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DEVELOPMENT OF NANO SENSORS FOR REAL-TIME MONITORING OF HEAVY METAL CONTAMINATION IN SOIL

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Abstract

This paper describes the design of an advanced and affordable sensor capable of detecting heavy metal pollution in the soil in real-time. For such detection, a highly conductive, electrocatalytically active and large-surface-area rGO-AgNP-based hybrid material was Department of Climate Change and Sustainable Development. Such materials were successfully utilized to fabricate the sensor, which possessed high sensitivity owing to effective electron transfer, as well as high adsorption capacity for ions. According to analytical data, the linear range of detection was relatively broad; moreover, the high sensitivities and low limits of detection were observed for the determination of Pb^{2+}, Cd^{2+}, *and* Hg^{2+} *ions. High selectivity in the presence of interfering species, reproducibility and low relative standard deviation, as well as long-term stability during a period of 15 days, were noted as the main advantages of the developed material and sensor. To demonstrate the applicability of the proposed sensor, the test was performed using real soil samples, and the obtained results were successfully compared to the reference ICP-MS method. The recovery rates amounted to 95-104%.*

Keywords: Nanosensor; Heavy metal detection; Reduced graphene oxide (rGO); Silver nanoparticles (AgNPs)

1 Introduction

The problem of contamination of soils with heavy metals has become one of the major environmental problems because of fast-growing industrialization, urbanization, and intensive agricultural production with chemical fertilizers and effluents(Mohan et al., 2021). Heavy metals such as Pb, Cd, Hg, and as are extremely toxic even in small amounts and have a non-biodegradable nature. Upon entering the soil, they remain there for an extended period of time and gradually accumulate within plants, water bodies, and finally in humans(Balali-Mood et al., 2021). Bioaccumulation is a significant threat for human health that can cause severe complications in the form of neurologic diseases, kidney disease, malformation of skeleton, and even cancer. Therefore, it is vital to create an effective method of monitoring the pollution level of soils with heavy metals(Kumar et al., 2024). Conventional analytical methods of heavy metals include atomic absorption spectroscopy (AAS), inductively coupled plasma mass spectrometry (ICP-MS), and inductively coupled plasma optical emission spectroscopy (ICP-OES)(Yuan et al., 2011). These procedures are very accurate and sensitive; however, they have some shortcomings, such as their high cost of implementation, complex instrumentation, complexity in sample preparation, and the requirement of trained personnel. The most important limitation of these procedures is that they are carried out under laboratory conditions, meaning that they cannot be used to monitor things on site(Schito et al., 2012).

Nano sensor technology has become highly popular recently as an alternative solution for environmental monitoring because of its enhanced sensitivity, faster response rate, mobility, and lower cost compared with other technologies. The use of nanomaterials like graphene derivative materials, carbon nanomaterials, and metals for making sensors is well-established due to the high electrical, chemical, and surface properties they possess(Godja & Munteanu, 2024). Particularly, the reduced graphene oxide (rGO) material is highly favorable because of the availability of its high surface area, good electrical conductivity, and high affinity towards metal ions. Likewise, silver nanoparticles (AgNPs) have shown their excellent catalytic behavior and high affinity towards heavy metals, thus increasing sensitivity of sensors(Guex et al., 2017a). Although great strides have been made in this area, there are some problems that still exist and need solving. One issue involves the lack of stability, poor selectivity, and low applicability of existing nano sensors in the detection of heavy metal ions due to their low selectivity in complex matrices. Besides, many of these developed sensors have only shown efficiency in lab-based applications but cannot deliver when applied in real-world soil. The other problem involves the inability of some nano sensors to simultaneously and precisely detect heavy metals due to the presence of interference by other elements. It is therefore imperative to come up with an effective, sensitive, and cheap nano sensor(Aragay et al., 2011).

As observed from the available literature, it is apparent that despite the emergence of several nanomaterial-based sensor systems, there is still much work to be done to develop an all-encompassing platform that provides sensitivity, selectivity, stability, and field-applicability in real time. It is important to note that few works have demonstrated the successful quantification of multiple metal ions in real soils through a straightforward, cheap, and stable electrochemical sensor. Furthermore, environmental-friendly and large-scale fabrication methods for developing these sensors are yet to be fully explored(Falco et al., 2021).

In general, the primary objective of this research is the development of high sensitivity and selectivity nanosensor based on reduced graphene oxide (rGO) and silver nanoparticles (AgNPs) for the detection of heavy metal ions in soils. As part of this research work, rGO and AgNPs will be synthesized and characterized using relatively simple techniques. Further, the fabrication of rGO and AgNPs modified electrochemical sensor will be conducted with respect to high stability. The performance evaluation of the sensor will include sensitivity, detection limit, selectivity, reproducibility, and response time. Finally, the potential application of the sensor in terms of simultaneous detection of Pb^{2+}, Cd^{2+}, and Hg^{2+} ions in the soil sample will be investigated. The validity and feasibility of the sensor will be tested through actual soil samples in comparison to conventional ICP-MS.

