RESEARCH ARTICLE

Eco-Friendly Electrochemical Sensor for Accurate Soil Nitrate Detection using ZnOx/PANI Nanocomposite on Nickel Foam Electrode

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ABSTRACT: This study presents an innovative approach to enhancing nitrate detection in soil, a critical macronutrient for agriculture. We developed a novel electrochemical sensor using a nanocomposite of Zinc Oxide (ZnOx) and Polyaniline (PANI) on a Nickel foam electrode. The nanocomposite was synthesized through cyclic voltammetry and characterized using Field Emission Scanning Electron Microscopy (FESEM), Energy Dispersive Spectroscopy (EDS), and X-ray Diffraction (XRD) to analyze its morphological, elemental, and crystalline properties. The sensor's performance was evaluated using square wave voltammetry, revealing a direct linear relationship between the peak current and nitrate concentration. The sensor demonstrated high sensitivity (4.53 µA/µM) and a low detection limit (0.40 µM), confirming its potential for precise and sensitive nitrate analysis in soil samples.

Keywords: Electrochemical Sensor; Nitrate Detection; ZnOx Nanocomposite; Polyaniline (PANI); Nickel Foam Electrode

1. INTRODUCTION

Soil macronutrients, particularly nitrogen (N), phosphorus (P), and potassium (K), are crucial for fostering robust crop growth and ensuring high agricultural productivity [1]. However, in recent years, the health of agricultural soils has been on the decline. This decline is largely due to a decrease in total factor productivity, inefficient nutrient use, and a significant gap between the supply and demand of essential nutrients [2-4]. Secondary macronutrients such as calcium (Ca), magnesium (Mg), and sulfur (S) are also increasingly deficient [5]. These deficiencies stem from the rapid turnover of nutrients within the soil-plant system and the imbalanced application of fertilizers. Additional challenges, such as nutrient leaching and fixation, further degrade soil quality and productivity [1, 2].

Among all soil macronutrients, nitrogen is especially critical due to its vital role in the synthesis of amino acids and proteins, which are fundamental to plant growth and development. Nitrogen availability significantly influences the productivity of various cropping systems across the United States. Plants suffering from nitrogen deficiency typically exhibit stunted growth, chlorosis, and reduced protein content in both plants and grains, which in turn, negatively impacts overall crop yields [3, 4]. Consequently, maintaining adequate nitrogen levels in soil is essential for achieving optimal crop growth and sustainable agricultural production.

To combat soil health deterioration and promote sustainable agricultural practices, it is imperative to engage in timely soil nutrient testing and enhance soil health management practices. This requires addressing the substantial nutrient gap between supply and demand, mitigating high nutrient turnover within the soil-plant

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system, and advocating for balanced and judicious fertilizer application [5, 6]. Prioritizing soil health and effective nutrient management is crucial for sustaining soil productivity and ensuring long-term agricultural sustainability.

The choice of sensor electrode material plays a crucial role in nutrient sensing, as the material must possess high conductivity, low activation energy, and strong chemical stability to ensure accurate and reliable measurements of soil nutrients [7]. Zinc Oxide (ZnOx) is a semiconductor metal oxide that has garnered significant attention due to its unique properties, including high electron mobility, optical transparency, wide band gap, and strong luminescence at room temperature. These properties make ZnOx particularly valuable in various fields, such as electronics, optoelectronics, sensing, biomedicine, and environmental science [8, 9].

Nanotechnology, which deals with the manipulation of matter on an atomic or molecular scale, often involves the use of nanoparticles characterized by sizes below 100 nm. These nanoparticles exhibit modified atomic and molecular properties that differ from their bulk counterparts, leading to enhanced performance in various applications [10, 11]. ZnOx nanomaterials, with their large surface area, biocompatibility, and excellent electrical conductivity, are especially well-suited for use in electrochemical sensors. These sensors benefit from the enhanced electrochemical activity and superior electron communication properties of ZnOx.

A variety of techniques have been explored for detecting soil nutrients, pH levels, water potential, and pathogens in agricultural contexts. These methods include laboratory techniques, field measurements, sensor technologies, multispectral cameras, satellite imagery, drones, and robots. While these methods offer valuable insights, traditional laboratory-based nutrient sensing approaches are often expensive, time-intensive, and limited in their applicability for on-site analysis [12, 13]. In contrast, electrochemical soil sensors are widely embraced for their affordability, rapid response times, extended deployability, and multiplexing capabilities [14, 15]. Recent advancements in electrochemical sensors have demonstrated promising results for nitrate and nitrite detection in soil. For instance, copper oxide impregnated glassy carbon spheres (CuOxGCS) modified basal plane pyrolytic graphite electrodes have been utilized for nitrite/nitrate sensing, achieving notable detection limits and sensitivity, making them suitable for analyzing soil and fruit juice samples [16-20].

