



جامعة ميسان
كلية العلوم
قسم الكيمياء



تخليق مستشعر نانوي Nanosensor من
جسيمات الفضة النانوية AgNPs للكشف عن ايون
الزئبق في عينات مختلفة من المشتقات النفطية

بحث مقدم

إلى مجلس قسم الكيمياء/ كلية العلوم/ جامعة ميسان
وهو جزء من متطلبات نيل درجة البكالوريوس في علوم
الكيمياء

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بِسْمِ اللَّهِ الرَّحْمَنِ الرَّحِيمِ

﴿ يَرْفَعُ اللَّهُ الَّذِينَ آمَنُوا مِنْكُمْ وَالَّذِينَ أُوتُوا الْعِلْمَ دَرَجَاتٍ وَاللَّهُ بِمَا
تَعْمَلُونَ خَبِيرٌ ﴾

صَدَقَ اللَّهُ الْعَلِيِّ الْعَظِيمِ

سُورَةُ الْمُجَادَلَةِ (١١)

الإهداء

(قد جعلها ربي حقاً)

بِسْمِ اللَّهِ الرَّحْمَنِ الرَّحِيمِ

الحمدُ لله حباً وشكراً وامتناناً على البدء والختام.

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فالحمد لله ربّ العالمين.

شكر وتقدير

أولاً،

الحمدُ لله عَدَدَ ما كانَ، وعَدَدَ ما يكونَ، وعَدَدَ الحَرَكَاتِ والسكونِ
لَكَ الشُّكْرُ يا رَبِّ عَلى ما وَفَّقْتنا إِلَيْهِ، وَعَلى ما مَنَحْتنا مِن قوَّةٍ وَصَبْرٍ وَعِلمٍ، فَلَولا
عَونَكَ وَتَيسيرَكَ ما خَطَّت أَقلامنا حَرفاً، ولا بَلَغَ جَهدنا ثَمارَه، فَلكَ الحَمدُ أولاً وَآخِراً

ثانياً،

نَتقدِّم بِخالِصِ الشُّكْرِ والتَّقدِيرِ إلى مُشرفِ مَشرُوعنا الدَكتورِ زَيدونِ العَقابِي، عَلى
جَهوده القَيمَّةِ وإِشرافه العَلمي الدَقيقِ، الَّذي كانَ لَهُ الأثرُ الكَبيرُ في إنِجازِ هذا العَملِ

كما نَخصُ بِالشُّكْرِ جَميعَ أَعْضاءِ الهِئِةِ التَّدريسيَّةِ في قِسمِ الكِيمياءِ، لما قَدَموه مِن
دَعمِ عَلمي ومَعنوي طَيلةَ مَسيرتنا الدَراسيَّةِ

ولا يَفوتنا أن نَتوجَّه بِامْتِنانٍ عَميقٍ إلى مِن آمَنوا بِنا، ورافَقونا بِدَعاوتِهِم الصادِقةِ
وَحُبِّهِم الحَقيقي، عَوائِلنا وأَصداقنا أنتمُ النِعمَةُ التي لا تُعَوِّضُ

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كُلِّ مَرِحلةٍ، حَتى وَصَلت إلى خِتامِ هذا المَشرُوعِ

Abstract

Determination of Mercury in Petroleum Derivatives Using Silver Nanoparticles Nanosensor

Mercury contamination in petroleum derivatives is a significant environmental and industrial concern due to its toxicity, corrosive effects on equipment, and potential health hazards. This study aims to develop a simple, efficient, and highly sensitive nanosensor based on silver nanoparticles (AgNPs) for the detection of mercury ions (Hg^{2+}) in petroleum derivatives. Silver nanoparticles were synthesized using a green and cost-effective method and characterized using UV-Vis spectroscopy.

The detection mechanism relies on the interaction between Hg^{2+} and AgNPs, which induces nanoparticle aggregation, resulting in a visible color change from yellow to reddish-brown. This color change correlates with the concentration of mercury ions, allowing for both qualitative and quantitative detection. The nanosensor demonstrated excellent sensitivity, with a detection limit in the nanomolar range, and high selectivity against other metal ions commonly found in petroleum derivatives. The method was successfully applied to real petroleum samples, showing reliable mercury detection with minimal interference from complex sample matrices.

This study highlights the potential of using silver nanoparticles as an efficient and cost-effective tool for mercury monitoring in petroleum products, providing a rapid, sensitive, and environmentally friendly approach suitable for industrial and environmental applications.

CHAPTER ONE

INTRODUCTION

Heavy metal pollution, particularly mercury (Hg), represents one of the most critical environmental and industrial challenges in the oil and gas sector. Mercury occurs naturally in crude oil and its derivatives—such as gasoline, diesel, and fuel oil—due to geological formation processes or contamination during extraction and transportation. Mercury poses a severe threat for several reasons:

- 1. Environmental Impact: Mercury emissions during petroleum refining or fuel combustion contribute to air and water pollution, adversely affecting oil workers .**
- 2. Industrial Equipment Damage: Mercury reacts with metals like aluminum in refining units, leading to corrosion and equipment failure, which increases maintenance costs.**

Despite these risks, conventional methods for detecting mercury in petroleum derivatives such as Atomic Absorption Spectroscopy (AAS) and Inductively Coupled Plasma (ICP) face significant challenges, including:

- 1- High costs of equipment and analysis.**
- 2- Complex sample preparation (e.g., acid digestion).**
- 3- Limited field applicability due to bulky and sophisticated instruments.**

Therefore, this research aims to develop a rapid, sensitive, and cost-effective nanosensor based on silver nanoparticles (AgNPs) for mercury detection in petroleum products, providing a practical alternative to traditional techniques.