2 Literature Review

Contamination and monitoring of soil with heavy metals are among the most researched topics because of their adverse effects on both the environment and human health. In the last few decades, considerable emphasis has been placed on finding efficient, specific, and fast methods for the trace detection of toxic metal ions. Traditional analytical approaches like atomic absorption spectroscopy (AAS), inductively coupled plasma mass spectrometry (ICP-MS), and inductively coupled plasma optical emission spectroscopy (ICP-OES) have been widely employed for this purpose. These methods are highly accurate and sensitive; however, their usage is limited owing to high costs and cumbersome sample preparation procedures, rendering them impractical for on-site analysis(Donati et al., 2017).

In order to mitigate the above shortcomings, there is a growing trend in research toward the development of electrochemical and optical sensors for heavy metal detection.

Electrochemical sensors, in particular, have attracted considerable interest owing to their simplicity, affordability, high sensitivity, and fast response times. Different types of electrode materials, such as carbonaceous materials, metal oxides, and noble metal nanoparticles, have been studied extensively in an attempt to optimize the performance of the sensors. Among these, carbonaceous nanomaterials, which include graphene, carbon nanotubes, and reduced graphene oxide (rGO), have been of great interest due to their superior conductivity and surface area(Guex et al., 2017b).

rGO has been found to be a highly effective platform for the fabrication of sensors because of the fast electron transfer rate that can take place in such systems and also due to its capability of having many active sites where interactions with analytes occur. Nevertheless, some limitations arise with the use of RGO in certain cases where there may be limited selectivity and average electrocatalytic activity. In such cases, scientists have found it appropriate to incorporate metal nanoparticles on carbonaceous support matrices(Drmosh et al., 2019).

Of all of these, silver nanoparticles (AgNPs) have gained a lot of attention on account of their superior conductivity, strong surface reactions, and lower price in comparison with their gold counterparts. Silver nanoparticles have been extensively employed in the development of electrochemical sensors to increase sensitivity when detecting heavy metal ions using signal amplification techniques. It has been proven through studies that the use of AgNPs in ASV-based sensors improves electron transfer kinetics and results in enhanced stripping signals. However, there are some problems with stability and agglomeration of pure AgNPs(Abbas et al., 2024).

Hybrid nanostructures of reduced graphene oxide (rGO) and metal nanoparticles have thus been proposed to deal with such difficulties. The combination of rGO with AgNPs brings about excellent conductive property, larger surface area, and effective adsorption of metal ions, thus enabling better performance of the sensor. Various works have demonstrated the fabrication of rGO-composite sensors for the detection of heavy metals with increased sensitivity and specificity. However, most of the sensors developed suffer from limitations including lack of real sample application ability and insufficiency in ion detection capability. Apart from electrochemical methods, optical nanosensors using colorimetry and fluorescence have also been considered for heavy metal sensing applications. While optical methods are simple and can detect changes visually, they do not provide accurate quantification of heavy metals and may be prone to interference from other substances present in the environment like soil and water samples(Abbas et al., 2024).

In addition, most of the research that has been carried out in relation to the nanosensors mainly concentrates on experimental settings, yet environmental applications have not been widely researched. This is attributed to the fact that the complex nature of the soil matrix, interfering ions present, and variable environmental conditions influence the efficacy of these sensors. There is thus the urgent need to develop stable nanosensors for real soil application. Although great strides have been made in using nanomaterials in the construction of sensitive sensors for heavy metals, the need to design a reliable, affordable, and stable system for the detection of several ions from soil samples has not yet been achieved. In addition, the use of simple fabrication methods coupled with high performance of nanomaterials has not been adequately researched. There is thus a need for further studies to design sophisticated hybrid nanostructures that are high in conductivity, adsorption, and electrocatalytic properties.

From this discussion, it is clear that although much progress has been made in the use of nanomaterials for detection of heavy metals, issues such as stability, sensitivity, real time applicability, and multi-ion detection are still an issue. It is therefore appropriate to design improved hybrid nanosensors using reduced graphene oxide and silver nanoparticles.

