and selectivity. In electrochemistry, these benefits arise from an increased surface-to-volume ratio, which enhances the overall rate of diffusion processes, as well as from the greater number of molecules that can attach to or adsorb on inorganic nanoparticles [15].

Due to numerous exposed metal sites, metal-organic frameworks (MOFs) have recently gained attention for their well-defined structures, large specific surface areas, and strong catalytic activity. These advantages make MOFs widely applicable in solar cells, catalysis, biopharmaceuticals, biosensors and electrochemical sensor development. Zeolitic imidazolate frameworks (ZIFs) are a subclass of MOFs that also share many of their general properties and demonstrate excellent

thermal and chemical stability, making them particularly promising for adsorption applications. ZIFs are especially well-suited for electrochemical sensing because of their excellent dispersion and high adsorption capacity for small molecules [16].

A ZIF-L (Zn) modified screen-printed graphene electrode (SPGE) was created, resulting in a sensitive method for the electrochemical analysis of sulphite. The modified electrode demonstrated improved electrochemical performance for sulphite detection compared to the unmodified SPGE. This engineered sensor was effectively used to detect sulphite in real samples.

Experimental

Chemicals and materials

All salts and solvents, including sulphite, *etc.*, were of high purity and obtained from Merck and Sigma Aldrich. The phosphate buffer solution, PBS, was prepared using H_3PO_4 and sodium hydroxide (NaOH) in specific proportions.

Instrumentation

Cyclic voltammetry (CV), linear sweep voltammetry (LSV), differential pulse voltammetry (DPV) and chronoamperometry were used for the electrochemical analysis. The measurements were carried out with a potentiostat/galvanostat Model PGSTAT 12 Autolab electrochemical system (Eco Chemie, Utrecht, The Netherlands), utilizing software linked to GPES (Eco Chemie). Electrochemical measurements were performed using an electrochemical cell containing a screen-printed electrode (Dropsense, Spain), including a silver pseudo-reference electrode, graphite working electrode, and graphite auxiliary electrode.

Synthesis of ZIF-L (Zn)

The synthesis and characterization of ZIF-L (Zn) were detailed in our previous study [16]. Figure 1 presents the FE-SEM image of ZIF-L (Zn).

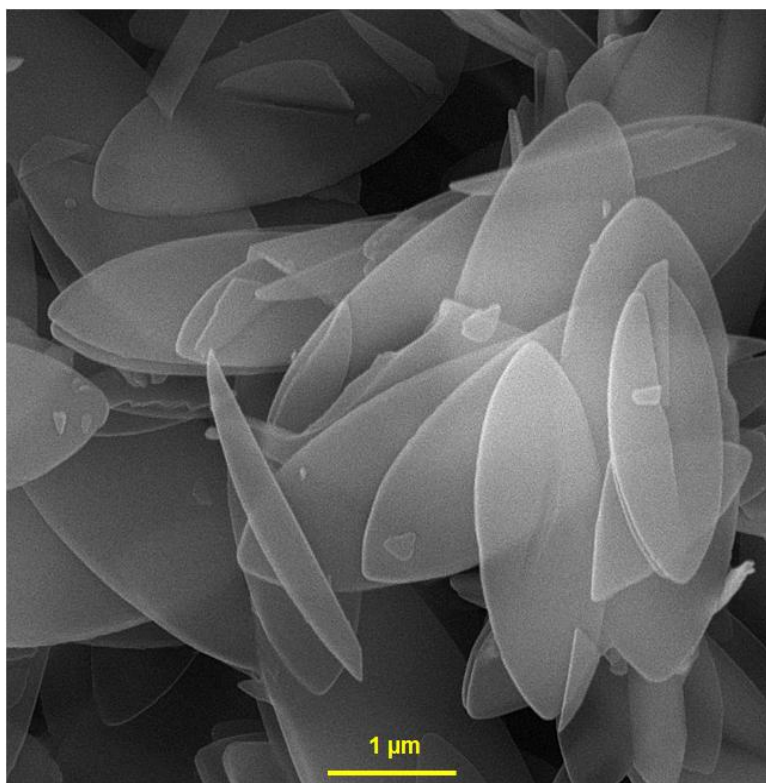


Figure 1. FE-SEM image of ZIF-L (Zn)

Preparation of modified SPGE

1.0 mg of ZIF-L (Zn) was suspended in 1000 mL of water. The suspension was dispersed using ultrasound for 20 min. Subsequently, 5 μL of the ZIF-L (Zn) solution was applied dropwise onto the surface of the SPGE working electrode.

