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# Detection of Malathion in *Ipomoea aquatica* Using a Plasmonic Sensor Based on Ag-Modified Gold Nanobipyramids

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***Abstract.*** *Malathion is an organophosphate pesticide commonly used in agriculture to protect various crops, including Ipomea aquatica. I. aquatica is a widely consumed vegetable that is vulnerable to pests, such as caterpillars, which damage its leaves. Malathion is an insecticide effective against caterpillars on Ipomoea aquatica without affecting its internal tissues. However, excessive use of this pesticide may leave residues that pose risks to the environment and human health. This study aims to develop a plasmonic sensor based on silver-modified gold nanobipyramids (Ag-GNBPs) for malathion detection. This plasmonic sensor employs anisotropic gold nanomaterials, specifically silver-coated gold nanobipyramids, to enhance localized surface plasmon resonance (LSPR) and improve detection sensitivity. Silver is used due to its high electrical conductivity and responsiveness to electrical and light stimuli. Ag-GNBPs were synthesized using the seed-mediated growth method, and their optical, structural, and morphological properties were characterized via UV-Vis spectroscopy, XRD, and FESEM. The UV-Vis absorption spectrum exhibited transverse (T-SPR) and longitudinal (L-SPR) surface plasmon resonance peaks at 500-600 nm and 700-900 nm, respectively. Testing involved adding the analyte to the solution and analyzing LSPR spectrum changes via UV-Vis spectroscopy. The observed LSPR peak shifts correlated with malathion concentration, with enhanced sensitivity due to silver modification. The results demonstrated that the plasmonic sensor based on silver-modified gold nanobipyramids not only detected malathion with high accuracy but also exhibited high sensitivity at low concentrations, which is essential for environmental monitoring and food safety applications. The optimal growth time for the seed-mediated growth method was 2 hours.*
***Keywords:*** *GNBPs; Ag-modified GNBPs; malathion; Ipomea aquatica; LSPR.*

**Type of the Paper:** Regular Article.

## 1. Introduction

Gold nanobipyramids possess unique plasmonic properties that are highly effective for various sensing applications, particularly in detecting environmental contaminants [1]. Silver modification enhances their optical properties, making them well-suited for localized surface plasmon resonance (LSPR) applications [2]. The synthesis and characterization of these nanobipyramids enable the customization of their plasmonic properties for specific sensing applications, such as pesticide detection [3]. Gold nanobipyramids, like other nanostructures, offer



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enhanced sensitivity in detecting chemical agents due to their large surface area and strong plasmonic effects [4]. Ongoing research on silver-modified gold nanobipyramids underscores their significant potential for developing more sensitive and efficient sensors [5].

With rising global living standards, food safety has become an increasing concern [6]. Agricultural chemicals, particularly pesticides, are widely used to protect crops and seeds before and after harvest. However, even at low concentrations, pesticide residues pose significant health risks to humans [7]. Although pesticides are essential for enhancing agricultural productivity, they also raise concerns regarding food safety, ecological damage, and adverse human health effects [8]. Thus, testing food, particularly fruits and vegetables, for harmful pesticide residues before consumption is crucial [9]. Even low-dose pesticide exposure can cause immediate side effects, including headaches, rashes, dizziness, and nausea, as well as long-term health effects such as cancer, multi-system toxicity, reproductive issues, and metabolic system disruption [10].

Malathion, a widely used organophosphate insecticide, is crucial for controlling agricultural pests and enhancing crop yields [11]. However, improper use can lead to environmental accumulation, posing risks to both ecosystems and human health [12]. This underscores the urgent need for accurate and sensitive detection techniques to ensure malathion levels remain within safe limits [13]. Monitoring pesticide residues, particularly malathion, is essential not only for human health but also for preserving biodiversity and maintaining ecosystem integrity [14]. Excessive malathion use can induce pest resistance, necessitating higher doses and more frequent applications, thereby exacerbating environmental contamination [15]. Numerous studies highlight the need for efficient detection methods to identify pesticide residues in agricultural products and ensure food safety [16].