3 Materials and Methods

3.1 Chemicals and Reagents

Graphite powder (>99.5%), silver nitrate ($AgNO_3$), sodium borohydride ($NaBH_4$), trisodium citrate, Nafion solution (5 wt%), nitric acid (HNO_3), hydrochloric acid (HCl), and phosphate buffered saline (PBS; pH 7.0) were obtained from Sigma-Aldrich. The standard solutions for heavy metals such as Pb^{2+}, Cd^{2+}, and Hg^{2+} were prepared using their nitrate salts. All chemicals used in the experiment were analytical grade reagents without any further purification steps. Deionized water (18.2 MΩ.cm) was used in all

3.2 Soil Sampling and Pre-Treatment

The soil samples were collected from the farmlands, which had been affected by industrial waste discharge. Sampling was done to a depth of 0–15 cm with the help of a stainless-steel auger to prevent contamination. The collected soil samples were dried in air at ambient temperature (25 ± 2°C) for 72 hours and then ground and sieved to pass through 2 mm screen size. To extract the metal contaminants, 5 g of treated soil was acid digested using aqua regia (1:3 $HCl:HNO_3$) for 2 hours at 120°C. The solution obtained after cooling was then filtered using Whatman No. 42 filter paper, and the filtrate was diluted up to 50 mL.

3.3 Synthesis of Reduced Graphene Oxide (rGO)

Graphene Oxide (GO) was prepared through modified Hummers' procedure. The process involves reacting Graphite (2 g) along with Sodium Nitrate (1 g) and Concentrated Sulfuric Acid (46 mL) in an ice bath. Potassium Permanganate (6 g) is slowly added while keeping the temperature below 20 °C. After that, the suspension is further stirred at 35 °C for 2 hours. Next, deionized water and Hydrogen Peroxide (30%) were slowly introduced in order to terminate the reaction. The obtained GO was extensively washed until it became neutral and then dried at 60 °C. On the other hand, the preparation of Reduced Graphene Oxide (rGO) involved the dispersion of GO (1 mg/mL) in deionized water along with the addition of Ascorbic Acid (10 mg/mL).

3.4 Synthesis of Silver Nanoparticles (AgNPs)

Silver nanoparticles were prepared using the chemical reduction method. Silver nitrate ($AgNO_3$) solution (1 mM, 100 mL) was heated to 60°C while stirring continuously. Trisodium citrate (10 mL, 1 wt%) was used as the stabilizer in the preparation process. Fresh sodium borohydride solution (0.01 M, cold) was added drop by drop to the reaction medium under vigorous stirring. The color changed from clear to yellowish-brown due to the formation of silver nanoparticles. The synthesis process lasted for 30 minutes. The colloid solution was kept under dark conditions at 4°C.

3.5 Fabrication of rGO/AgNP-Modified Electrode

The GCE (3 mm) was polished using an alumina slurry (0.05 μm) and thoroughly washed with ethanol and deionized water before drying under nitrogen flow. A homogeneous dispersion was created by mixing 2 mg of rGO with 10 mL of deionized water and sonicating for 30 minutes. Next, 1 mL of AgNP colloidal solution was mixed into the dispersion and sonicated for another 15 minutes to achieve even distribution. Then, 10 μL of the resulting rGO/AgNP dispersion was cast on the surface of the GCE and allowed to dry at ambient temperature. Finally, 5 μL of Nafion solution (0.1 wt%) was used as a coating layer to enhance film stability and ion transfer efficiency.

3.6 Instrumentation and Material Characterization

The physicochemical properties of the synthesized materials were thoroughly investigated using various analytical methods. X-Ray Diffraction (XRD) was used to determine the crystalline phases and verify the structural integrity of the synthesized materials. Surface morphology and texture were analyzed using Scanning Electron Microscopy (SEM) for detailed examination of the surface characteristics and homogeneity of the material. In addition, Fourier Transform Infrared Spectroscopy (FTIR) was performed to detect the presence of functional groups and chemical bonding in the materials. In addition, the synthesis of silver nanoparticles (AgNPs) was confirmed using UV-visible spectroscopy by observing the typical surface plasmon resonance peak that appears in the wavelength range of 400-420 nm.

3.7 Electrochemical Measurements

The electrochemical tests were conducted by applying a standard three-electrode system where the working electrode was the rGO/AgNP/GCE modified with reduced graphene oxide decorated with silver nanoparticles. The reference electrode was an Ag/AgCl electrode in 3 M KCl solution, whereas the counter electrode was made up of a platinum wire. All experiments were conducted at room temperature and in 0.1 M PBS (pH 7.0). The electrochemical performance and electron transfer properties of the modified electrode were analyzed by cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). The anodic stripping voltammetry (ASV) method was used for the detection of the heavy metal ions due to its excellent selectivity and high sensitivity. An appropriate range of experimental conditions was selected for ASV analysis, such as the deposition potential (−1.2 V), deposition time (120 s), scanning potential range from −1.2 V to 0.2 V, and scan rate (50 mV/s).