To determine the electroactive surface area of unmodified and modified SPGE, the CV responses of unmodified SPGE and ZIF-L (Zn) modified-SPGE were recorded for redox probe (1.0 mM $\text{K}_3[\text{Fe}(\text{CN})_6]$) in the presence of 0.1 M KCl solution at different scan rates. The Randles-Ševčík equation was applied to determine the surface areas. The electroactive surface area of unmodified SPGE (0.034 cm^2) and ZIF-L (Zn) modified-SPGE (0.14 cm^2) were calculated.

Procedure

All the experiments were performed at room temperature. After transferring the modified SPGE into a phosphate buffer solution, the oxidation signal of sulphite was obtained using DPV, with a scan rate of 40 mV s^{-1} (step potential = 0.008 V and pulse amplitude = 0.01 V, initial potential = 580 mV, final potential = 960 mV). The data were baseline-corrected with GPES software. Five modified SPGEs were prepared identically, and the average signal of sulphite was obtained prior to each experiment for sulphite determination.

Results and discussion

Electrochemical oxidation of sulphite in the surface of bare SPGE and ZIF-L (Zn) modified-SPGE

Figure 2 shows the CVs in pH 7.0 PBS with 500.0 μM sulphite. The anodic oxidation potential for bare SPGEs (trace a) is observed at 845 mV, with peak currents of 5.5 μA , corresponding to the electrochemical oxidation of sulphite. In contrast, the ZIF-L (Zn)/SPGE (trace b) displays a peak at 750 mV, with peak currents of 11.0 μA . This indicates that the ZIF-L (Zn)/SPGE achieves a higher peak current, making it more favourable for electroanalytical applications and potentially increasing sensitivity at lower concentrations. Therefore, modifying the SPGE with ZIF-L (Zn) enhances sensitivity and reduces overvoltage.

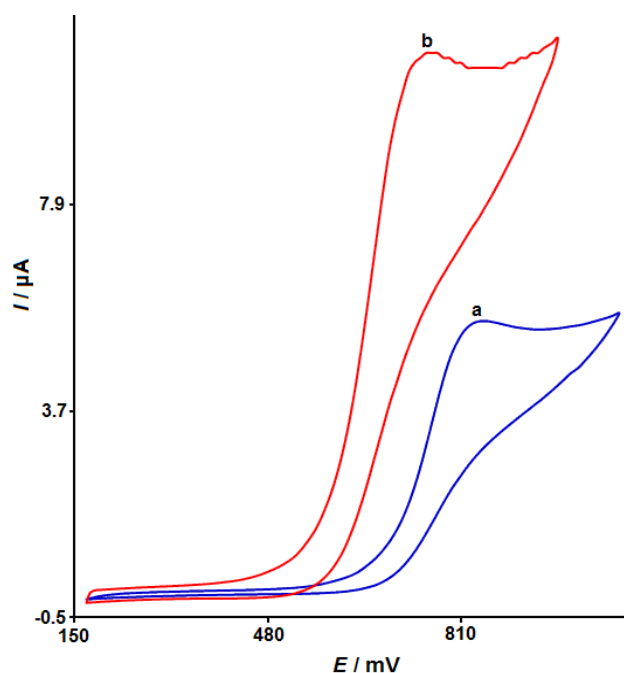


Figure 2. Cyclic voltammograms of bare SPGE (a) and ZIF-L (Zn) modified SPGE (b) for 500.0 μM sulphite in 0.1 M PBS at pH 7.0 (scan rate: 50 mV/s)

Effect of scan rate

The influence of scan rate on the redox behaviour of 300.0 μM sulphite was examined in 0.1 M PBS using LSV (Figure 3). As illustrated in Figure 4, the oxidation peak currents (I_p) of sulphite were directly proportional to the square root of the scan rate ($v^{1/2}$), which varied from 10 to 400 mV s^{-1} . These findings suggest that the electrochemical reaction of sulphite is a diffusion-controlled process.