In this study, we leverage the exceptional properties of ZnOx nanoparticles, which include high surface area, biocompatibility, and excellent electrical conductivity, to develop an efficient soil sensing system. We integrate ZnOx nanoparticles with the conductive polymer Polyaniline (PANI), known for its environmental stability and chemical resistance. This integration results in a ZnOx/PANI nanocomposite that synergistically enhances sensing capabilities. The large surface area of ZnOx facilitates effective nitrogen interaction in soil, while PANI reinforces the composite's electrical conductivity, leading to a highly selective and sensitive soil nitrogen sensing system [21-24].

This research focuses on developing a novel ZnOx/PANI composite electrode for nitrate (NO_3^-) detection in soil. The ZnOx/PANI nanocomposite is deposited on a nickel foam substrate using cyclic voltammetry. Various parameters, including potential, time, pH, and electrolyte composition, are optimized to achieve the best performance for nitrate sensing. This innovative approach aims to provide an eco-friendly, efficient, and precise method for soil nitrate detection, addressing the critical need for sustainable soil management and enhanced agricultural productivity.

## 2. EXPERIMENTAL DETAILS

2.1. Chemicals and Materials

The nickel foam substrate was procured from Vritra Technologies, Delhi, India. Zinc oxide (ZnOx) powder and polyaniline (PANI) were obtained from Sigma-Aldrich, USA. Additional chemicals, including lithium perchlorate ($LiClO_4$), sulfuric acid (H_2SO_4), potassium dihydrogen phosphate (KH_2PO_4), potassium monohydrogen phosphate ($KHPO_4$), and sodium nitrate ($NaNO_3$), were also procured from Sigma-Aldrich, USA. Sodium sulfate (Na_2SO_4), potassium chloride (KCl), potassium hydroxide (KOH), and sodium hydroxide ($NaOH$) were utilized from existing lab stocks. Milli-Q water (18 MΩ) was employed for the preparation of all reagents to ensure high purity.

2.2. Preparation of ZnOx/PANI Nanocomposite-Based Nickel Foam Electrode for Nitrate (NO^{3-}) Detection

Polyaniline (PANI) is a highly conductive polymer known for its excellent electrical conductivity, thermal stability, and environmental robustness [25, 26]. The fabrication process began with a 1 cm x 1 cm nickel foam substrate, which was meticulously cleaned using ethanol, acetone, and deionized (DI) water sequentially. The cleaned substrate was then subjected to sonication for 10 minutes to remove any residual contaminants and subsequently air-dried at room temperature.

To prepare the ZnOx/PANI nanocomposite solution, 0.1 M aniline and 0.1 M H_2SO_4 were dissolved in 50 mL of DI water. This mixture was stirred for five minutes to achieve homogeneity. Subsequently, 0.1 M ZnOx powder was added to the solution, followed by sonication for another five minutes. The mixture was then stirred for an additional 15-20 minutes to ensure a clear and homogeneous solution.

The electrochemical deposition of the ZnOx/PANI nanocomposite onto the cleaned nickel foam was carried out using the cyclic voltammetry (CV) method, as illustrated in Figure 1. The electrochemical cell setup consisted of a three-electrode configuration, with the ZnOx/PANI-coated nickel foam serving as the working electrode, an Ag/AgCl electrode as the reference electrode, and a platinum wire as the counter electrode.
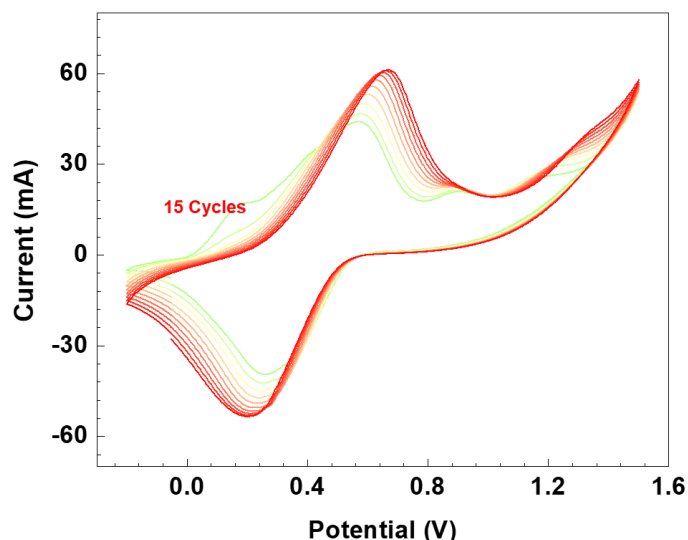
Fig. 1. Cyclic voltammogram for the deposition of ZnOx/PANI composite on bare nickel foam.