Conventional methods for detecting pesticide residues, such as gas chromatography (GC) and high-performance liquid chromatography (HPLC), are often complex and time-consuming [17]. These techniques require extensive sample preparation and may lack the sensitivity needed to detect contaminants at low concentrations, which is crucial for food safety [18]. Consequently, many harmful substances may go undetected, posing health risks to consumers. Plasmonic sensor technology presents a promising alternative for detecting chemical contaminants, particularly pesticide residues [19]. These sensors leverage the surface plasmon resonance (SPR) effect, where light interacts with conductive nanomaterials such as gold and silver [20]. This resonance greatly amplifies the electromagnetic field at the nanomaterial surface, enabling the sensitive detection of specific compounds through spectral changes [21]. Silver-modified gold nanobipyramids exhibit strong plasmonic resonance properties, substantially enhancing detection sensitivity [22]. Their distinctive shape increases surface area and enhances optical properties, making them highly effective for detecting low concentrations of pesticides such as malathion [23]. Recent studies indicate that plasmonic sensors can achieve detection limits in the nanomolar range, which is crucial for identifying hazardous pesticide residues that conventional methods may overlook [24]. Additionally, their rapid response time and simplicity make them well-suited for real-time monitoring in agricultural settings [6].

This study aims to develop and optimize a plasmonic sensor based on silver-modified gold nanobipyramids for detecting malathion in *Ipomoea aquatica*. The primary objective is to design a sensor with enhanced specificity, sensitivity, and efficiency by leveraging plasmonic spectral shifts induced by malathion interaction with gold nanobipyramids. This method is expected to significantly advance pesticide detection technology and enhance the understanding of nanomaterial applications in environmental monitoring. Additionally, this study aims to provide a more reliable malathion detection method while contributing to the broader development of plasmonic sensor technology. By improving detection and monitoring capabilities, this study contributes to environmental safety and public health while establishing a foundation for the future development of similar technologies.

## 2. Materials and Methods

### *2.1. Materials*

The materials used for the synthesis of silver-modified gold nanopyramids (Ag-GNBPs) include gold (III) chloride hydrate ($HAuCl_4{:}3H_2O$, ≥99.9%), chloroplatinic acid ($H_2PtCl_4.H_2O$, ≥ 99.9%), cetyltrimethylammonium bromide (CTAB, ≥98.0%), sodium borohydride ($NaBH_4$, ≥98.0%), and ascorbic acid ($C_6H_8O_6$), all of which were purchased from Sigma-Aldrich, USA. Additionally, silver nitrate ($AgNO_3$ ≥99.9%) was obtained from Honeywell, USA and hydrogen chloride (HCl) was sourced from RCI Labscan, Thailand.

### *2.2. Synthesis*

The synthesis of these anisotropic nanomaterials employs the Seed-Mediated Growth (SMG) method, which consists of two main steps: seeding and growth. In the seeding process, small nanoparticles (seeds) are synthesized, typically through a reduction method [25], serving as nucleation sites for the formation of larger nanostructures [26]. The seeding process is conducted by mixing 0.15 mL of gold (III) chloride acid ($HAuCl_4{:}3H_2O$) 0.01 M and 0.1 mL of chloroplatinic acid ($H_2PtCt_4$) 0.01 M into 20 mL of cetyltrimethylammonium bromide (CTAB) 0.1 M, followed by gentle shaking until the solution is thoroughly mixed. Subsequently, 0.9 mL of sodium borohydride ($NaBH_4$) 0.01 M, pre-cooled on ice, is added to the solution and gently shaken. The seeding process is conducted for 2 hours at room temperature.

During the growth process, the seed nanoparticles are expanded into larger or more complex structures by the addition of metal ions or other precursors, which undergo reduction and subsequent deposition onto the seeds. The growth process is conducted by sequentially adding 0.875 mL of gold (III) chloride acid ($HAuCl_4$:$3H_2O$) 0.01 M, 0.025 mL of chloroplatinic acid ($H_2PtCl_4$) 0.01 M, 0.225 mL of silver nitrate ($AgNO_3$) 0.01 M, 20 mL of CTAB 0.1 M, 0.4 mL of hydrochloric acid (HCl) 1 M, and 0.16 mL of ascorbic acid ($C_6H_8O_6$) 0.1 M. The solution is then gently shaken before adding 0.05 mL of the previously prepared seed solution. The mixture is left undisturbed for different durations of 0.5 hours, 1 hour, 2 hours, and 3 hours.