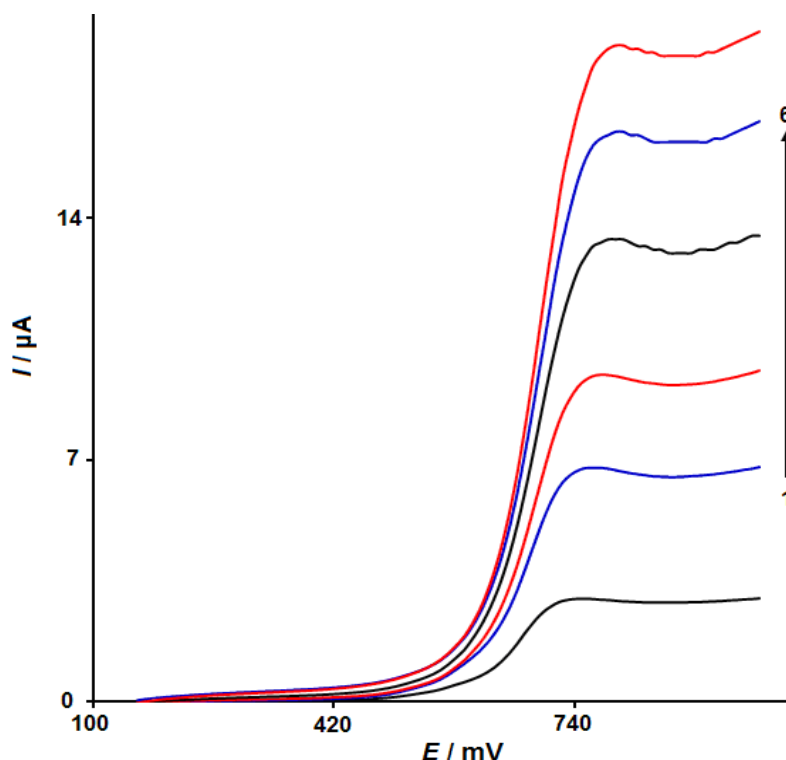


Figure 3. LSVs of ZIF-L (Zn) modified SPGE for 300.0 μM sulphite in 0.1 M PBS at pH 7.0 at varying scan rates (1 - 10, 2 - 50, 3 - 100, 4 - 200, 5 - 300 and 6 - 400 mV/s)