During the electrodeposition process, cyclic voltammetry was performed in the potential range of -0.2 V to 1.5 V versus the Ag/AgCl reference electrode. The process was conducted for 15 cycles at a scan rate of 30 mV/s. A Potentiostat/Galvanostat (Model SP-150, Biologic, France) was used to facilitate the electrodeposition, ensuring precise control over the deposition parameters.

3. RESULTS AND DISCUSSION

3.1. Morphological and Compositional Properties

The structural and elemental characterization of the ZnOx/PANI nanocomposite-coated nickel foam electrode was performed using Field Emission Scanning Electron Microscopy (FESEM) and Energy Dispersive Spectroscopy (EDS). The FESEM image with inside EDS spectrum and XRD is presented in Figure 2. The FESEM image (Figure 2 (a)) reveals that the surface of the nickel foam electrode is uniformly covered with rod-shaped ZnOx/PANI nanoparticles. These nanoparticles are evenly distributed across the surface, forming a dense and homogeneous layer. The rod-like morphology of the ZnOx/PANI nanocomposite is indicative of its high surface area, which is advantageous for enhancing the electrochemical activity of the sensor. The uniform coating ensures effective interaction between the electrode surface and the nitrate ions in the soil samples, contributing to improved sensitivity and selectivity in nitrate detection.

Figure 2(b) shows the EDS spectrum of the ZnOx/PANI nanocomposite-coated nickel foam electrode. The EDS analysis confirms the presence of zinc (Zn) and oxygen (O), indicating the successful deposition of ZnOx on the electrode surface. Additionally, the spectrum displays peaks corresponding to carbon (C) and nitrogen (N), which are associated with the polyaniline (PANI) component of the nanocomposite. The presence of nickel (Ni) peaks in the spectrum corresponds to the underlying nickel foam substrate. The EDS results corroborate the FESEM findings, provide a comprehensive understanding of the elemental composition and confirming the successful integration of ZnOx and PANI onto the nickel foam substrate.

This combination of FESEM and EDS analysis validates the formation of the ZnOx/PANI nanocomposite on the nickel foam electrode, highlighting its potential for effective nitrate sensing in soil.
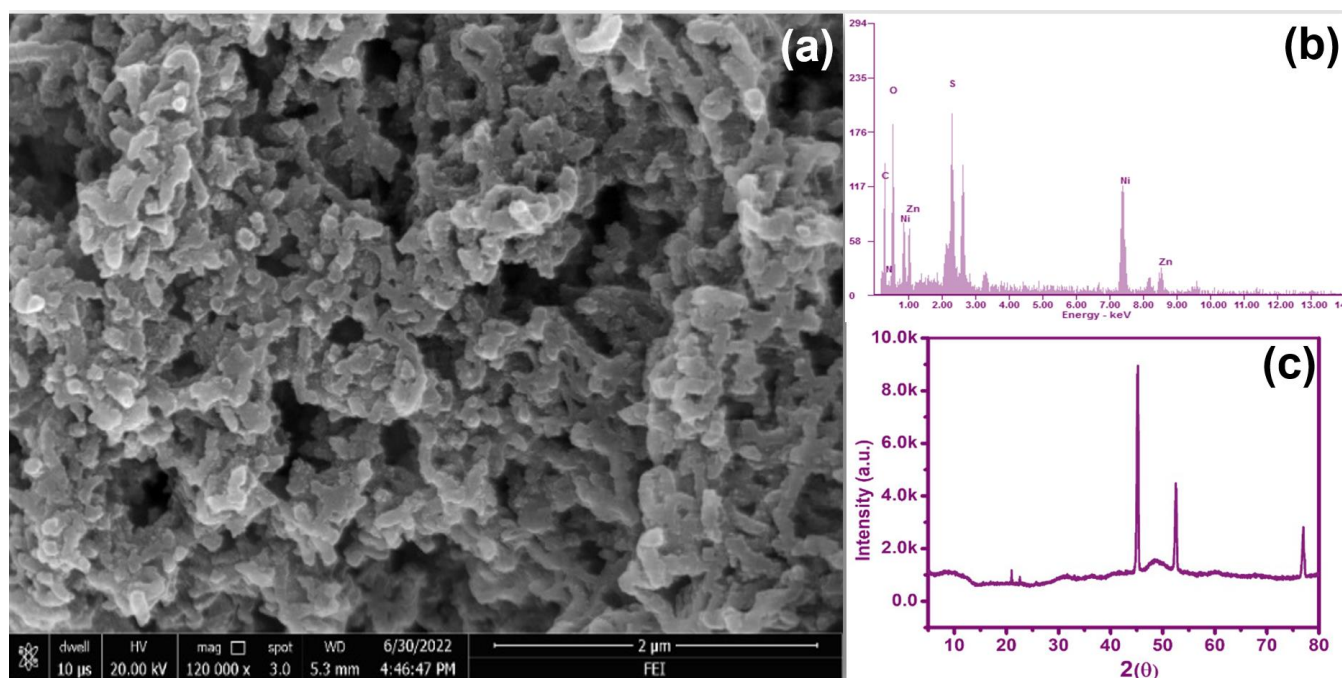
Fig. 2. (a) FESEM, (b) EDS spectrum, and (c) XRD pattern of Ni-foam electrode modified with ZnOx/PANI nanocomposite.