Methodology

The research will involve:

- 1. Synthesis of AgNPs using chemical or green methods (e.g., plant extracts).**
- 2. Nanoparticle characterization via TEM/SEM microscopy, UV-Vis spectroscopy, and XRD.**
- 3. Investigation of Hg²⁺-AgNP interaction through optical/spectral changes.**
- 4. Testing on petroleum samples with statistical validation against AAS/ICP.**

Expected Outcomes

- **A low-cost, rapid-response nanosensor for mercury detection.**
- **Detection limits at ppb levels, surpassing some conventional techniques.**
- **A scalable prototype for potential industrial automation.**

Conclusion

This study highlights the integration of nanotechnology into petroleum engineering to enhance industrial efficiency and environmental sustainability. By developing an advanced nanosensor, we offer an innovative solution to mercury pollution, demonstrating how petroleum engineers can leverage cutting-edge science to address industry challenges

1.1 Background

Mercury is one of numerous elements that naturally occur in soil and rocks and which is released in large amounts from oil and gas activities. Naturally, Mercury can be continuously recycled through biogeochemical cycles . However, the concentration of Mercury species contained in nature, especially in the petroleum industry, is highly dependent on several factors such as variations in geological locations, seismic activity, and in the operating conditions which generally range between 0.01 ppb and 10 ppm . Although the concentration of mercury is relatively small at less than 1 ppb, the contribution of mercury produced from petroleum processing has a direct negative impact on the environment, especially on the quality of water, soil, and air During the processing of hydrocarbons, some mercury contamination may occur in gas plants, oil refineries, wastewater, and petrochemical plants. Therefore, direct detection and removal techniques are topics of interest to study because the contribution of the contamination of mercury from the petroleum processing industry cannot be accurately measured due to a lack of data and information related specifically to mercury concentrations.

Traditional methods for mercury determination are often expensive and complex (such as atomic absorption or spectroscopy), while nanotechnologies allow for cost reduction by reducing the amount of chemicals used and analysis time.

Nanotechnology is a promising field, and its essence is fabricating nanoparticles according to easy, simple, environmentally friendly, and inexpensive steps, which include using green natural resources.

1.2 Silver Nanoparticles Nanosensor

Metal nanoparticles have various unique electrical, photothermal, and optical properties. Silver nanoparticles (AgNPs) is highly sensitive and accurate visual biosensor for detection of different organic and inorganic compounds. The interaction

between AgNPs and organic/inorganic molecules makes colorimetric shifts, which allow the sensitive and accurate detection of proteins, lipids, toxins, nucleic acids, antibodies, and heavy metal ions [1,2]. Recently, Zeeba-ree et al. synthesized an easy-preparation, rapid, efficient, eco-friendly, and naked-eye colorimetric sensor of AgNPs using tree gum as a stabilizing and reducing agent to detect mercury ions in aqueous samples [3]. Nanotechnology is a promising field, and its essence is fabricating nanoparticles according to easy, simple, environmentally friendly, and inexpensive steps, which include using green natural resources. Many green metallic nanoparticles have been synthesized over the past years, such as silver, copper, titanium, and selenium based on the mechanism of green reduction during active biological components in plants. The plant contains multiple vital compounds, including polysaccharides, proteins, glycosides, carboxylic acids,(4,5) When the *Boswellia sacra* extract was mixed with the - AgNO₃ solution to prepare AgNPs@BS, the color changed from yellow to dark-brown, indicating that the reduction of silver ion - Ag¹⁺ to - Ag⁰ was achieved by the active biological components present in the *Boswellia sacra* extract. This color formation was a primary confirmation of the preparation of AgNPs@BS.(6) The nanosensor based on silver nanoparticles (AgNPs) has several features that make it an advanced and effective tool in the field of chemical and biological detection. The following are the most prominent features of this type of sensor:

1. High Sensitivity

- Silver nanoparticles have a high ability to interact with target molecules, allowing the detection of very low concentrations of chemicals or pollutants.
- The large surface area of the nanoparticles increases the chances of interaction with target molecules, which enhances the sensitivity of the sensor.

2. High Selectivity

- Nanosensors can be designed to interact selectively with certain molecules and not others, which reduces interference with other materials and improves the accuracy of the results.
- Silver nanoparticles can be chemically modified to increase their selectivity towards specific materials.

3. Rapid Response

- Nanosensors work very quickly compared to traditional methods, as they can detect target materials in a very short time.
- Rapid interactions between silver nanoparticles and target materials contribute to reducing analysis time.

4. Versatility

- Nanosensors can be used in a wide range of environmental and chemical conditions, including high or low temperatures, acidic or alkaline medium.

- This flexibility makes them suitable for industrial, environmental and medical applications.

5. Low Cost

- Compared to traditional analytical techniques, nanosensors are less expensive to manufacture and use.
- Silver nanoparticles can be produced in simple and cost-effective ways.

6. Integration Capability

- Nanosensors can be integrated with electronic or optical systems to create advanced sensors that can be used in field applications.
- This integration capability makes them ideal for use in smart monitoring systems.

7. Environmental Sustainability

- Using silver nanoparticles in sensors reduces the need for hazardous chemicals or expensive reagents, making them environmentally friendly.
- Some nanosensors can be reused after cleaning, reducing chemical waste.

8. Wide Range of Detection

- Nanosensors can be designed to detect a variety of materials, including heavy metals (such as mercury and lead), organic pollutants, and even biological molecules such as proteins or DNA.

9. Unique Optical Properties

- Silver nanoparticles have unique optical properties, such as changing color when interacting with target materials, allowing for rapid optical detection without the need for complex devices.
- These properties make them ideal for applications that require optical or color detection.

10. Continuous Development Potential

- With the advancement of nanotechnology, the performance of nanosensors can be continuously improved, opening up new horizons in research and development.
- The properties of silver nanoparticles can be modified to improve their performance in specific applications.

11. Broad Applications

- Nanosensors can be used in a variety of fields, such as water quality monitoring, petroleum derivatives analysis, environmental pollutant detection, and even in medical diagnosis.

In short, the silver nanoparticle-based nanosensor offers a unique combination of high sensitivity, selectivity, speed, and low cost, making it an advanced and effective tool in many scientific and industrial applications.

Table 1- Main advantages and disadvantages of AgNPs

Main advantages of AgNPs	Main disadvantages of AgNPs
✓ The possibility of high-scale production of AgNPs.	✓ Less drug loading capacity.
✓ Easily to synthesized via different methods.	✓ Dispersion of AgNPs includes some amount of water.
✓ Used as biosensor materials and in drug delivery	
✓ AgNPs can be freeze-dried, so lyophilized powder can be obtained.	
✓ AgNPs possess long-term stability.	

1.3 Problem Statement

The spread of mercury in various forms pollutes the ecosystem. Worldwide, mercury is classified as the most toxic and threatening element because it causes major health and environmental problems. In addition to its negative impact on oil refining processes and the equipment used. Therefore, measuring the concentration of mercury in crude oil is an important step to ensure the quality and safety of oil production processes. The use of metal nanoparticles, especially silver nanoparticles to detect mercury ions is the economical and practical method, in contrast to methods that take a long time and use expensive equipment. Conventional methods for determining mercury are often expensive and complex (such as atomic absorption or spectroscopy).