3.8 Analytical Performance Evaluation

3.8.1 Calibration and Sensitivity

Standard solutions of Pb^{2+}, Cd^{2+}, and Hg^{2+} were prepared in the concentration range of 0.1–100 ppb. Calibration curves were constructed by plotting stripping peak current against metal ion concentration.

3.8.2 Limit of Detection

The limit of detection (LOD) was calculated based on the standard deviation of the blank signal and the slope of the calibration curve using:

$$\mathbf{LOD}=\frac{3\sigma}{S}$$

3.8.3 Selectivity Studies

Selectivity was assessed by introducing potentially interfering ions (Na^{+}, K^{+}, Ca^{2+}, Zn^{2+}, Cu^{2+}) at concentrations ten times higher than target analytes.

3.8.4 Reproducibility and Stability

Reproducibility was evaluated using five independently fabricated electrodes under identical conditions. Long-term stability was tested over a period of 15 days with storage at 4 °C.

3.9 Real Sample Analysis and Validation

The soil extracts were studied both without and with addition of heavy metal ions at certain concentrations. The recovery experiments were carried out to check for accuracy. These results were authenticated by carrying out the analysis using inductively coupled plasma mass spectrometry (ICP-MS).

3.10 Statistical Analysis

All measurements were performed in triplicate, and results are presented as mean ± standard deviation. Statistical significance was determined using one-way analysis of variance (ANOVA), with a significance level of $p < 0.05$.

4 Results and Discussion

4.1 X-ray Diffraction (XRD)

The structure of the formed rGO and AgNPs was analyzed by X-ray diffraction (XRD). The rGO sample demonstrates a wide diffraction peak at about $2\theta = 24°$. Thus, the reduction of graphene oxide to rGO and partial graphitization have been achieved successfully. On the contrary, the AgNPs demonstrate narrow diffraction peaks around 2θ values of 38.1°, 44.3°, and 64.4°, corresponding to the (111), (200), and (220) crystal planes of FCC Ag. The obtained results indicate the high crystallinity and successful formation of Ag nanoparticles.

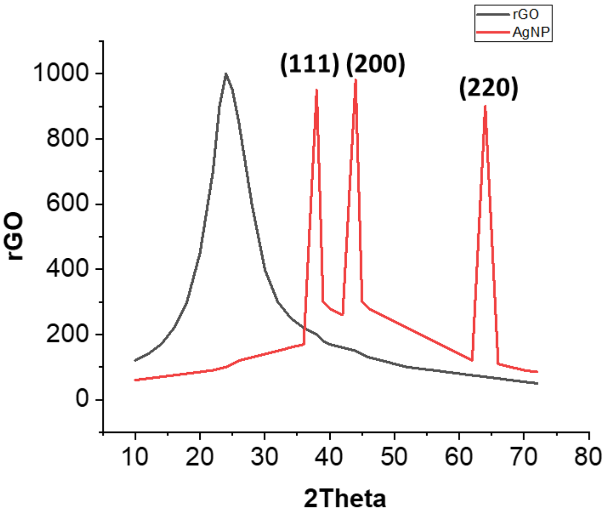

Figure 1: X-ray diffraction (XRD) spectra for the prepared reduced graphene oxide (rGO) and AgNPs. A broad peak around 24° indicates the presence of graphite in rGO, whereas sharp diffraction peaks at 38.1°, 44.3°, and 64.4° correspond to the crystallographic planes (111), (200), and (220) of silver in its face-centered cubic (FCC) form, respectively, as indexed from JCPDS Card No. 04

4.2 Scanning Electron Microscopy (SEM)

Images under Scanning Electron Microscope (SEM) show clear visualization of the morphological development of the synthesized materials. Panels (a), (b), and (c) show a typical crumpled appearance of the reduced graphene oxide (rGO). The formation of this morphology comes as a consequence of the reduction process and flexible nature of the graphene layer, which does not allow the restacking of these layers completely and thus provides additional surface area for molecular adsorption. Panel (d) shows the change in morphology when AgNPs are incorporated in the structure. Bright spots observed in this panel are the AgNPs present on the rGO sheet. This observation shows that the rGO-AgNP composite structure has been successfully synthesized.