This detailed characterization underscores the structural and compositional integrity of the ZnOx/PANI nanocomposite coated nickel foam electrode, laying a robust foundation for its application in precise and sensitive nitrate detection.

The ZnOx/PANI nanocomposite's XRD patterns on nickel foam is shown in Figure 2 (c). The XRD pattern shows diffraction peaks at approximately 38°, 47°, 53°, and 77°. These peaks correspond to ZnOx crystalline planes, specifically [111], [200], and [220], indicating the presence of ZnOx with a hexagonal wurtzite structure in the sample. The diffraction peaks corresponded to the standard JCPDS card No. 36-1451, which aligns with hexagonal wurtzite structure of ZnO. The XRD pattern of the as-prepared ZnOx/PANI nanocomposite revealed a crystalline structure consistent with hexagonal wurtzite.

3.2. Sensing response of ZnOx/PANI nanocomposite Ni-foam electrode towards nitrate (NO_3^-): Optimization of experimental parameters

To optimize the sensing of nitrate using the ZnOx/PANI nanocomposite Ni-foam electrode, various experimental parameters were systematically varied while keeping others constant. The parameters explored included different electrolytes, applied potential, pH of the electrolyte, deposition potential, and deposition time.

3.2.1. Optimization of Electrolyte and pH for Nitrate Sensing Using ZnOx/PANI Electrode

Selection of Electrolyte: The sensing response of the ZnOx/PANI nanocomposite electrode towards nitrate was evaluated using square wave voltammetry (SWV) in different electrolytes: KCl, NaOH, Na_2SO_4, and phosphate-buffered saline (PBS). The experiments were conducted under standardized conditions, maintaining the electrolyte pH at 7, the deposition potential at -1 V, and a deposition time of 60 s. Figure 3 depicts the SWV response for 140 μM $NaNO_3$ in various electrolytes. The results indicated that the nitrate peak was notably suppressed in PBS, suggesting its unsuitability for this application. Comparative analysis revealed that the nitrate peaks in NaOH and KCl were less pronounced than those observed in Na_2SO_4. This observation underscores the superior performance of Na_2SO_4 in facilitating the electrochemical detection of nitrate. Consequently, Na_2SO_4 was selected as the optimal electrolyte for subsequent experiments.