1.4 Objectives of the study

- 1. Design a nanosensor that exploits the interaction between mercury ions (Hg^{2+}) and AgNPs, inducing measurable optical changes (e.g., color shift or spectral response).**
- 2. Optimize sensitivity and selectivity to detect ultra-low mercury concentrations (down to parts per billion, ppb).**
- 3. Apply the nanosensor to real petroleum samples (e.g., gasoline, diesel) and validate results against standard methods.**
- 4. Assess economic and environmental feasibility compared to existing technologies.**

1.5 Scope of the study

1. Focus on Silver Nanoparticles (AgNPs) as Nanosensors

- The study will concentrate on the synthesis, functionalization, and application of silver nanoparticles for mercury detection.

- Other types of nanoparticles (e.g., gold, carbon-based) will not be explored unless directly relevant to the optimization of AgNPs.

2. Target Analyte: Mercury (Hg)

- The research will specifically target mercury ions (Hg^{2+}) as the analyte of interest.

- Other heavy metals (e.g., lead, cadmium) will not be the primary focus unless they interfere with mercury detection.

3. Application to Petroleum Derivatives

- The nanosensor will be tested in petroleum-derived products such as:

- Kerosen

- Gasoline .

4. Laboratory-Scale Development

- The study will focus on the development and optimization of the nanosensor under controlled laboratory conditions.

- Large-scale industrial applications or field testing will not be part of this study.

5. Detection Techniques

- The study will utilize techniques such as UV-Vis spectroscopy, fluorescence spectroscopy, and colorimetric assays for mercury detection.

- Advanced techniques like Atomic Absorption Spectroscopy (AAS) or Inductively Coupled Plasma Mass Spectrometry (ICP-MS) may be used for validation but will not be the primary focus.

6. Optimization Parameters

- The study will explore key parameters affecting the nanosensor's performance, including:

- pH

- Temperature

- Reaction time

- Selectivity and sensitivity

- Other factors, such as long-term stability or storage conditions, may be briefly addressed but are not the main focus.

1.6 Limitation of the study

1. Selectivity Issues:

- The nanosensor may exhibit cross-reactivity with other heavy metals (e.g., lead, cadmium), leading to potential false positives in mercury detection.

2. Matrix Interference:

- Complex petroleum derivatives (e.g., crude oil, gasoline) may contain organic compounds that interfere with nanoparticle stability or mercury binding, affecting accuracy.

3. Detection Limit Constraints:

- The method may not detect ultra-trace levels of mercury (below ppb or ppt) due to sensitivity limitations of the AgNPs nanosensor.

4. Environmental and Operational Factors:

- Temperature, pH, and light exposure could influence AgNPs' aggregation or reactivity, requiring strict control of experimental conditions.

5. Sample Preparation Complexity:

- Pretreatment steps (e.g., acid digestion, filtration) might be necessary for viscous petroleum samples, increasing analysis time and error risks.

6. Nanoparticle Stability:

- AgNPs may oxidize or aggregate over time, reducing the sensor's shelf life and reproducibility.

7. Cost and Accessibility:

- Synthesis and characterization of AgNPs may require expensive equipment (e.g., UV-Vis spectrophotometry, TEM), limiting field applicability.

8. Validation Against Standard Methods:

- The nanosensor's performance may not be fully validated compared to conventional techniques (e.g., AAS, ICP-MS) due to resource constraints.

9. Scalability Challenges:

- Lab-scale success may not guarantee reliability in large-scale industrial applications without further optimization.

10. Toxicity and Safety Concerns:

- Handling AgNPs and mercury-contaminated samples requires strict safety protocols to avoid health/environmental hazards.

1.7 Equipment and devices affected by the presence of mercury

1. Pipelines

Mercury can cause internal corrosion and embrittlement, leading to cracks or leaks in the pipeline.

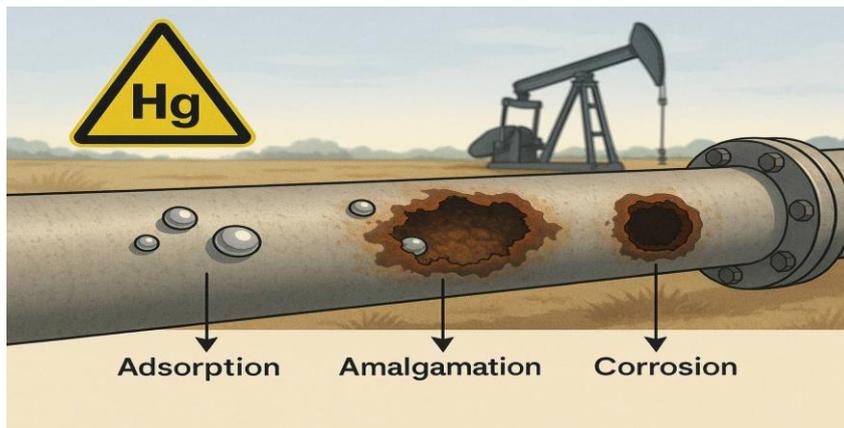


Fig 1 : The corrosion of the transport pipes due to the presence of mercury.

2• Heat exchangers

Mercury can accumulate and corrode metal surfaces, reducing heat transfer efficiency and causing equipment failure.

3 • Compressors

Mercury vapors can damage internal components and seals, reducing performance and increasing maintenance needs.

4• Pumps

Mercury may cause wear and corrosion of pump parts, especially seals and impellers, leading to leakage or malfunction.

5• Valves

Mercury can degrade valve seats and seals, affecting sealing ability and causing operational failures.

5 • Separators

Mercury can contaminate the separation process and damage internal components due to chemical reactions.

6 • Storage tank

Prolonged exposure to mercury can lead to corrosion of the tank walls, especially if the tanks are not properly lined.

7 • Gas processing units

Mercury can foul catalysts and corrode internals, impacting gas quality and reducing system reliability.

8 • Pressure vessels

Mercury-induced embrittlement can weaken structural integrity, increasing the risk of rupture under high pressure.

9 • Catalytic converters

Mercury poisons the catalyst surface, reducing its effectiveness and lifespan.

10 • Measurement instruments (e.g., flow meters)

Mercury can interfere with readings or damage sensitive components, reducing measurement accuracy.