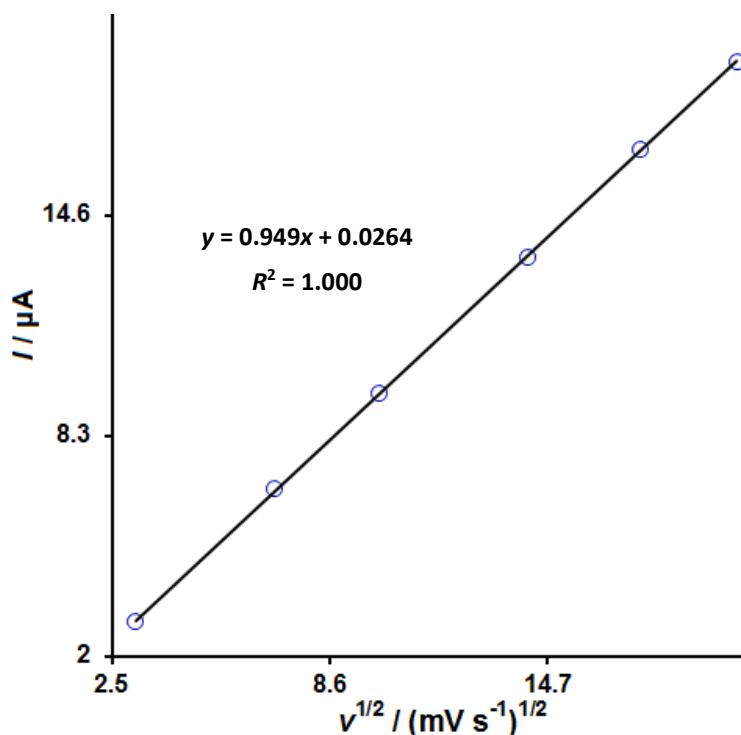


Figure 4. Linear dependence of peak currents on the square root of the scan rate

Chronoamperometry

To determine the diffusion coefficient (D) of sulphite at the ZIF-L (Zn)/SPGE, chronoamperometry was employed. Figure 5 presents the chronoamperometry studies conducted using ZIF-L (Zn)/SPGE at various sulphite concentrations, with the electrode potential set to 790 mV. The chronoamperometry data were analysed using the Cottrell equation [16]. Under diffusion-controlled conditions, the plot of current (I) versus time $t^{-1/2}$ is linear, allowing for the calculation of D from its slope. The plots of I versus $t^{-1/2}$ for sulphite are shown in Figure 6. The slopes of these linear plots were then plotted against the sulphite concentration (Figure 7), with the estimated value of D being $1.34 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$.

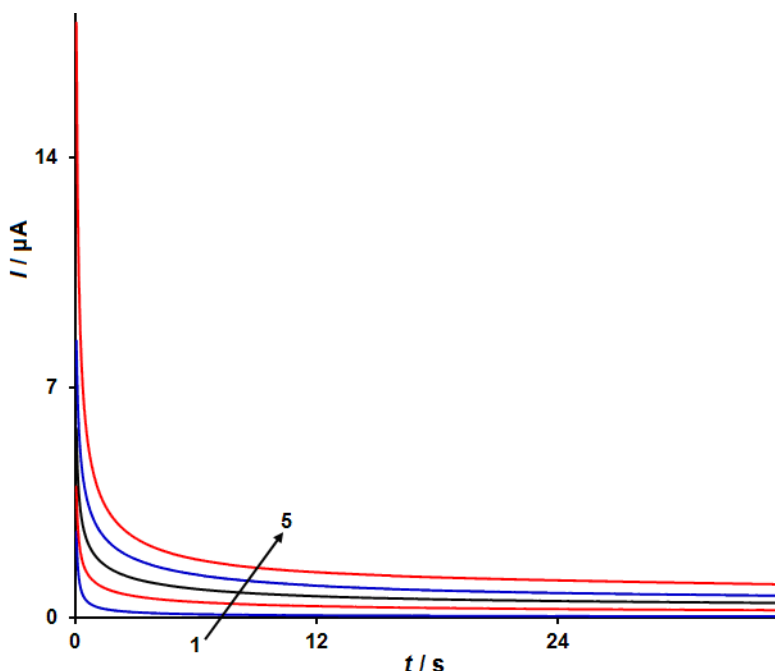


Figure 5. Chronoamperogram curves of ZIF-L (Zn) modified SPGE in 0.1 M PBS (pH 7.0) with sulphite concentrations of 1 - 0.1, 2 - 0.2, 3 - 0.3, 4 - 0.5 and 5 - 1.0 mM