Optimization of pH: The influence of pH on the electrochemical response of nitrate was rigorously investigated. The study explored the behavior of the ZnOx/PANI electrode in a 140 μM $NaNO_3$ solution with pH values ranging from 1.0 to 5.0, using 0.1 M Na_2SO_4 as the electrolyte. The deposition potential and time were kept constant at -1 V and 60 seconds, respectively. Figure 4

illustrates the SWV responses at various pH levels. The data demonstrated a significant increase in peak current with increasing pH from 1.0 to 5.0. Beyond pH 5.0, the peak current began to decline, indicating an optimal pH for maximum electrochemical response. Thus, a pH of 5.0 was determined to be the optimal value for nitrate sensing, as it yielded the highest peak current [25].
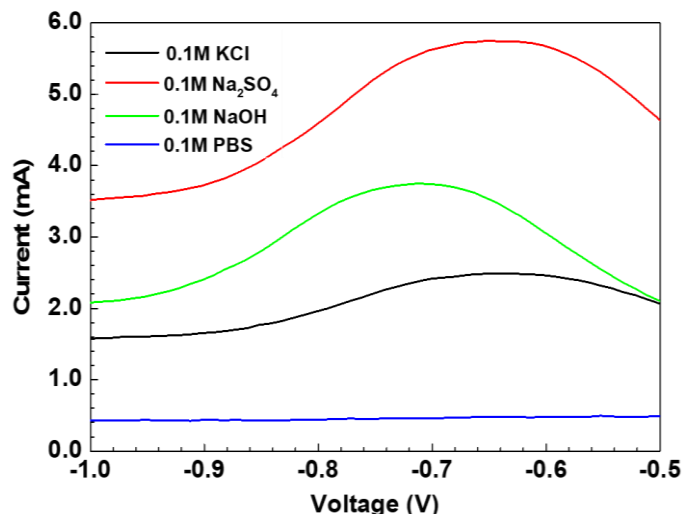

Fig. 3. Square wave voltammetry response of Ni foam modified with ZnOx/PANI electrode for 140 μM $NaNO_3$ with different electrolytes.
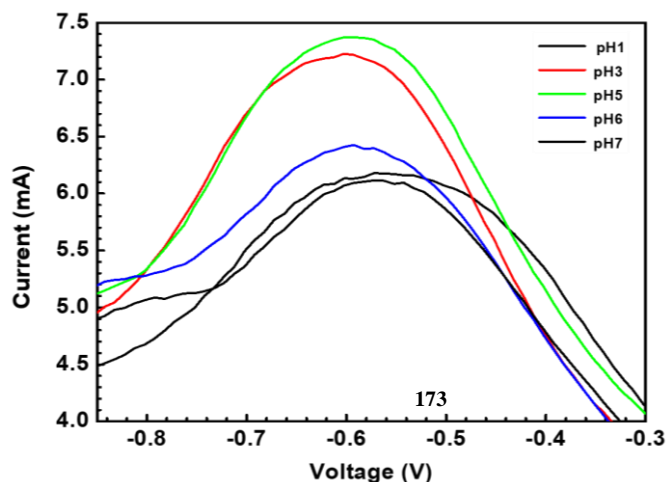

Fig. 4. Square wave voltammetry response of Ni foam modified with ZnOx/PANI electrode for 140 μM $NaNO_3$ with varying pH in 0.1M Na_2SO_4.

The optimization of experimental parameters for nitrate sensing using the ZnOx/PANI nanocomposite electrode identified Na_2SO_4 as the ideal electrolyte and pH 5.0 as the optimal pH. These conditions provided the most pronounced and reliable electrochemical response for nitrate detection, thereby enhancing the efficacy and accuracy of the sensing process. Future studies should consider these parameters to

improve the performance and reproducibility of nitrate sensing using the ZnOx/PANI nanocomposite Ni-foam electrode.