### *2.3. Characterization*

The samples were characterized using three techniques: FESEM, UV-Vis spectroscopy, and XRD. FESEM was employed to analyze the morphology of the gold nanomaterials [27]. The FESEM system used in this study was a Schottky JSM-7600F (Jeol, Japan) with a magnification of 100,000x. The optical spectrum was analyzed using UV-Vis spectroscopy [28] with a Shimadzu UV-1800 spectrophotometer, covering a wavelength range of 200-100 nm. XRD analysis was performed to determine the phase and crystallinity of the gold nanomaterials, utilizing Eva Diffrac Plus Evaluation software (version 10.00.3) within the 2θ range of 30°–60° [29].

### *2.4. Preparation of target analyte*

The target analyte was prepared by applying malathion to 3-week-old *Ipomoea aquatica* leaves. A 2.5 mL volume of malathion was dissolved in 500 mL of distilled water to create the insecticide solution. After application and an exposure period, the water spinach was harvested and rinsed to assess residual insecticide levels. The rinsing process was performed twice: the first rinse resulted in a malathion concentration of 11 ppm, while the second rinse reduced it to 2 ppm. This suggests that the second rinse provides optimal removal of residual malathion.

### *2.5. LSPR sensor testing*

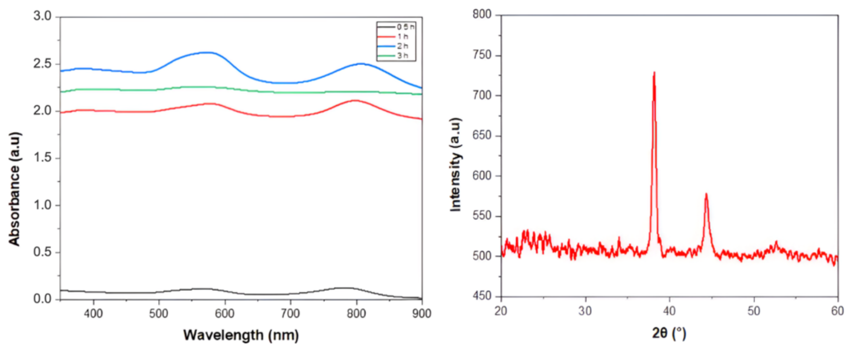
After a 3-hour growth period, the GNBPs were ready to be used as sensing materials in LSPR sensors. The sensor testing was conducted using a custom-designed setup comprising four main components: a light source, a cuvette holder, a spectrometer, and a computer equipped with Ocean View software. The GNBP-based sensor was then tested with the prepared analytes. During testing, the sensor is placed in a testing cell and exposed to light with wavelengths ranging from 450 to 750 nm. The spectral response is monitored by measuring changes in absorption or scattering intensity at specific wavelengths, which indicate interactions between the analyte and the nanoparticle surface [30]. The observed spectral shifts indicate the analyte's affinity and concentration, as well as the sensor's effectiveness in detecting environmental changes [28]. Data analysis from these tests evaluates the sensor's performance, including sensitivity, repeatability, and stability under various conditions, and assesses the practical application of GNBPs as sensing materials in LSPR systems [31].

## 3. Results and Discussion

### *3.1. Optical and structural properties*

The optical and structural properties of a material are crucial for its performance, particularly in plasmonic sensors. Optical properties define how the material interacts with light, including absorption, reflection, and scattering. Optical characterization of silver-coated gold nanobipyramids (Ag-GNBPs) using UV-Vis spectroscopy reveals localized surface plasmon resonance (LSPR), with absorption peaks at ~500-600 nm (transverse) and ~700-900 nm (longitudinal), consistent with previous studies that reported similar LSPR peaks for silver-coated gold nanoparticles.