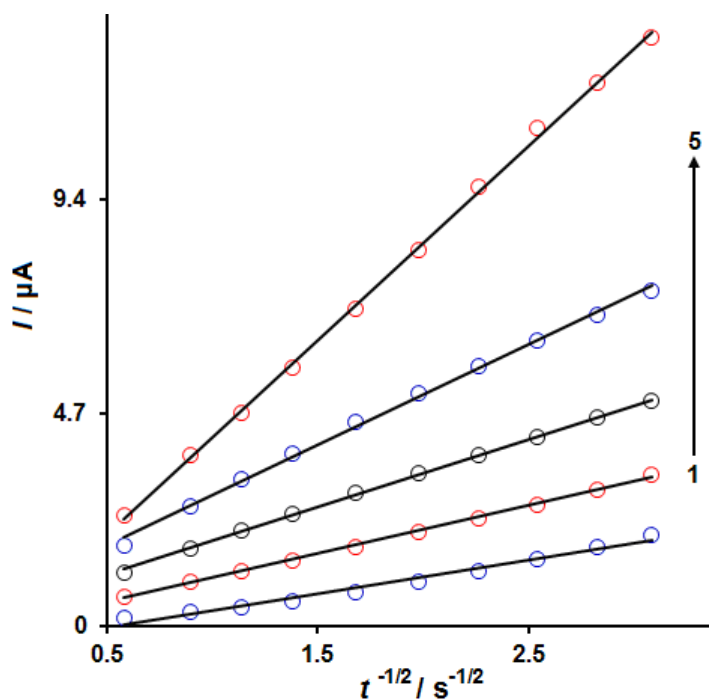


Figure 6. Plots of I versus $t^{-1/2}$ obtained from chronoamperograms for various sulphite concentrations (1 - 0.1, 2 - 0.2, 3 - 0.3, 4 - 0.5 and 5 - 1.0 mM)

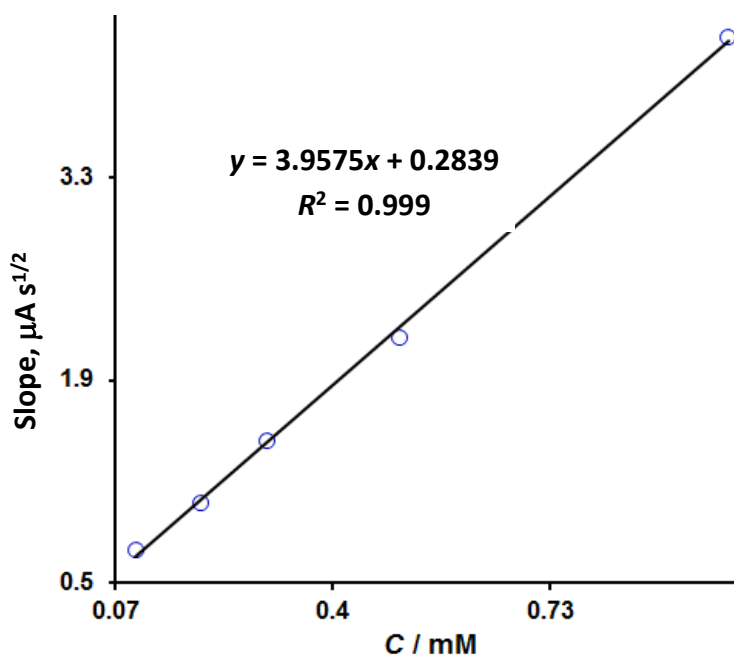


Figure 7. Plot of slope versus various concentrations of sulphite derived from chronoamperograms

DPV technique

The DPV technique was employed to quantitatively assess ZIF-L (Zn)/SPGE with varying sulphite concentrations from 0.04 to 900.0 μM (Figure 8). A noticeable increase in peak current was observed as the sulphite concentration rose.