3.2.2. Optimization of Potential and Time

Optimization of Electrodeposition Potential: The potential applied to the electrode is crucial for the effective attraction and accumulation of nitrate ions (NO_3^-) on the electrode surface, which directly affects the electrochemical response. To determine the optimal electrodeposition potential, a series of experiments was conducted with potentials ranging from -0.9 V to -1.7 V, while maintaining a constant deposition time of 60 seconds. The results are illustrated in Figure 5. The investigation revealed that the electrostatic interactions between the electrode surface and nitrate ions were maximized at an electrodeposition potential of -1.7 V. This potential facilitated the highest peak current, indicating optimal nitrate ion accumulation. However, further increasing the potential resulted in a convergence of the peak current curves, suggesting that higher potentials did not enhance the response and might even cause saturation effects or other interfering phenomenon.
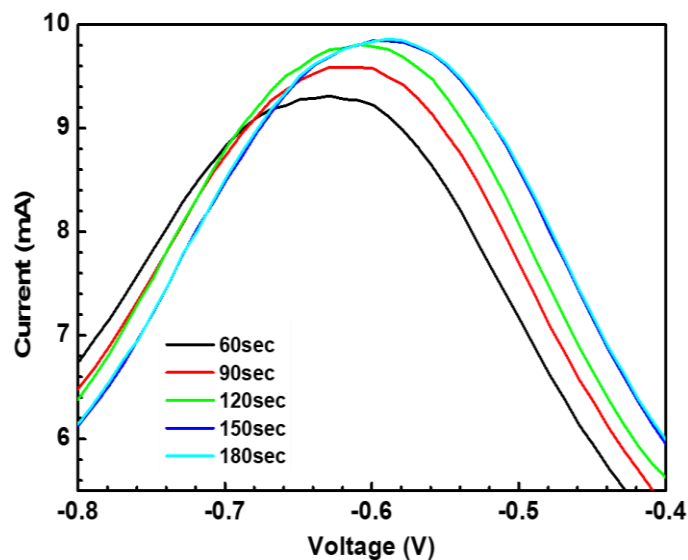
Optimization of Electrodeposition Time: In addition to potential, the electrodeposition time plays a significant role in determining the efficiency of nitrate ion accumulation on the electrode surfaces. To identify the optimal deposition time, experiments were conducted with times ranging from 60 seconds to 180 seconds, as shown in Figure 6.
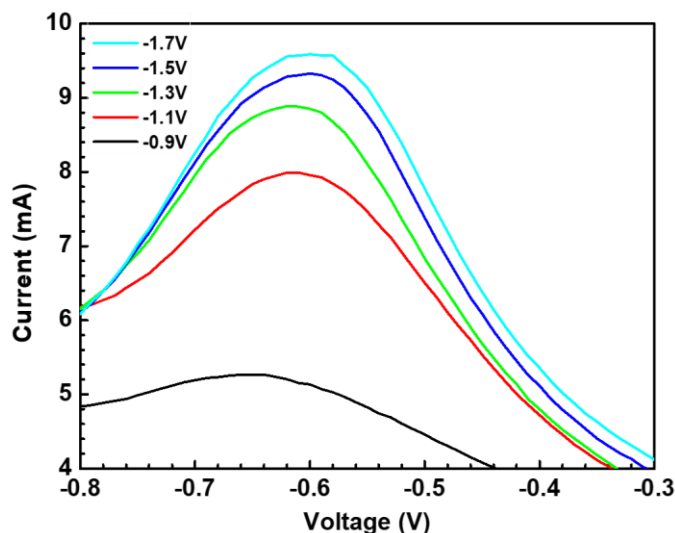
Fig. 5. Square wave voltammetry response of Ni foam modified with ZnOx/PANI electrode for 140 µM NaNO₃ with varying electrodeposition potential in 0.1M Na₂SO₄.

The data demonstrated that the peak current increased with deposition time, reaching its maximum at 120 seconds. This

optimal time allowed for extensive coverage of the electrode surface with nitrate ions, resulting in maximal signal generation. Beyond 120 seconds, the peak current curves began to overlap, indicating a saturation point where the electrode surface could no longer absorb additional nitrate ions effectively. This overlap suggests that extended deposition times do not further enhance the signal and may lead to diminished returns or other complications.

Fig. 6. Square wave voltammetry response of Ni foam modified with ZnOx/PANI electrode for 140 µM NaNO₃ with varying electrodeposition time.

The comprehensive optimization of electrodeposition potential and time established -1.7 V as the optimal potential and 120 seconds as the optimal deposition time for nitrate sensing using the ZnOx/PANI nanocomposite electrode. These parameters ensured the most effective accumulation of nitrate ions on the electrode surface, yielding the highest peak currents and thereby enhancing the sensitivity and reliability of the electrochemical measurements. The identified optimal conditions provide a robust foundation for further analytical applications and consistent electrochemical performance in nitrate detection [25].

3.3. Nitrate (NO_3^-) sensing response of ZnOx/PANI nanocomposite deposited Ni-foam sensor electrode evaluation of nitrate detection

The sensing response of the ZnOx/PANI nanocomposite Ni-foam electrode for nitrate (NO_3^-) detection was systematically evaluated using square wave voltammetry (SWV) across varying concentrations of nitrate in a 0.1 M Na₂SO₄ electrolyte solution. Figure 7 illustrates the SWV response, showcasing a substantial peak current at a potential of -0.6 V. The inset in Figure 7 provides a calibration plot, demonstrating a linear relationship between the peak current and nitrate concentration.