Structural properties refer to the atomic arrangement, and particle morphology. In this study, X-ray diffraction (XRD) is used to analyze the crystal structure of Ag-GNBPs. XRD analysis showed diffraction peaks at 38.46° and 44.01°, corresponding to the (111) and (200) crystal planes, consistent with Nafisah et al. [6]. Additionally, field emission scanning electron microscopy (FESEM) was used to examine the morphology of the particles, including their dimensions, shape, and distribution. These optical and structural properties collectively influence the sensor's performance in detecting target molecules, such as malathion, through changes in the LSPR spectrum.




(a) (b)

**Fig. 1.** (a) UV-Vis absorption spectrum of Ag-GNBPs sample with growth time variation (b) XRD Spectrum

Fig. 1 (a) displays a graph of light intensity distribution as a function of wavelength. The variation parameters for Ag-Modified gold nanobipyramids include different growth durations: 30 minutes (0.5 hours), 1 hour, 2 hours, and 3 hours. The graph shows peaks within the 500-900 nm wavelength range, indicating plasmonic resonance. The curve corresponding to the 2-hour growth duration (blue line) exhibits the highest intensity, suggesting optimal plasmonic interaction under these conditions. As the growth duration increases, the spectral intensity rises, reaching its peak at 2 hours. However, at 3 hours (green line), the intensity slightly decreases, suggesting that the optimal condition is achieved at 2 hours. The decrease in intensity after 2 hours results from the increasing density of gold nanoparticles, which disrupts bipyramidal structures formation and induces a shift when the growth time exceeds 2 hours. This also alters the sample's size and morphology, making it larger. Resonance peaks appear in the 500–600 nm (transversal) and 700–900 nm (longitudinal) wavelength ranges, with slight shifts in different curves, indicating variations in the material's optical properties with changing growth times.

Graph (b) presents an X-ray diffraction (XRD) pattern, essential for examining the material's crystalline structure. The X-axis represents the 2θ angle (20°-60°), while the Y-axis shows the diffracted X-rays intensity in arbitrary units (a.u.). A notable peak near 2θ = 38° suggests a specific crystalline phase, likely corresponding to the (111) plane of gold (Au), a characteristic feature of gold nanomaterials. The peak's clarity and intensity indicate a well-organized crystalline structure, confirming the successful synthesis of gold nanobipyramids. Secondary peaks around 44° and 64° further support the crystalline nature of the sample, suggesting the formation of various crystallographic planes.