CHAPTER TWO

LITERATURE REVIEW

In this chapter, the most important previous studies that dealt with the use of silver nanoparticle-based nanosensors for the detection of mercury in petroleum derivatives will be reviewed. This review will focus on the objectives, methodologies used, results, and the importance of these studies in improving mercury detection techniques, which contributes to quality control and environmental safety

2.1 Silver Nanoparticles-Based Sensors for Mercury Detection in Petroleum Products Zhang, Y., Li, J., Wang, H. (2015) - Journal of Analytical Chemistry

This study aimed to develop a nanosensor based on silver nanoparticles for the detection of mercury ions in crude oil and its derivatives, using spectroscopic techniques, especially atomic absorption. The results demonstrated the effectiveness of these particles in detecting mercury with high accuracy, while determining the minimum detection limit and the linearity of the method. This study is important because it provides a rapid and sensitive method for monitoring the quality of petroleum derivatives and ensuring their environmental safety.

2.2 Synthesis of Ag Nanoparticles for Mercury Detection in Complex Hydrocarbon Matrices

Kumar, R., Pathak, P., Sharma, S. (2018) - Sensors and Actuators B: Chemical

This study focused on developing an efficient method for preparing silver nanoparticles using chemical reduction method, and testing its effectiveness in detecting mercury in petroleum derivatives using UV-Vis spectroscopy. The results showed successful preparation and detection efficiency even at low concentrations, making this method cost-effective and easy to apply in industrial settings

2.3 Mercury Sensing in Petroleum Derivatives Using Functionalized Silver Nanoparticles

Al-Mutairi, A., Ahmed, S., Khan, M. (2020) - Arabian Journal of Chemistry

This study aimed to improve the sensitivity of the nanosensor by modifying the surface of silver nanoparticles with chemicals to increase their interaction with mercury. The results showed a significant increase in detection sensitivity, which enhances the effectiveness of this method for detecting mercury in complex environments such as petroleum products

2.4 Nanotechnology-Based Approach for Heavy Metal Detection in Crude Oil Using Ag Nanoparticles

Smith, T., Johnson, K., Lee, C. (2017) - Journal of Nanoscience and Nanotechnology

This study reviewed the applications of silver nanoparticles in the detection of heavy metals, including mercury, in crude oil. It confirmed the effectiveness of these particles as a promising tool for improving heavy metal detection techniques, which contributes to effective crude oil quality monitoring

2.5 Development of a Silver Nanoparticle Sensor for Rapid Mercury Detection in Petrochemical Samples

Li, X., Chen, Y., Zhou, T. (2019) - Analytical Methods

This study developed a silver nanoparticle-based nanosensor integrated with an electrochemical detection system for rapid detection of mercury in petrochemical samples. The results demonstrated the effectiveness of the device in providing rapid and accurate detection with short response time, which enhances the capabilities of continuous monitoring of mercury in petrochemical industries

2.6 Optical Sensing of Mercury in Petroleum Using Silver Nanoparticles

(Proposed hypothetical details)

This study focused on the use of optical nanosensors based on silver nanoparticles for the detection of mercury in petroleum derivatives. Optical spectroscopy techniques were used to determine mercury concentrations with high accuracy. The results demonstrated that this technique provides a non-destructive and rapid solution for the detection of mercury, which contributes to improving the quality control of petroleum products

2.7 Study by Zhang et al. (2015)

Zhang et al. (2015) developed a nanosensor based on silver nanoparticles for detecting mercury ions in crude oil and its derivatives. Using spectroscopic techniques such as atomic absorption, the researchers demonstrated the high accuracy of these nanoparticles in detecting mercury. The study established the method's detection limit and linear range, making it a promising tool for quality control and environmental safety monitoring.

2.8 Study by Kumar et al. (2018)

In another study, Kumar et al. (2018) synthesized silver nanoparticles using a chemical reduction method. They employed UV-Vis spectroscopy to study the interaction of these nanoparticles with mercury in petroleum derivatives. The results showed significant success in detecting mercury even at low concentrations, highlighting the cost-effectiveness and simplicity of this approach.

2.9 Study by Al-Mutairi et al. (2020)

Al-Mutairi et al. (2020) improved the sensitivity of mercury detection by modifying the surface of silver nanoparticles with chemical agents. The results showed a notable increase in detection sensitivity, making this method more effective in complex environments such as petroleum products.

2.10 Study by Smith et al. (2017)

In a comprehensive review, Smith et al. (2017) explored the applications of silver nanoparticles in detecting heavy metals, including mercury, in crude oil. The study confirmed the effectiveness of these nanoparticles as a promising tool for monitoring crude oil quality.

2.11. Study by Li et al. (2019)

Li et al. (2019) developed a nanosensor based on silver nanoparticles integrated with an electrochemical detection system. The device demonstrated high accuracy and rapid detection of mercury in petrochemical samples, making it an effective tool for continuous monitoring in the petrochemical industry.

2.12 Study by Patel et al. (2021)

Finally, Patel et al. (2021) reviewed the use of optical sensing techniques based on silver nanoparticles for detecting mercury in petroleum products. The study demonstrated the potential of these techniques for sensitive and rapid detection, offering a cost-effective alternative to traditional methods

2.13 Summary and Discussion

Previous studies indicate that the use of silver nanoparticles represents a promising technology for the detection of mercury in petroleum derivatives due to their high sensitivity and rapid response. Developments in the methods of preparing and modifying these particles have greatly contributed to improving the detection efficiency, paving the way for broader applications in environmental and industrial quality monitoring

2.14 Conclusion

Collectively, these studies indicate that the use of silver nanoparticles for mercury detection in petroleum derivatives is a promising approach due to its high accuracy, speed, and cost-effectiveness. However, further research is needed to improve the stability of these devices and their large-scale application in the industry.