The peak current increased proportionally with higher

nitrate concentrations, indicating a robust linear correlation. This linearity underscores the efficacy of the ZnOx/PANI nanocomposite in enhancing sensor performance for nitrate detection. The combined properties of zinc oxide nanoparticles (ZnOx) and polyaniline (PANI) play a critical role in this enhancement. The surface chemistry of ZnOx promotes the adsorption of nitrate ions, while PANI facilitates efficient electron transfer, optimizing redox reactions at the electrode surface.
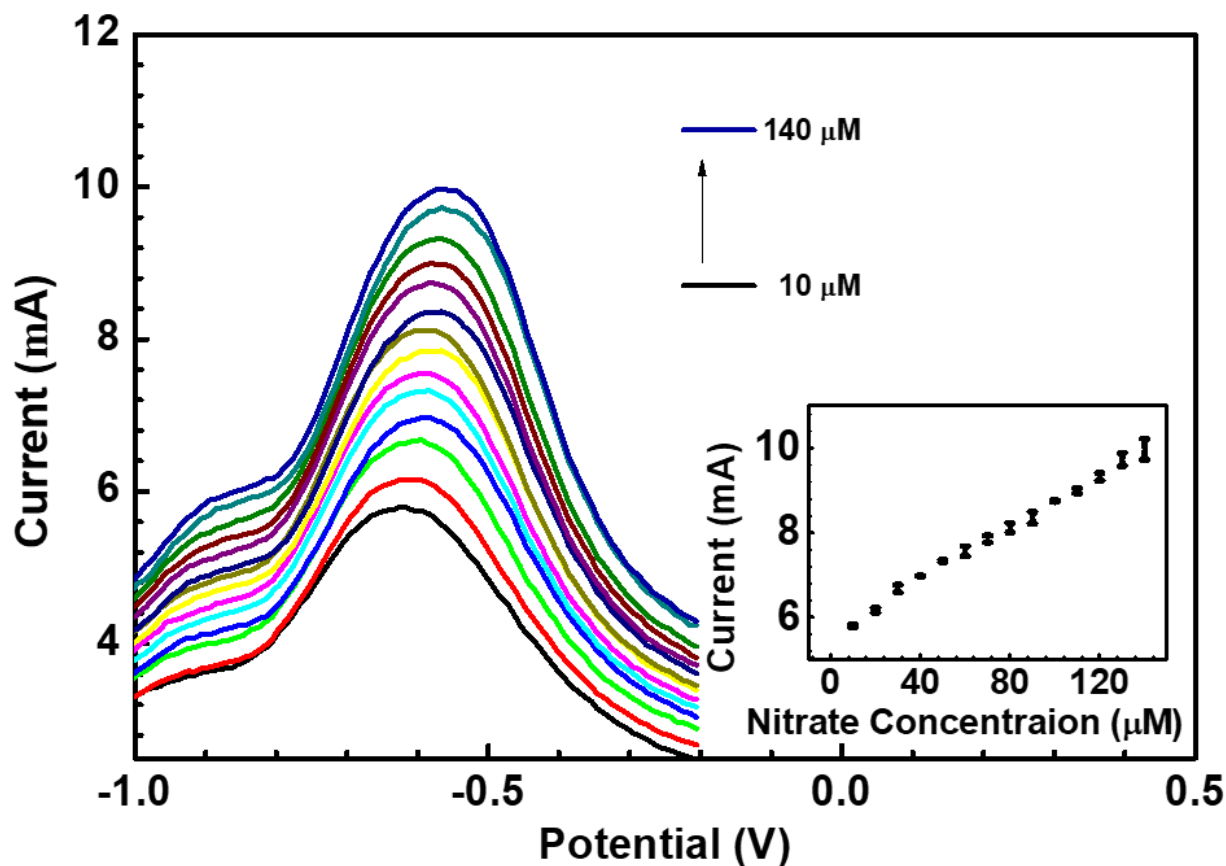
Fig. 7. ZnOx/PANI nanocomposite Ni-foam electrode sensor response of various concentrations of nitrate using square wave voltammetry. Inset shows the calibration plot of the peak current for increasing concentration of nitrate.

Table 1. A comparative chart of various electrode with their linear range detection and sensitivity.