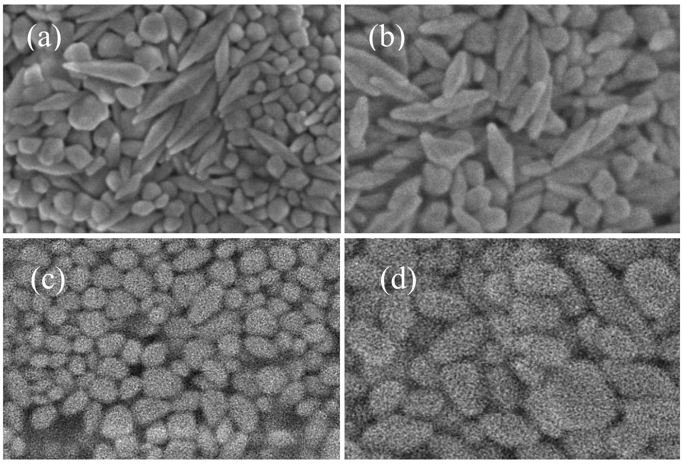



**Fig. 2.** Morphology FESEM of A-GNBPs (a) 0.5 hour (b) 1 hour (c) 2 hours (c) 3 hours

Field Emission Scanning Electron Microscopy (FESEM) analysis at 100,000 x magnification reveals that the synthesized nanoparticles predominantly exhibit well-defined bipyramidal shapes, consistent with the intended design. High-resolution FESEM images, particularly in Fig. 2 (a) and (b), confirm that most nanoparticles exhibit well-defined bipyramidal morphology with clear edges and facets, indicating the successful synthesis. Fig. 2 (c) still displays bipyramidal shapes, though fewer in number. Meanwhile, Fig. 2 (d) reveals a decline in the desired bipyramidal morphology. However, a small fraction of nanoparticles shows variations in shape and size, indicating minor imperfections in the synthesis or modification process. While these imperfections are not significant, they may affect the optical properties and performance of the LSPR sensor, highlighting the need for further optimization to improve material consistency and quality. These findings affirm the overall effectiveness while providing important insights for refining the process to achieve more uniform and optimal results for sensor applications.

The study by Abdul-Moqueet et al. [32], published in the journal *Nanotechnology*, discusses the synthesis of bipyramidal gold nanoparticles and highlights that well-defined bipyramidal shapes are crucial for applications such as biosensing and Surface-Enhanced Raman Spectroscopy (SERS). They also noted that deviations in shape and size can affect the optical characteristics of the nanoparticles. Compared to these studies, our research emphasizes the need to achieve a uniform bipyramidal morphology to enhance the performance of LSPR sensors. The morphological inconsistencies observed in the synthesized nanoparticles indicate that refining the synthesis parameters is essential to minimize variations in shape and size. This optimization is crucial, as even minor deviations can alter the optical response of the nanoparticles, thereby affecting the sensor's accuracy and reliability.