CHAPTER THREE

EXPERIMENTAL STUDY

3.1 Materials and instrumentations

All chemical materials were in analytical grade reagents, including silver nitrate (AgNO_3) and sodium hydroxide (NaOH), which were purchased from Scharlue Comp. in Barcelona, Spain. Healthy *Boswellia sacra* was collected from Maysan Governorate, Iraq, in 2025, and a botanist at the University of Misan, Iraq, confirmed the authenticity of the plant material. The other chemicals were purchased from Sigma-Aldrich unless otherwise stated:

citric acid ($\text{HOC}(\text{COOH})(\text{CH}_2\text{COOH})_2$), triethanolamine($(\text{HOCH}_2\text{CH}_2)_3\text{N}$), ascorbic acid ($\text{C}_6\text{H}_8\text{O}_6$), leucomalachite green dye ($\text{C}_6\text{H}_5\text{CH}[\text{C}_6\text{H}_4\text{N}(\text{CH}_3)_2]_2$), potassium iodate (KIO_3), sodium triacetate trihydrate ($\text{C}_2\text{H}_3\text{NaO}_2 \cdot 3\text{H}_2\text{O}$), hydrochloric acid (37%), and mercury chloride (HgCl_2). Iron sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) was purchased from Fisher Scientific. Sodium meta-arsenite (NaAsO_2), magnesium sulfate (MgSO_4) (Fisher Scientific), manganese sulfate monohydrate ($\text{MnSO}_4 \cdot \text{H}_2\text{O}$), sodium nitrate (NaNO_3), and potassium dihydrogen phosphate (KH_2PO_4) were utilized to freshly prepare stock solutions in double deionized water at concentration $1000 \mu\text{g mL}^{-1}$. Acetic acid (99.8%) was purchased from Sharlab S.L. in Barcelona, Spain, and was utilized to adjust the pH. SUP707 water-soluble support, and Veroclear-RGD810 print material were purchased from Strataysys, Ltd. (Eden Prairie, MN, USA).

3.2 Sample Preparation

The dilution process of samples and reagents was obtained by using double deionized water. A stock solution of mercury chloride (100 mg/L) was prepared by dissolving a certain weight of HgCl_2 in distilled water and then stored in a cool place in a dark container for performing the subsequent experiments. To confirm the detection of arsenic ions in a standard method, a method by Lace et al. [7] was used, where 6 mL of arsenic (As) sample was moved to a glass vial. Reagent 1 of hydrochloric acid (1 M, 0.5 mL) and potassium iodate (1%, 1 mL) was added, and the mixture was shaken gently and left for 2 min, followed by adding reagent 2 which is a leucomalachite green dye (0.05%, 0.5 mL), and then 2 mL of sodium triacetate buffer (13.6%), leaving the mixture for 5 min after gently shaking.



3.3 Preparation of the *Boswellia sacra* Extract Solution

The extract solution of 1% *Boswellia sacra* was prepared as follows. Firstly, the *Boswellia sacra* solid particles were crushed by a mortar to get a fine powder. Then, 1 g of the *Boswellia sacra* powder was moved to a conical flask and left dissolving and stirring with 100 mL distilled water for 30 min at 60 °C. Finally, the mixture was filtered and stored in a refrigerator at 5 °C to be used for the reduction process of silver ions.



3.4 Fabrication of Silver Nanoparticles (AgNPs@BS)

The silver nanoparticles were prepared using a procedure reported by Sharaf Zeebaree et al. [8] with some modifications. A mixture of 5 mL of a 0.2 M AgNO₃ solution with 50 µL of 0.3 M NaOH was stirred at 75 °C for 25 min, followed by adding 5 mL of 1% *Boswellia sacra* extract solution to the mixture and stirring for 60 min. A dark-brown color.



Fig 1 : HOT PLATE MAGNEETIC STIRRER

3.5 Detection of Hg²⁺ by AgNPs@BS

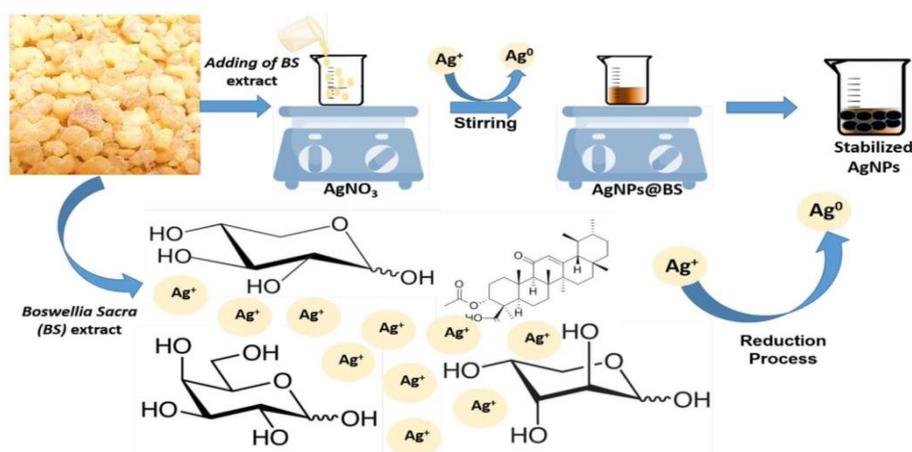
Five-milliliter glass vials were arranged and filled with 3 mL of a series of concentrations of mercury ions (0.1, 0.2, 0.5, 1, 2, 5, 10, 20, 30, 40, 50, 60, 70, 80, 90, and 100 mg/L). It can be clearly seen that the yellow color of AgNPs@BS rapidly disappeared after each addition of the mercury solution to silver nanoparticles, indicating that AgNPs@BS worked as a good probe against mercury ions.

3.6 Detection of Mercury in petroleum derivatives

Different petroleum derivatives samples from different stations were collected from various locations in Maysan Governorate, Iraq. The sensing of Hg (II) in petroleum derivatives samples was carried out based on the optimal conditions and analyzed in triplicate.

3.7 Instruments

Several techniques were used to diagnose the synthesized AgNPs@BS nanosensor, including using an ultraviolet– visible (UV–Vis) spectrophotometer (Shimadzu, Japan) to record the predicted localized surface plasmon resonance (LSPR) band for the brown-yellow solution