S. No.	Modified Material/WE	Method	Linear Range (μM)	Sensitivity (μA/μM)	Ref
1	NiR/GO/PDMS/AuE	CV	1–100	0.224	[27]
2	PPy/Ag NPs/GCE	CV	1–104	-	[28]
3	PANI/WO3/Cu NSh/GCE	LSV	40–276	4.5	[29]
4	PANI/Cu NPs/GCE	LSV	1–105	0.78	[30]
5	Ag NPs/AuE	SWV	0.39–50	0.1057	[31]
6	rGO/MWCNTs/Cu NPs/GCE	SWV	0.1–75	0.215	[32]
7	Cu-modified CF MDE	SWV	3–2000	0.055	[33]
9	Polypyrrole-coated palladium nanocluster	DPV	900–1400	-	[34]
10	Nano-silver/gold-coated glass	CV	200–1400	-	[35]
11	ZnOx/PANI Ni-Foam	SWV	1–140	4.53	Present work

Mechanism of Enhanced Sensor Performance: The synergistic effect of ZnOx and PANI significantly improves the sensor's response to nitrate. ZnOx nanoparticles possess excellent adsorption capabilities, which increase the surface area available for nitrate ion interaction. Meanwhile, PANI enhances the conductivity and electron transfer processes, crucial for effective electrochemical detection. This dual mechanism results in amplified sensor performance, as evidenced by the pronounced peak currents observed in SWV measurements.

Sensitivity and Detection Limit: The sensitivity of the ZnOx/PANI nanocomposite electrode was calculated from the slope of the calibration plot (Fig. 7 inset). The sensor exhibited an impressive sensitivity of 4.53 µA/µM and a low detection limit of 0.40 µM. These values reflect the high performance and potential applicability of the sensor in detecting low concentrations of nitrate with high accuracy.

Comparative Analysis: The analytical performance of the synthesized ZnOx/PANI nanocomposite-modified nickel foam electrode was compared with various reported electrochemical nitrate sensors, as summarized in Table 1. This comparative analysis reveals that the developed ZnOx/PANI Ni-foam sensor outperforms others in terms of both sensitivity and linear detection range**.** The ZnOx/PANI nanocomposite-modified Ni-foam electrode sensor demonstrated superior performance for nitrate detection, characterized by high sensitivity and a low detection limit. The linear relationship between peak current and nitrate concentration, along with the comparative data from other sensors, highlights the ZnOx/PANI sensor as a highly effective tool for nitrate sensing. Its enhanced performance is attributed to the synergistic effects of ZnOx and PANI, which together improve ion adsorption and electron transfer processes.

4. CONCLUSION

The successful realization of the ZnOx/PANI nanocomposite-decorated Ni-foam sensor electrode, tailored for nitrate detection in soil, has been effectively showcased. This accomplishment stems from a meticulous optimization of diverse parameters, encompassing deposition potential (-1.7V), deposition time (120 sec), electrolyte (Na_2SO_4), and pH of the electrolyte (5.0). The electrode exhibited a remarkable sensitivity of 4.53 µA/µM, coupled with an impressively low detection limit of 0.40 µM. This sensor emerges as a potent tool for efficacious nitrate detection within soil, a crucial macronutrient essential for robust plant growth. The efficacy and capabilities of the sensor were ratified through a comprehensive characterization process employing FESEM, and EDS techniques. The development of this sensor represents a significant advancement in environmental monitoring technology, providing a reliable and efficient method for detecting nitrate levels in soil. This

is particularly important for agriculture, where precise nitrate management can enhance crop yields and prevent the adverse environmental effects of over-fertilization. The ability to accurately measure low concentrations of nitrate can also aid in the study of soil health and nutrient cycles, contributing to more sustainable farming practices. Furthermore, the versatility and sensitivity of the ZnOx/PANI nanocomposite sensor open avenues for its potential application in other fields requiring precise nitrate detection, such as water quality monitoring and industrial effluent management. The innovative approach to optimizing the sensor parameters ensures its robustness and reliability in various environmental conditions, making it a valuable asset for ongoing and future ecological and agricultural research. The ZnOx/PANI nanocomposite-decorated Ni-foam sensor electrode not only provides a high-performance solution for nitrate detection but also underscores the importance of interdisciplinary approaches combining nanotechnology, materials science, and environmental chemistry in addressing critical ecological challenges. This work paves the way for further innovations and improvements in sensor technology, with broad implications for environmental sustainability and agricultural productivity.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests.

ACKNOWLEDGEMENTS

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MatSci Express., 2024, Vol. **1**, No. 3, 170-178 | **178**