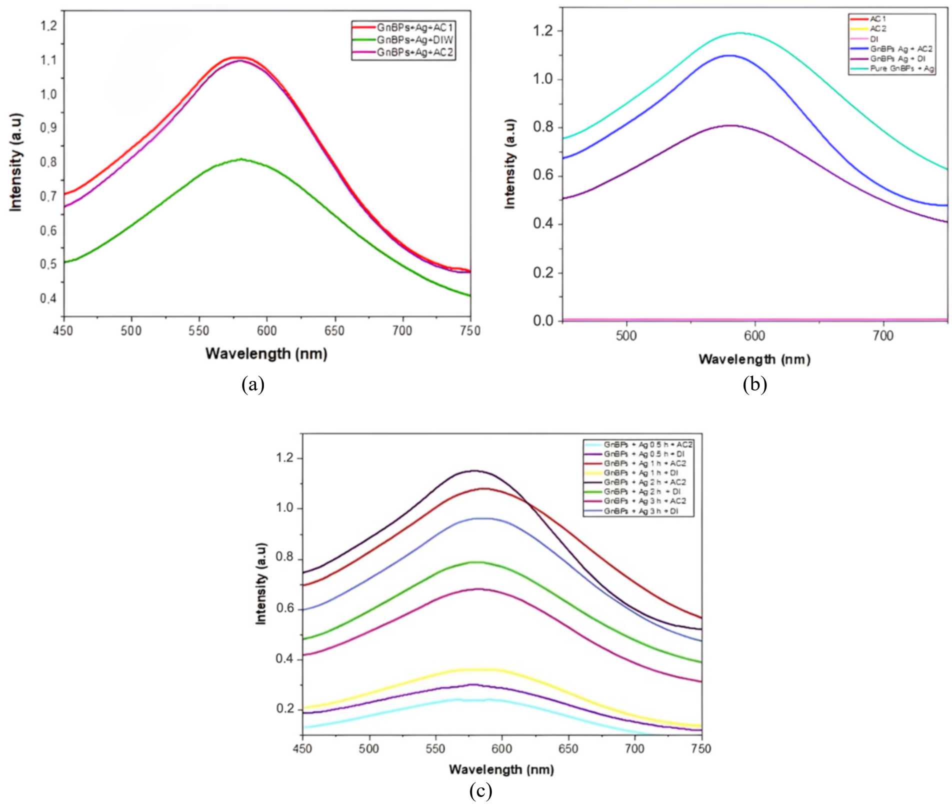



**Fig. 3.** Sensitivity Ag-GNBPs (a) Effect Concentration (b) Plasmonic Response (c) Effect Growth Time.

### *3.2. Sensor testing*

In sensor evaluation, three main aspects are typically tested: sensitivity, stability, and repeatability. Sensitivity measures the sensor's ability to detect small changes in analyte concentration by assessing variations in the analytical signal. Stability measures the consistency over time and under various conditions, ensuring reliable results despite environmental changes. Repeatability measures result consistency when tests are repeated under identical conditions, reflecting the sensor's accuracy and reliability in practical applications. Evaluating these three aspects is crucial to ensure that the sensor meets the required performance standards for its intended use. The following figure illustrates the three main aspects of sensor testing: sensitivity, stability, and repeatability. Sensitivity indicates how well the sensor can detect small changes in the concentration of the target analyte, assessing its ability to respond to variations in the analytical signal. Stability measures the consistency of the sensor's performance over time and under various conditions, ensuring reliable results despite environmental changes. Meanwhile, repeatability assesses how consistent the results are when the test is repeated under the same conditions, reflecting the sensor's accuracy and reliability in practical applications. Evaluating these three aspects is crucial to ensure that the sensor meets the performance standards required for its intended use. The following figure illustrates the three main aspects of sensor testing.

Fig. 3 (a) presents the absorbance spectra of three GNBPs samples: AC1, AC2, and DI. All three samples exhibit two main peaks around 450-700 nm range, corresponding to the localized surface plasmon resonance (LSPR) of silver-modified gold nanobipyramids (Ag-GNBPs). Absorbance intensity is highest in Ag-GNBPs+AC2, showing the highest absorbance (~1.1), followed by Ag-GNBPs+AC1 (~1.05), and Ag-GNBPs+DI has the lowest absorbance (~0.75). This indicates that increasing the concentration of AC enhances plasmonic sensitivity, with AC2 showing a 4.76% increase over AC1 and a 46.67% increase over DI, without affecting nanoparticle size or shape stability.

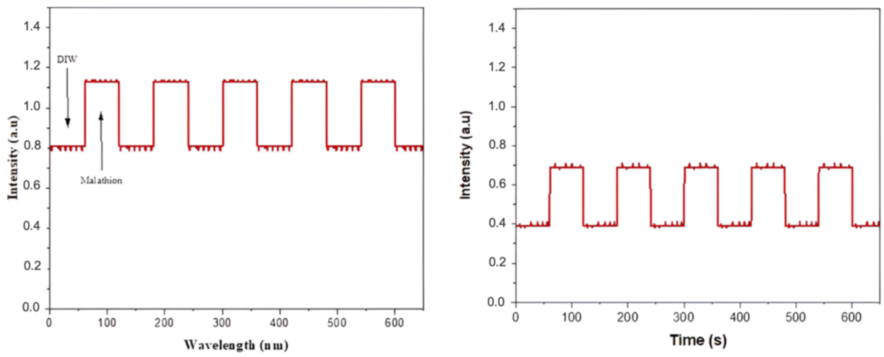
Fig. 3 (b) illustrates the Plasmonic Response of the silver-modified gold nanobipyramids (Ag-GNBPs), exhibiting the highest intensity when tested in deionized (DI) water, with a peak around 500-700 nm, indicating strong plasmonic interaction. The AC2 medium also produces a fairly good response, although slightly lower than DI, while AC1 shows minimal change, indicating weak interaction. Pure Ag-GNBPs exhibit lower intensity compared to GNBPs in DI or AC2 but maintain a peak at the same wavelength, confirming surface resonance even without an additional medium. The analytes AC1 and AC2 alone show no significant plasmonic response, confirming that interaction occurs only in the presence of metal nanoparticles. Overall, the graph demonstrates the medium's significant effects on plasmonic intensity, with DI being the most optimal medium for generating the highest response, a crucial factor in plasmonic sensor applications.