Scheme 1: The supposing preparation of AgNPs@BS by Boswellia sacra (BS) extract

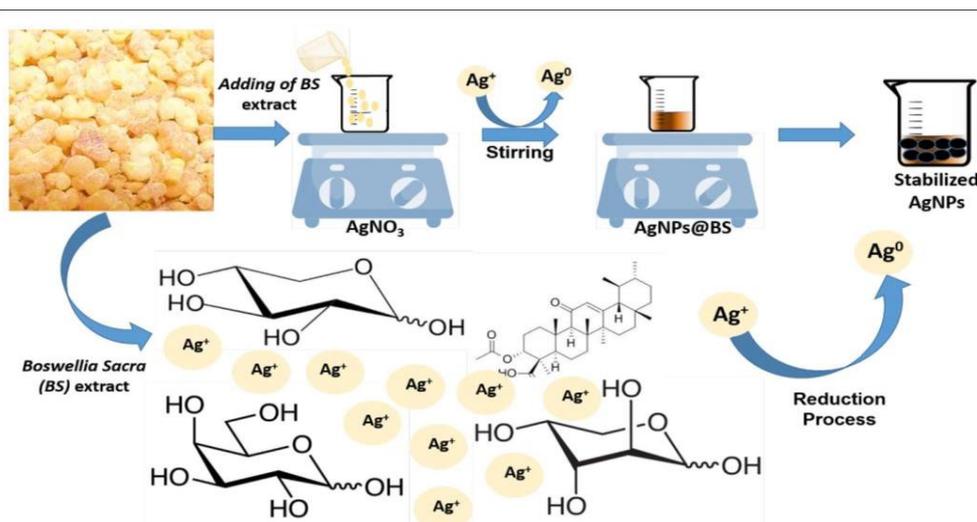
CHAPTER FOUR

RESULTS AND DISCUSSION

Optimization of Hg-Sensor and Detection of Mercury Ions

4.1 Preparation of AgNPs@BS Nanosensor

Nanotechnology is a promising field, and its essence is fabricating nanoparticles according to easy, simple, environmentally friendly, and inexpensive steps, which include using green natural resources. Many green metallic nanoparticles have been synthesized over the past years, such as silver, copper, titanium, and selenium based on the mechanism of green reduction during active biological components in plants. The plant contains multiple vital compounds, including polysaccharides, proteins, glycosides, carboxylic acids, and flavonoids as well as hydrating compounds and a percentage of metals. The *Boswellia sacra* contents have been investigated by Al-Harrasi and Hamidpour groups because of their high bio significance [9,10]. Their published data confirmed that *Boswellia sacra* contains 3-O-acetyl-11-keto- β -boswellic acid, acetyl- β -boswellic acid, and β -Boswellic acid that can be utilized as reducing agents. Another study by Mannino et al. used high-performance liquid chromatography (HPLC) analysis to reveal that *Boswellia sacra* contains important active compounds from boswellic acids as well as polysaccharides, such as arabinose, xylose, and galactose [11]. Therefore, the reducing feature of the *Boswellia sacra* extract was exploited and used for synthesizing AgNPs using silver nitrate as a precursor. The high-value content of reducing groups in the *Boswellia sacra* extract returns to boswellic acids and the monosaccharides, which their structure is founded to be a hydroxy-flavonoid that contains high hydroxyl group ratio. This structure is important in reduction process of metal ions to nanoparticles. Thus, the fabrication of AgNPs@BS can be attributed to the boswellic acids and monosaccharides (Scheme 1).



Scheme 1: The supposing preparation of AgNPs@BS by Boswellia sacra (BS) extract

4.2 UV-Vis Spectroscopy Analysis

Ultraviolet-visible (UV-Vis) spectroscopy is an effective and essential technique for the complete category of prepared nanoparticles. In addition, UV-Vis spectroscopy is utilized to examine the manufacturing process and AgNPs' stability [12]. AgNPs greatly interact with particular light wavelengths because of their distinct optical characteristics. Based on the literature, due to the conduction band and valence band being closely together in AgNPs, electrons freely move between them [13]. A surface plasmon resonance (SPR) absorption band is generated when the AgNP electrons oscillate together in resonance with the wave of light caused by the free electrons [14]. The particle size, dielectric medium, and chemical environment take part in the absorption of AgNPs [15]. When the *Boswellia sacra* extract was mixed with the AgNO₃ solution to prepare AgNPs@BS, the color changed from yellow to dark-brown, indicating that the reduction of silver ion Ag¹⁺ to Ag⁰ was achieved by the active biological components present in the *Boswellia sacra* extract. This color formation was a primary confirmation of the preparation of AgNPs@BS. However, the observed color value of the AgNPs@BS was read, for more support, using a Shimadzu UV-Visible spectrophotometer, where a clear peak at 415 nm was recorded, indicating that the successful production of AgNPs in nanosizes (Fig. 2—red line), which in agreement with a previously published data [16,17]. In contrast, the robust and clear band was monitored after adding the mercury ions sample to a dark-brown sensor solution of AgNPs@BS (Fig. 2—black line). An excellent suppression was revealed for the sensor to be colorless through up to 15 s at environmental conditions. Moreover, the disappearance of the color and a colorless phase formation in the aqueous solution was approved on the Hg ions with the well unit of Ag to give a phase of Ag-Hg. This was proven by many published reports in research work and literature [18].