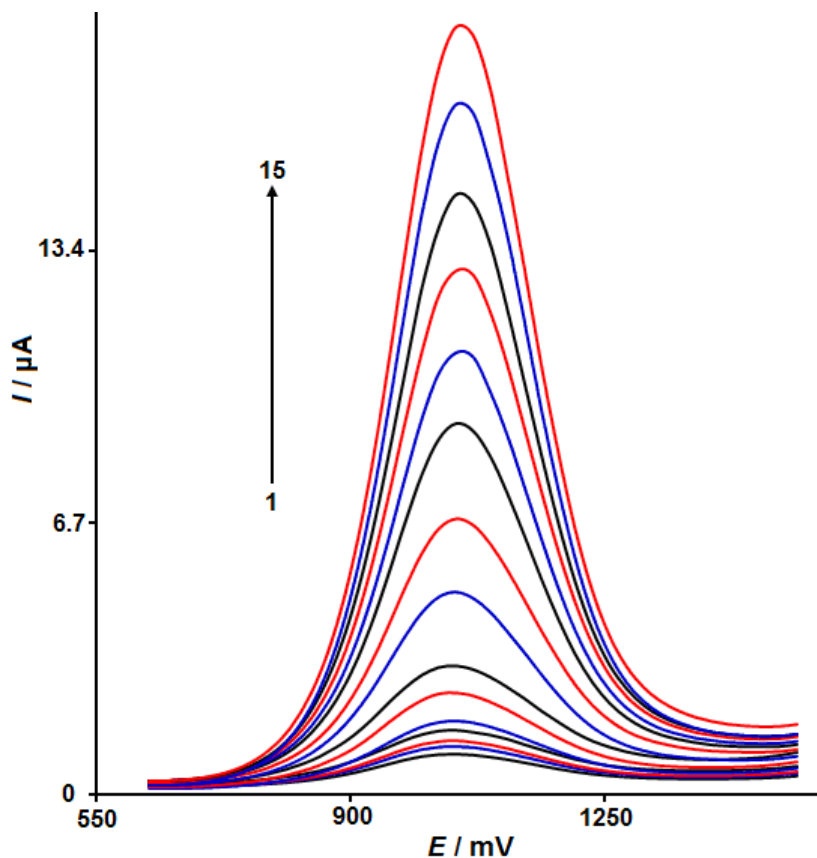


Figure 8. DPVs of ZIF-L (Zn) modified SPGE at different sulphite concentrations: 0.04, 0.5, 5.0, 15.0, 30.0, 70.0, 100.0, 200.0, 300.0, 400.0, 500.0, 600.0, 700.0, 800.0 and 900.0 μM , curves 1 to 15, respectively

As illustrated in Figure 9, the peak current signals at ZIF-L (Zn)/SPGE increased progressively with sulphite concentration, establishing a strong linear relationship within the concentration range, LDR, of 0.04-900.0 μM . The limit of detection, LOD, was calculated to be 0.01 μM . This value of LOD can be compared with some recent works, 16.5 μM [17] and 3.3 μM [18]. As can be seen, the obtained LOD in this work is better than the values obtained in these previous works.