Fig. 3 (c) illustrates the effect of growth time on the plasmonic intensity of Ag-GNBPs, showing an increase with longer growth durations, peaking at 2 hours within the 500-700 nm range. This indicates that at this duration, the nanoparticles reach an ideal size and shape for maximum plasmonic resonance. At shorter times (0.5 and 1 hour), lower intensity indicates incomplete nanoparticles formation. However, extending the growth time to 3 and 4 hours results in decreased intensity, likely due to morphological changes that reduce plasmonic resonance efficiency. Thus, 2 hours is identified as the most ideal growth duration.

The repeatability analysis ensures consistency in the plasmonic response between samples rinsed with and without malathion. Each sample underwent five rinsing and testing cycles, with a 60-second interval between measurements. The results were analyzed to determine the sensor's reliability and reproducibility. Consistent readings across all repetitions, as shown in Fig. 4 (a) and (b), confirm the sensor's ability to distinguish the presence of malathion. This repeatability is crucial for validating the sensor's effectiveness and accuracy in practical applications, demonstrating its reliability under repeated testing conditions. By comparing with previous studies, the evaluation of sensitivity, stability, and repeatability remains the primary focus in modern sensor development. Differences may lie in the type of sensor, the analyte being detected, and the data analysis methods used. However, the fundamental principles for ensuring reliable and accurate sensor performance remain consistent.

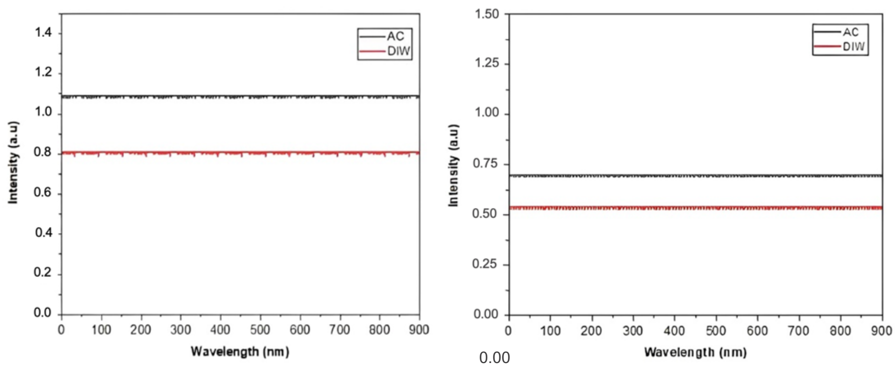
0.2

0.0




(a) (b)

**Fig. 4.** Repeatability Ag-GNBPs (a) t-SPR Ag-GNBP (b) l-SPR Ag-GNBP




(a) (b)

**Fig. 5.** Stability Ag-GNBPs (a) t-SPR Ag-GNBP (b) l-SPR Ag-GNBP

Fig. 5 (a) and (b) shows the stability test of the Ag-Modified GNBP sample at the t-SPR and l-SPR peaks, evaluating the stability of the sensor's plasmonic response. This test is important to ensure that the sensor provides consistent results at the relevant peak wavelengths, 559.753 nm for t-SPR and 875.273 nm for l-SPR, under identical environmental conditions. The results confirm that the sensor maintains its effectiveness in detecting plasmonic changes over time performance degradation, which is crucial for practical applications, particularly in repeated detection of pesticides such as malathion. The repeatability analysis in this study demonstrates the consistency of the plasmonic response between samples rinsed with and without malathion, through five rinsing and testing cycles with a 60-second interval between measurements. These results confirm the sensor's ability to repeatedly detect the presence of malathion, which is crucial for validating its effectiveness and accuracy in practical applications.

These findings align with research published in *Bioelectrochemistry* by Aghoutane et al. [33], where an electrochemical sensor based on molecularly imprinted polymer (MIP) was developed to detect malathion in fruits and olive oil. That study assessed the repeatability and operational stability of the sensor, finding that it had a dynamic concentration range between 0.1 pg $mL^{-1}$ and 1000 pg $mL^{-1}$, with a low detection limit of 0.06 pg $mL^{-1}$. Additionally, the sensor demonstrated a recovery rate of 87.9% with a relative standard deviation of 8% for malathion detection in olive oil samples, confirming its reliability and consistency in practical applications.