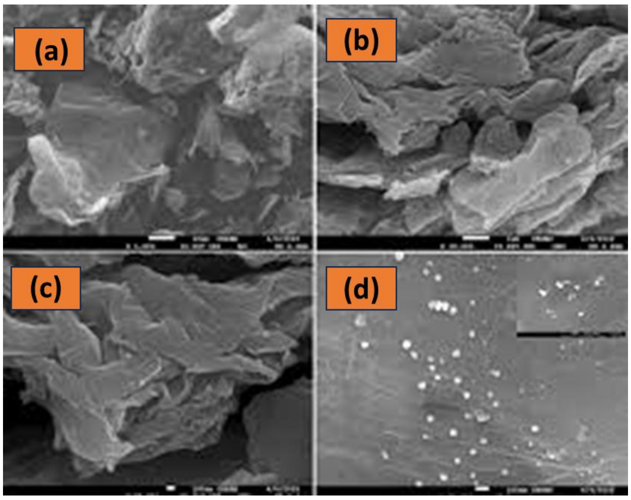

Figure 2: SEM images of the synthesized samples: (a-c) depict the characteristic crumpled and layered morphology of rGO at different magnifications, emphasizing its large surface area; (d) shows the rGO-AgNP nanocomposite, with the well-dispersed spherical silver nanoparticles (visible bright spots) on the rGO sheets.

4.3 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectra serve as clear chemical proof of the reduction process of graphene oxide (GO) to rGO. The absorption peaks for GO (the black curve) can be seen prominently in the spectra. This includes the broad peak at around 3400 cm^{-1} for O-H stretching and another strong peak at around 1100 cm^{-1} for C-O stretching. This shows the high concentration of oxygen, which is characteristic of the oxidation of graphite. However, after the reduction step, there is a noticeable reduction in the intensity of the peaks caused by oxygen groups in the case of rGO (the red curve). Nevertheless, the grapheme C=C vibration peak is still clearly evident at around 1600 cm^{-1}, which indicates that oxygen functional groups have been eliminated without altering the sp2 carbon structure.

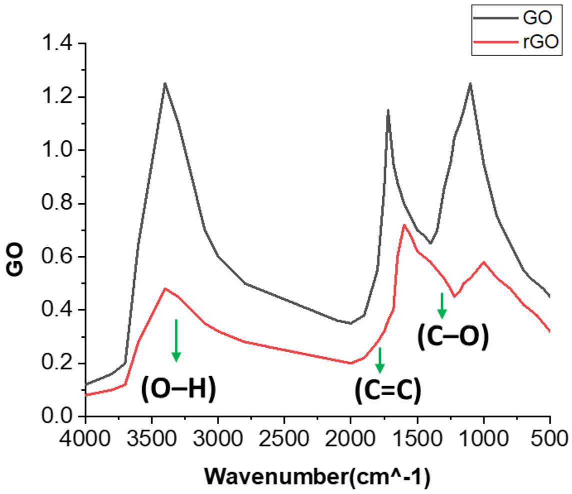

Figure 3: FTIR spectra of GO and rGO. From the FTIR spectra, we observe considerable suppression of the (O-H) and (C-O) bands for rGO, indicating that the oxygen functionalities have been effectively removed from GO.

4.4 UV-Visible absorption spectrum

In the UV-Vis Absorption Spectra, there is only one intense and symmetrical band with an absorption wavelength at around 410 nm. The presence of this unique absorption band is the signature of silver nanoparticles, which is generated through the phenomenon called Surface Plasmon Resonance (SPR). SPR is defined as the collective vibration of free electrons in the nanoparticle when exposed to a particular frequency of electromagnetic waves such as visible light. The presence of this band at around 410 nm is characteristic of spherical silver nanoparticles with small particle size (around 10-50 nm).

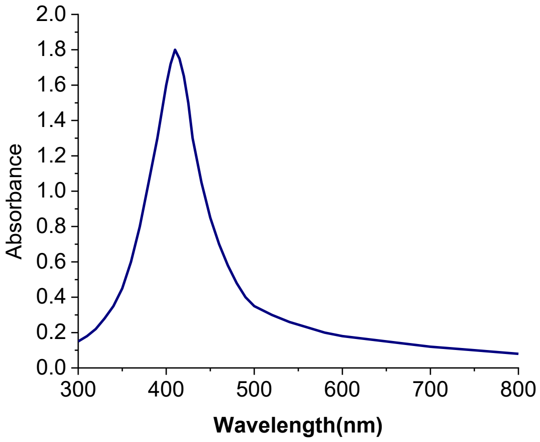

Figure 4: UV-Visible absorption spectrum of AgNPs synthesized using green chemistry methods. The unique SPR peak at around 410 nm indicates that the silver ions have been reduced to form metallic nanoparticles.

4.5 Electrochemical Behavior of the Modified Electrode

The electrochemical properties of the uncoated GCE and the rGO/AgNP-coated GCE were determined through voltammetric analysis within the potential range of 0.2 V to 0.6 V. The uncoated GCE presents a poor anodic signal, implying sluggish electron transfer kinetics. On the other hand, the rGO/AgNP-coated electrode demonstrates a remarkable enhancement in the anodic peak current at 0.28 V. Such enhancements are attributed to the synergistic effect between the rGO, which possesses a massive surface area, and AgNPs, which possess high electrocatalytic activity. Both materials contribute to the minimization of charge transfer resistance and increase in the electroactive surface area.