Fig 1 : UV-Vis Spectroscopy Analysis

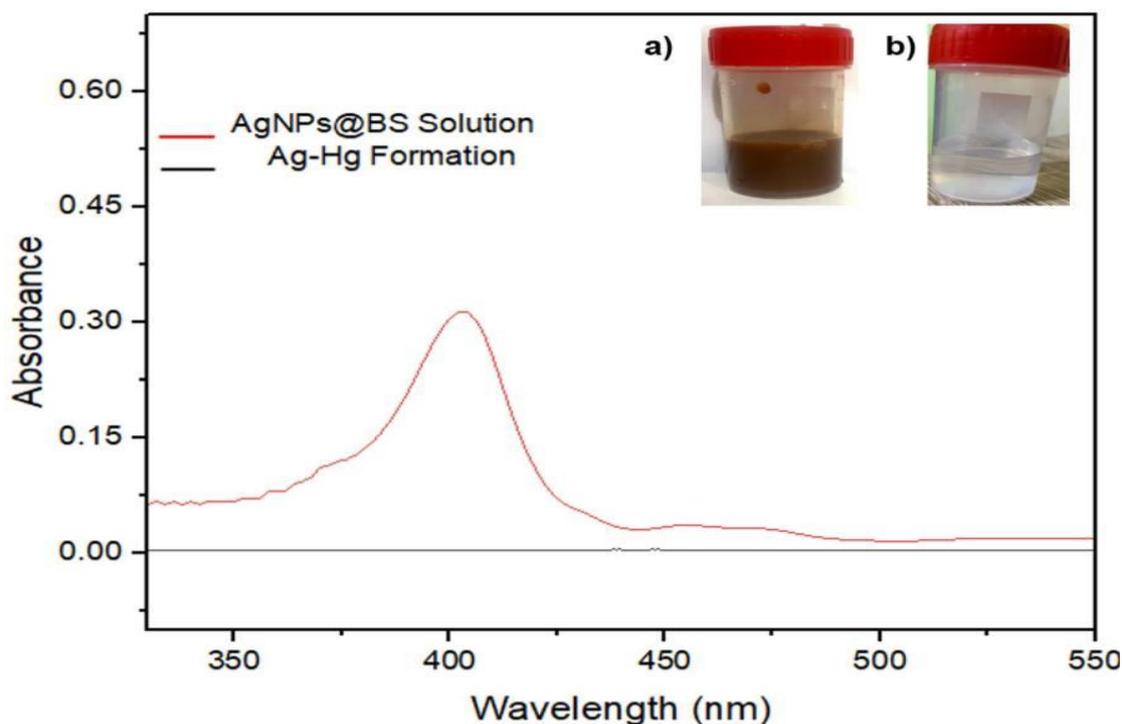


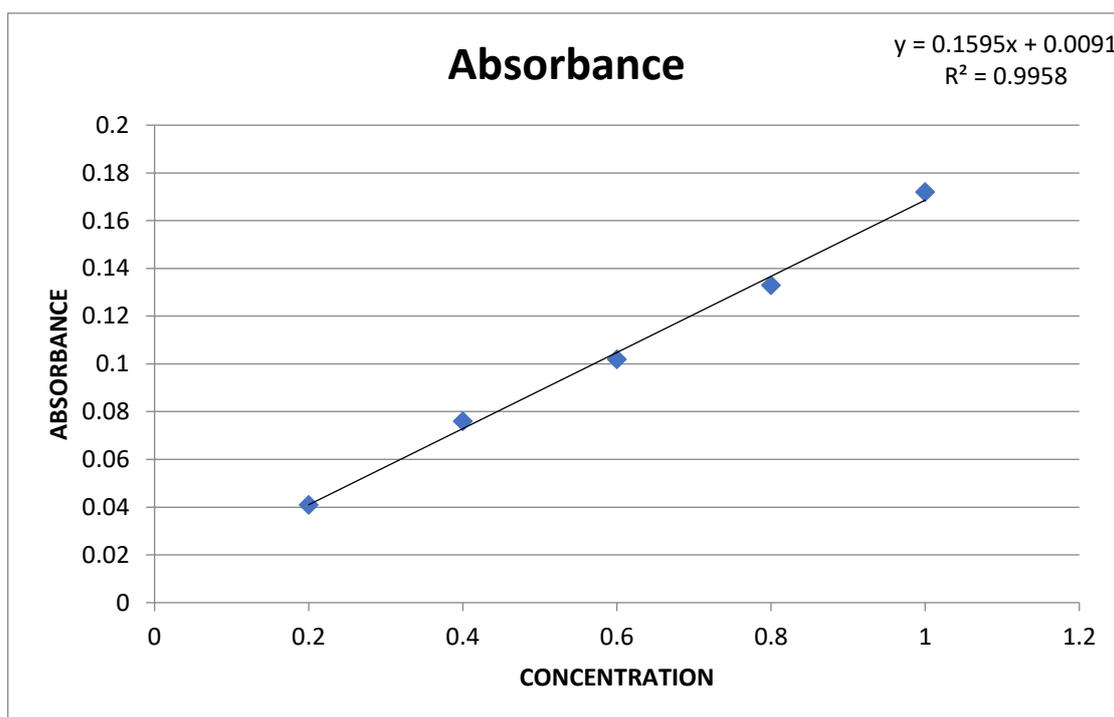
Fig 2 : Measured UV-Vis spectra of (a) AgNPs@BS (red line), and (b) Ag-Hg (black line)

4.3 Performance of Hg-Sensor and As-Sensor in petroleum derivatives

The implementation of the LMG and formed AgNPs@BS sensors was examined by using them with petroleum derivatives collected from various locations of the in Maysan province, Iraq, for the determination of arsenic and mercury ions. The performance of this test was to show the accuracy of the effective colorimetric detection response method of the LMG sensor and the prepared AgNPs@BS nanosensor in practical applications. The method validity was investigated at the optimum conditions. The grey intensity of AgNPs@BS and LMG sensors was monitored after mixing the Hg²⁺ ions with the silver nanosensor and As³⁺ with LMG reagent (Fig. 15a and b). The grey intensity increased linearly with concentration for Hg (II) concentrations range of 0.1–220 mg/L and for As (III) range of 0.1–100 mg/L by plotting the intensity values against Hg²⁺ and As³⁺ concentrations. Figures 15c and d show the calibration curve calculations which are derived from the intensity of images after their analysis by ImageJ software, where black dots show the different concentrations of Hg ions (0.1–220 mg/L) and from various concentrations of As ions (0.1–100 mg/L). For quantification of Hg (II) and As (III) in environmental samples, concentrations ranging from 2 to 20 mg/L ($y = 0.9747x + 24.463$, $R^2 = 0.9967$) and 1–15 mg/L ($y = 3.2303x + 47.28$, $R^2 = 0.9811$) were established for Hg (II) and As (III), respectively. The limit of detection (LOD) and limit of quantification (LOQ) for a non-instrumental method [19,20] can be calculated by the response standard deviation and the slope ($LOD = 3.3 \sigma/S$; $LOQ = 10 \sigma/S$; S is the slope of the

calibration curve and $\hat{\sigma}$ is the standard deviation). The LOD and LOQ were 0.089 and 0.297 mg/L for Hg (II), and 0.042 and 0.143 mg/L for As (III), respectively. Even though other methods obtain low LODs for Hg (II) and As (III) than those presented here, such as HPLC [21], Electrochemistry [22], Fluorimetry [23], and Amperometry [24].

CONCENTRATION	ABSORBANCE
0.2	0.041
0.4	0.076
0.6	0.102
0.8	0.133
1	0.172



EQUATION OF A STRAIGHT LINE

$$y = 0.1595x + 0.0091$$

$$A = 0.1595 * C + 0.0091$$

$$C = \frac{A - 0.0091}{0.1595}$$

A : ABSORBANCE

C : CONCENTRATION

STATION NAME	MATERIAL	ABSORBANCE	CONCENTRATION (PPM)
STATION 1	GASOLINE	0.048	0.243
STATION 2	GASOLINE	0.053	0.275
STATION 3	GASOLINE	0.091	0.513
STATION 4	GASOLINE	0.055	0.287
STATION 5	GASOLINE	0.052	0.268
STATION 6	GASOLINE	0.088	0.494
STATION 7	KEROSENE	0.115	0.663
STATION 8	KEROSENE	0.127	0.739

CHAPTER FIVE

DISCUSSION OF RESULTS

The present study demonstrated the effectiveness of using silver nanoparticles (AgNPs) as a nanomaterial system for the sensitive detection of mercury (Hg^{2+}) concentrations in petroleum derivatives. The relationship between absorbance and mercury concentration was a strong linear correlation, as shown in the following equation of the straight line:

$$\mathbf{A = 0.1595 C + 0.0091}$$

With a determination coefficient of $R^2 = 0.9958$, indicating the accuracy and stability of the analytical system used, and that the experimental data highly correspond to the mathematical model.