Furthermore, research by Iwantono et al. [3] in *Trends in Sciences* reported the development of a plasmonic sensor based on gold nanobipyramids (AuNBPs) for detecting malathion in lettuce. This sensor exhibited increased sensitivity to malathion, as indicated by an enhancement in signal corresponding to residue concentration. The intensity of AuNBPs in the presence of malathion significantly increased compared to deionized water, demonstrating a strong and effective response to malathion residue detection. Overall, the results of this study are consistent with previous findings, confirming that the plasmonic sensor based on Ag-GNBPs exhibits high repeatability and can reliably detect malathion under various testing conditions. This highlights the sensor's great potential for practical applications in detecting pesticide residues, particularly malathion, in agricultural products and environmental samples.

## 4. Conclusions

This study successfully developed a plasmonic sensor utilizing silver-modified gold nanobipyramids (Ag-GNBP) to detect malathion, a widely used organophosphate pesticide. By synthesizing and characterizing gold nanobipyramids and modifying their surface with silver, the sensor demonstrated enhanced sensitivity and specificity in identifying low levels of malathion. Experimental results confirmed a significant optical response, as indicated by shifts in the localized surface plasmon resonance (LSPR) wavelength. Additionally, the sensor effectively detected malathion residues on *Ipomoea aquatica*, demonstrating its potential for practical pesticide detection applications.

The results indicated that malathion residues on *Ipomoea aquatica* require multiple washes for significant reduction. The sensitivity of Ag-GNBPs+AC2 (after two washes) increased by 4.76% compared to AC1 and a 46.67% compared to DI (distilled water), highlighting the persistence of malathion and the importance of thorough washing practices for pesticide-exposed vegetables. Detection using silver-modified gold nanobipyramids yielded more accurate results than distilled water, demonstrating the sensor's high sensitivity in detecting malathion residues. Repeatability tests showed the consistency of the tested samples over five cycles within a 60-

second duration. Stability tests demonstrated consistent results at the relevant peak wavelengths, 559.753 nm for t-SPR and 875.273 nm for l-SPR. However, this study has certain limitations, such as the absence of Energy Dispersive X-ray Spectroscopy (EDX) characterization, which limits information regarding the elemental composition of *Ipomoea aquatica*. Additionally, the effect of varying malathion concentrations was not examined. Future research should explore the application of gold nanobipyramids to different plant species and insecticides while incorporating more comprehensive characterizations.

## Abbreviations

| | |
|---|---|
| AC | Air Cucian |
| DIW | Deionized Water |
| FESEM | Field Emission Scanning Electron Microscopy |
| EDX | Energy Dispersive X-ray |
| UV-Vis | Ultraviolet Visible |
| T-SPR | Transversal Surface Plasmon Resonance |
| L-SPR | Longitudinal Surface Plasmon Resonance |
| XRD | X-ray Diffraction |
| PPM | Parts per Minutes |

## Data availability statement

All crop images are publicly available via the following link: (https://docs.google.com/document/d/1xeGaWVYP15zu2TDs4j781unq29WKWDDN/edit?usp=sharing&ouid=117641264646910336383&rtpof=true&sd=true). We also glad to provide reasonable help involving our original images and data if the corresponding author is contacted.

## CRediT authorship contribution statement

**Iwantono**: Conceptualization, Methodology, Resources, Formal analysis, Investigation, Data curation, Funding acquisition & Writing. **Marlia Morsin**: Writing, Validation, Data curation, Formal analysis, Conceptualization. **Ananda Febri Yudani**: Conceptualization, Supervision, Data curation, Writing – original draft. **Hidayati Syajali**: Editing. **Friska Ziliwu**: Project administration, Writing & Editing. **Norsinta Ida Simbolon**: Editing. **Suratun Nafisah**: Data curation, Funding acquisition & Writing. **Mayta Novaliza Isda**: Writing & Editing. **Tengku Emrinaldi**: Writing & Editing.

## Declaration of Competing Interest

The authors declare no competing interests or the authors of this manuscript declare no conflict of interest or competing interest.

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