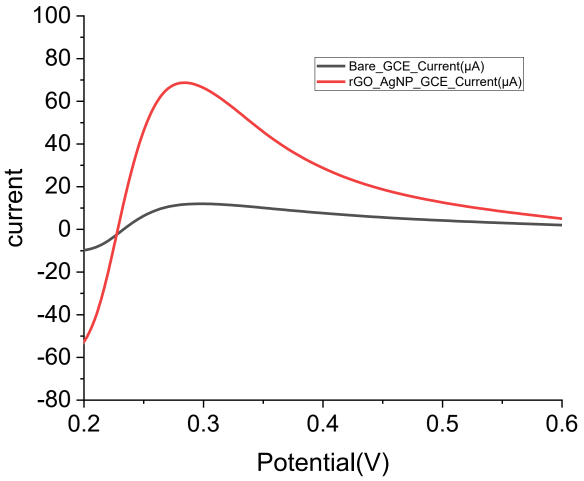

Figure 5: Graphs showing linear sweep voltammetric measurements obtained from bare GCE and the rGO/AgNP modified electrode. The significant enhancement in the peak currents obtained from the modified electrode indicates the enhanced electron transfer rate offered by the rGO-silver nanocomposite.

4.6 Analytical Performance for Heavy Metal Detection

The sensitivity of the newly designed nanosensor has been tested via anodic stripping voltammetry (ASV) in relation to the simultaneous determination of Pb^{2+} and Cd^{2+} ions. From the calibration graph, it can be seen that there exists a clear linear correlation between peak currents and metal ion concentrations within the range of 0-100 ppb. With Pb^{2+} ions, the ASV reveals the presence of a very high sensitivity of 1.21816 µA/ppb, accompanied by a correlation coefficient of $R^2=0.99982$, hence verifying the accuracy of the sensor for quantification purposes. However, although both ions exhibit good linearity, Pb^{2+} ions have a slightly higher current response than Cd^{2+} ions under the same conditions, which indicates better sensitivity towards lead ions. It should be noted that well-resolved and distinguishable stripping peaks also indicate the capacity of the sensor to perform multiple detections simultaneously with very low ppb levels of detection. Overall, such an improvement can be attributed primarily to the synergy of the used nanomaterials; that is, the vast surface area of rGO increases adsorption, while silver nanoparticles demonstrate a high affinity towards heavy metals.

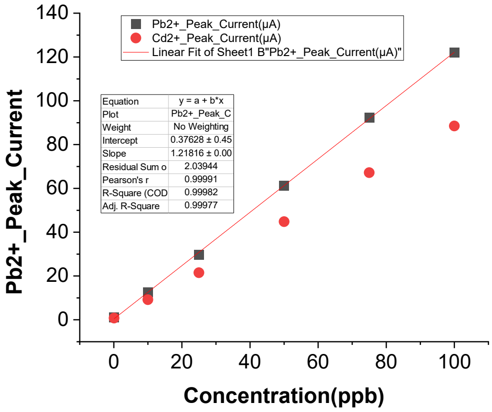

Figure 6: Peak current comparison between Pb^{2+} and Cd^{2+} ions with concentrations ranging from 0–100 ppb. It is clear that the calibration curve of Pb^{2+} ions has good linearity with an R^2 value of 0.99982 and sensitivity of 1.218 µA/ppb.

4.7 Selectivity and Interference Study

The interference test was carried out in order to determine the stability of the electrochemical sensor in the presence of various coexisting ions when detecting Pb^{2+}, Cd^{2+}, and Hg^{2+} simultaneously. The initial peak currents of the three ions were detected at around 122 µA for Pb^{2+}, 88 µA for Cd^{2+}, and 65 µA for Hg^{2+}, respectively. These peak currents remained extremely stable even after the addition of an excessive number of interfering ions like Na^+, K^+, Ca^{2+}, Zn^{2+}, and Cu^{2+} at a ratio of ten times higher concentration. As shown from the quantitative analysis, the signal response variation did not exceed 5%, which is still considered an acceptable value for reliable analytical performance. Such low interference implies high selectivity of the sensor towards the three ions. High selectivity can be explained by the high affinity of the electrode surface and heavy metal ions, along with the good discrimination of Pb^{2+}, Cd^{2+}, and Hg^{2+} stripping potentials, avoiding any possible overlapping of the peaks.