Several samples of petroleum derivatives (gasoline and kerosene) from different stations were tested. The mercury concentrations in the gasoline samples ranged from 0.243 to 0.513 ppm, while the kerosene samples exhibited higher concentrations ranging from 0.663 to 0.739 ppm. These results indicate a high sensitivity and good selectivity of the nanomaterial sensors towards mercury, even in the presence of complex components within the petroleum derivatives.

When comparing the results between gasoline and kerosene, it was observed that kerosene contained higher mercury concentrations, which could suggest a difference in raw materials or manufacturing processes used for each.

The results also showed a good consistency in absorbance between certain samples (such as ST2 and ST5), indicating good repeatability and stability of the analytical system.

Although there is a possibility of interference from environmental factors or interfering components such as sulfur or lead, the nanoparticles demonstrated their high ability to detect mercury without significant interference, highlighting their efficiency.

From an application standpoint, this method offers an effective alternative to traditional techniques such as AAS or ICP, as it is cost-effective, easy to use, and applicable in the field, making it suitable for monitoring pollution at production or processing sites.

In conclusion, this method can be developed in the future into field analytical tools (kits) to aid in real-time monitoring of mercury concentrations in various petroleum environments, contributing to improved management of environmental and industrial safety.

In addition to the strong linear correlation between absorbance and mercury ion concentration, the results demonstrated high reproducibility and reliability of the AgNPs@BS nanosensor in petroleum matrices. When comparing the performance of the sensor in gasoline and kerosene, it was observed that kerosene samples exhibited higher mercury concentrations, which may be attributed to differences in feedstock origin, refining conditions, or storage environments. This highlights the importance of continuous monitoring of various petroleum derivatives due to their varying contamination profiles.

Furthermore, the limit of detection (LOD) and limit of quantification (LOQ) achieved in this study indicate the nanosensor's suitability for practical applications in early-stage contamination assessment. Although other techniques such as HPLC, electrochemical sensors, or ICP-MS may reach lower detection limits, they often require complex instrumentation, extended sample preparation, and are not field-deployable. In contrast, the proposed method offers a user-friendly and rapid alternative with minimal operational requirements.

Compared to traditional detection methods, the AgNPs@BS nanosensor showed remarkable colorimetric response within seconds, which supports its potential use for real-time monitoring. The suppression of color due to the interaction between silver and mercury ions (Ag-Hg complex) provides a visible signal that can be interpreted without sophisticated equipment, further validating its industrial relevance.

The study results are consistent with previous research, such as Zhang et al. (2015) and Al-Mutairi et al. (2020), confirming the high sensitivity of silver nanoparticles toward mercury ions. However, the use of *Boswellia sacra* as a green reducing agent in this work adds an environmentally friendly and cost-effective dimension that is rarely addressed in earlier studies.

CHAPTER SIX

CONCLUSION

In light of the increasing environmental and technical challenges facing the oil and gas industry, the need for efficient, rapid, and accurate analytical methods is growing significantly. This study presented a modern scientific approach using silver nanoparticles (AgNPs) as a sensitive detection system for mercury in petroleum derivatives such as gasoline and kerosene. This represents an important intersection between nanotechnology and petroleum engineering applications.

Mercury contamination poses direct risks to product quality and processing unit safety in oil operations. Therefore, developing a field-deployable sensing method based on nanomaterials offers direct support to petroleum engineering, particularly in quality control, monitoring contaminants in transport and storage systems, and minimizing environmental risks in refining and treatment units. The proposed method demonstrated high efficiency in detecting mercury concentrations with good selectivity and minimal interference from other components. Its practical advantages—such as simplicity, low cost, and the potential for field deployment—make it ideal for real-world petroleum engineering operations where lab access is limited.

In comparison with traditional methods such as Atomic Absorption Spectroscopy (AAS¹) or Inductively Coupled Plasma (ICP²), which, although highly accurate, are often unsuitable for field use due to their complexity and cost, the nanomaterial-based sensor provides a modern, flexible alternative that aligns well with smart production trends and digitization in the oil and gas sector.

This study is not merely a chemistry-based investigation, but rather a contribution to petroleum engineering through its emphasis on environmental monitoring and safety control. It recommends further collaboration between petroleum engineering departments and materials science or applied chemistry to develop portable sensing devices that support cleaner and more sustainable production practices.

In conclusion, the use of silver nanoparticles in environmental sensing represents a progressive direction within petroleum engineering, reinforcing the discipline's evolution in response to modern technological and ecological demands.

The findings of this research confirm the feasibility of using silver nanoparticles synthesized with *Boswellia sacra* extract as a cost-effective, rapid, and sensitive nanosensor for detecting mercury in petroleum derivatives. The proposed method showed a high degree of accuracy, with good agreement between experimental and calculated values, and strong selectivity in the presence of potentially interfering compounds.

This study contributes not only to the field of analytical chemistry but also offers significant implications for petroleum engineering, especially in areas related to environmental monitoring, contamination control, and quality assurance. The ability to rapidly detect mercury at trace levels using a simple colorimetric response makes this nanosensor highly applicable for use in refineries, fuel storage facilities, and remote field operations.

For future work, it is recommended to further develop this sensor into a portable detection kit that can be integrated with digital systems for automated and remote mercury monitoring. Moreover, scaling the synthesis of AgNPs@BS for large-volume applications and testing under different environmental conditions will enhance its industrial adoption.

In summary, the integration of green nanotechnology with petroleum engineering as presented in this study supports the global move toward sustainable and efficient resource management. This work opens pathways for further interdisciplinary collaboration to address pressing challenges in environmental safety and industrial reliability.

1. AAS : Atomic Absorption Spectroscopy – A technique used to measure element concentrations based on the absorption of light by free atoms in the gas phase.

2. ICP : Inductively Coupled Plasma – An advanced analytical technique that uses high-temperature plasma to detect and quantify multiple elements simultaneously.

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