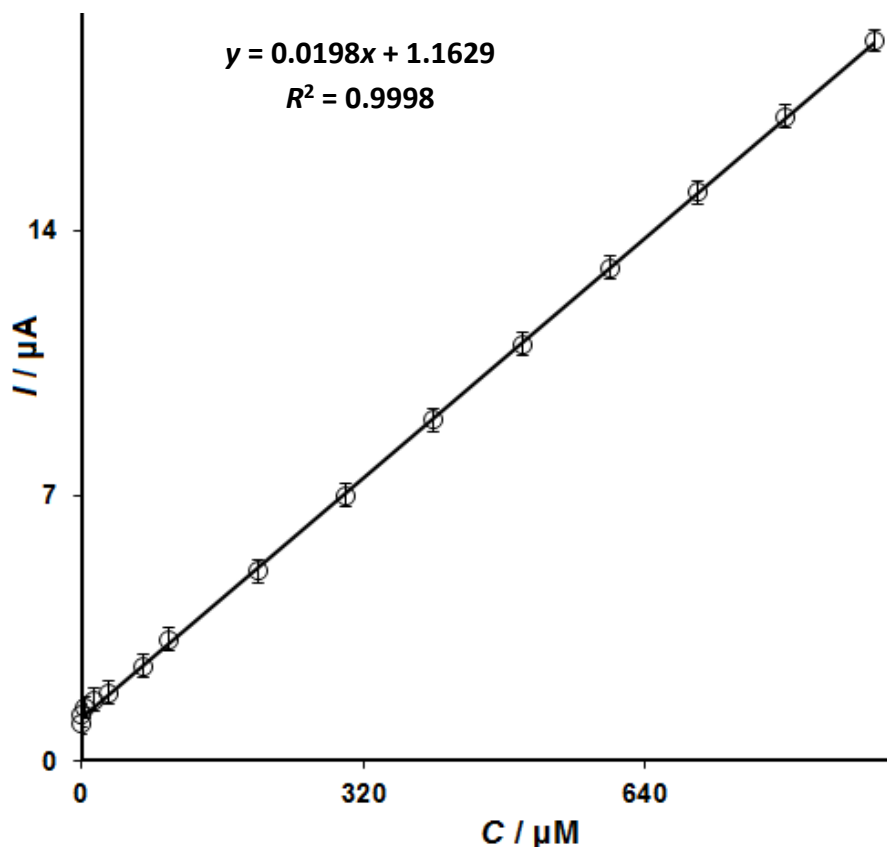


Figure 9. Plot of the linear relationship between peak current and sulphite concentrations

Stability of the ZIF-L (Zn)/SPGE

The long-term stability of the ZIF-L (Zn)/SPGE was evaluated by storing the electrode at room temperature for 6 days. After this period, the current response decreased by just 3.7 %, confirming the stability of the modified electrode.

Interference studies

Real samples contain various species that can influence the detection and sensitivity capabilities of electrodes. To study the interference effects of these species, we observed changes in the oxidation peak current of sulphite. Consequently, the anti-interference ability of the modified electrode is a critical factor affecting monitoring accuracy. This study shows that the presence of various interferences at concentrations up to several times greater than that of sulphite does not significantly impact the sensitivity and detection capabilities of the modified electrode. The tolerance limit was defined as the maximum concentration of the interfering substance that caused an approximately ± 5 % relative error in the determination. For example, in the detection of sulphite using modified, a 20-fold concentration of KCl, MgCl_2 , NaNO_3 , NaCl, CaCl_2 , Na_2SO_4 , fructose, citric acid, tartaric acid, glucose, malic acid, iodide, oxalic acid, nitrite, sulphide, thiosulfate, and bromide resulted slight changes in the peak current (less than 5 %). Table 1 shows the effect of some possible interfering compounds on the signal change of sulphite (30.0 μM).

Table 1. The effect of some possible interfering compounds in determination of 20 time lower concentration of sulphite (30.0 μM) in phosphate buffer solution (0.1 M with pH 7.0)

Interfering compounds	Signal change, %
KCl	2.2
MgCl ₂	2.7
NaNO ₃	3.1
NaCl	1.9
CaCl ₂	3.0
Na ₂ SO ₄	4.2
Fructose	4.1
Citric acid	4.3
Tartaric acid	3.4
Glucose	3.1
Malic acid	4.9
Iodide	2.2
Oxalic acid	3.1
Nitrite	2.6
Sulphide	4.0
Thiosulfate	2.1
Bromide	3.2

Analysis of real samples

To assess the usability of the ZIF-L(Zn)/SPGE sensor for determining sulphite in real samples, the DPV technique was applied to various water samples. The standard addition method was employed, and the results are presented in Table 2. The recoveries of sulphite obtained were acceptable, and the reproducibility of the results is indicated by the mean relative standard deviation (RSD).

Table 2. Determination of sulphite in real samples (n=5).

Sample	Concentration, μM		Recovery, %	RSD, %
	Spiked	Found		
Well water	5.0	4.9	98.0	3.3
	7.0	7.1	101.4	2.7
	9.0	8.8	97.8	2.5
	11.0	11.4	103.6	2.2
Tap water	5.0	5.1	102.0	2.1
	7.5	7.4	98.7	3.0
	10.0	9.9	99.0	2.4
	12.5	12.9	103.2	2.6

Conclusions

With the continuous emergence of food additives, there is a growing interest in developing new analytical tools for detecting and quantifying food additives using a reliable and simple method. In this study, we present the development of ZIF-L(Zn)/SPGE sensor for the detection of sulphite in real samples. The electrochemical properties of ZIF-L(Zn) modified SPGE were analysed using CV and DPV. This sensor showed a very good practical application for sulphite detection in real samples. The sensitivity of the sensor was determined and obtained a detection limit of 0.01 μM .

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