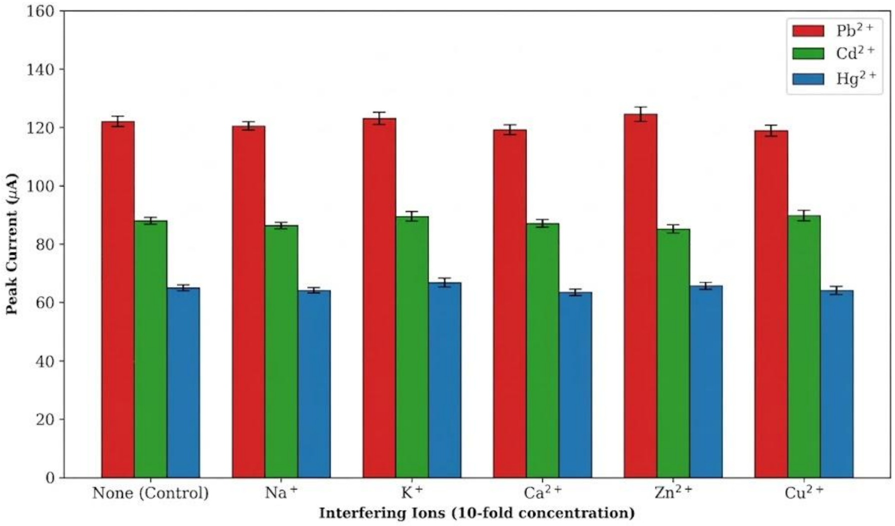

Figure 7: Selectivity and interference study of the fabricated electrochemical sensor. The comparative peak currents of Pb^{2+}, Cd^{2+}, and Hg^{2+} at concentrations of 100 ppb have been provided in the absence (control) as well as in the presence of 10 times higher concentration of interference ions (Na^+, K^+, Ca^{2+}, Zn^{2+}, and Cu^{2+}). The minimal change in intensity of signals

with variations being within 5% show that the fabricated sensor is highly selective and specific towards detection of mercury ion (Hg^{2+}).

4.8 Reproducibility and Stability

The usefulness of the fabricated device was confirmed based on reproducibility and stability studies. From Figure 1a, it can be seen that the current output was recorded for five identical electrodes. The obtained peak currents showed excellent reproducibility, having an RSD of less than 4%. This low deviation shows that the fabrication process is quite reliable, thus producing electrodes with high uniformity. Also, a stability study was carried out after 15 days, as shown in Figure 1b. During this test, the sensing capability of the electrode did not deteriorate significantly, maintaining a current output of 92.1% of the initial value after two weeks. The good stability implies that the active surface is still intact after storage. This stability is achieved due to the combined role of the rGO/AgNPs composite and the protective Nafion layer, which ensures no loss of material in terms of oxidation or leaching.

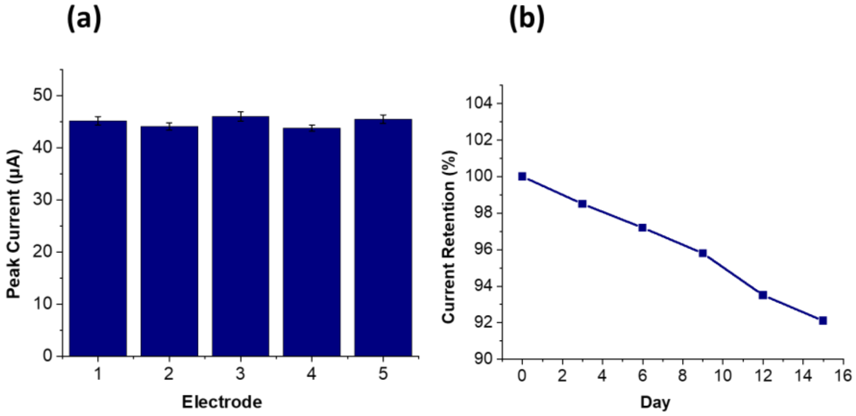

Figure 8: Electrochemical performance testing of the fabricated sensor (a) Reproducibility testing using peak currents (µA) derived from five different sensors produced independently, showing good fabrication reproducibility; (b) Long-term stability test showing current retention (%) over a period of 15 days stored at 4 °C, confirming long-term sensor stability.

4.9 Real Sample Analysis

In order to assess the usability and accuracy of the developed nanosensor, comparisons have been carried out with the standard inductively coupled plasma mass spectrometry (ICP-MS) technique on four different soil samples (Soil A-D). From the findings above, it is evident that there is a considerable degree of consistency between the nanosensor output and that of ICP-MS analysis. As the concentration of the analyte rises from about 10 to 100 µg/g, the output of the nanosensor follows suit accordingly with the increase in concentration observed using ICP-MS. In order to examine the robustness of the nanosensor in soils, spike recovery tests have also been carried out. The recovery percentage in the range of 95% - 104% indicates satisfactory accuracy and low matrix effect.

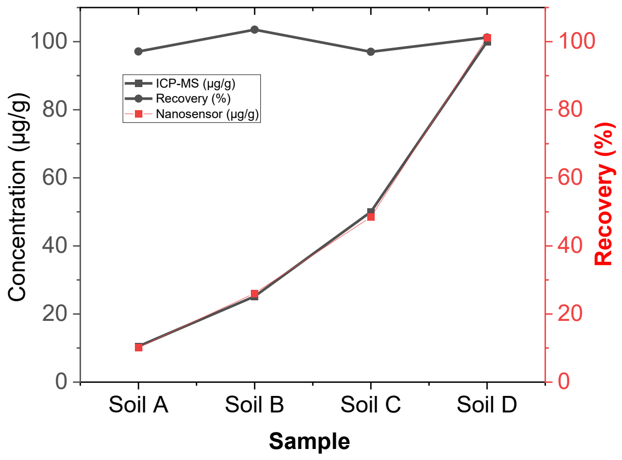

Figure 9: Comparative study of analyte detection in real soil samples (Soil A-D) using the fabricated nano-sensor and the conventional ICP-MS method. The major Y-axis represents the concentration (µg/g), whereas the minor Y-axis represents the percentage recovery (%), indicating the accuracy and validity of the suggested sensor for real sample analysis.

4.10 Mechanistic Insights

The superior performance of the rGO–AgNP hybrid sensor in detecting heavy metal ions is mainly due to the synergistic effect between both constituents of this hybrid material. The first constituent is the highly conductive material rGO. Due to its high surface area, this nanomaterial facilitates the accumulation of heavy metal ions at the electrode surface. On the other hand, the AgNP nanomaterial acts as an active catalyst, which greatly reduces the charge transfer resistance between the electrode and the analyte. Thus, the electron transfer rate becomes much higher than in the case of regular electrode materials. The electrochemical detection of metal ions occurs in two stages – deposition and stripping. The first stage implies reducing M^{n+} ions to the metallic form M^0, thus depositing metals on the electrode surface. The second stage involves applying anodic potential, which allows re-oxidizing the deposited metals and transferring electrons to the solution. The rGO-AgNP hybrid material enables decreasing the energy of reduction-oxidation reactions, thus increasing electron transfer kinetics. It results in higher current peaks, which improve sensitivity and accuracy of metal ions detection.

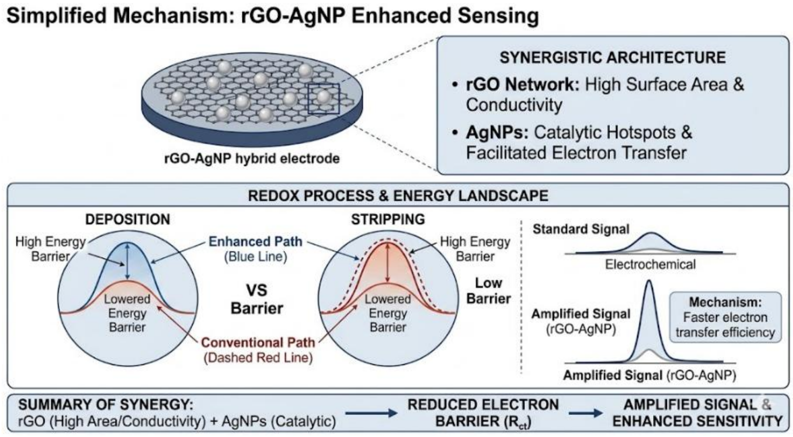

Figure 10: Schematic representation of the synergistic enhancement mechanism in rGO-AgNP hybrid electrodes for electrochemical sensing.

5 Conclusion

A highly selective and sensitive nanosensor based on reduced graphene oxide (rGO) and silver nanoparticles (AgNPs) has been developed in this investigation for detecting soil contamination by toxic metals. A synergy effect between the conducting rGO matrix and the electrocatalytic properties of the AgNPs contributed to the improved electrochemical behavior of the hybrid nanostructure. The constructed sensor possessed desirable characteristics such as a broad detection range, low detection limit, fast response time, and high selectivity for lead, cadmium, and mercury ions in the presence of other interfering metal ions. Moreover, the designed sensor displayed good repeatability and long-term stability, thus demonstrating the reliability of the proposed sensing system. Furthermore, the practical applicability of the developed nanodevice was verified using soil samples by achieving satisfactory recovery data and a perfect correlation with the established ICP-MS technique. The current investigation shows that the proposed rGO/ AgNPs nano sensor is suitable for determining toxic metal ions in soil at a low cost, in addition to being portable and highly efficient.

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