

Research Article

Eco-Friendly Au@Al-MOF Nanocomposites Fabricated with *Eleutherine bulbosa* Extract for Mercury Detection in Cosmetic Product

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Abstract

Mercury (Hg^{2+}) contamination in cosmetics, particularly skin whitening products, poses significant public health risks due to its well-documented toxicity and bioaccumulative nature. This study reports the development of an environmentally benign colorimetric sensor for Hg^{2+} detection by incorporating gold nanoparticles (AuNPs) within aluminum-based metal-organic frameworks (Al-MOF), utilizing *Eleutherine bulbosa* extract as a green reducing agent. Extensive characterization (XRD, FTIR, TGA, TEM, SEM, FESEM) verified successful AuNPs incorporation (average diameter 25.96 nm) while maintaining MOF structural integrity. Spectrophotometric analysis revealed a distinct red shift in surface plasmon resonance from 541 nm (pristine AuNPs) to 548 nm (Au@Al-MOF), confirming strong interactions between the AuNPs and the MOF framework. The sensor exhibited exceptional Hg^{2+} selectivity with minimal cross-reactivity to interfering metal ions, achieving a 3.46 ppm detection limit and 54-day stability. Validation studies using commercial skin whitening creams demonstrated excellent correlation between the UV-Vis method (4.53 ppm Hg^{2+}) and atomic absorption spectroscopy (4.59 ppm), with 98.7% agreement ($\pm 1.3\%$ variance), confirming method reliability. These findings establish Au@Al-MOF as a robust, sensitive, cost-effective colorimetric platform for Hg^{2+} detection. The technology holds significant potential for integration into other heavy metal detection systems and portable devices, addressing critical needs in cosmetic safety, environmental monitoring, and food quality control.

Keywords: Au@Al-MOF nanocomposite, Colorimetric sensor, Cosmetic, *Eleutherine bulbosa*, Gold nanoparticles, Mercury detection, Metal-organic frameworks

1 Introduction

Mercury (Hg^{2+}) contaminants, such as mercuric chloride (HgCl_2), mercurous chloride (Hg_2Cl_2), and mercuric ammonium chloride ($\text{Hg}(\text{NH}_2)\text{Cl}$), are frequently found in cosmetics, particularly in skin whitening creams [1]. These compounds can

temporarily lighten the skin by increasing melanin production through melanogenesis [2], [3]. However, prolonged use can accumulate Hg^{2+} in the body, causing significant harm [2]. These symptoms include weakening the immune system, triggering carcinogenic effects, and causing skin issues such as irritation, allergic reactions, blemishes, and dark scars.



Additionally, Hg^{2+} exposure can reduce the skin's resistance to bacterial and fungal infections. During pregnancy, Hg^{2+} exposure can impair fetal development [4]. Long-term skin exposure to mercury may also result in severe neurological disorders, including movement and speech impairments, hearing loss, narrowed vision, paralysis, and even death [5]. To mitigate these risks, regulatory agencies such as Indonesia's Food and Drug Administration (BPOM) and the U.S. Food and Drug Administration (FDA) have established safe limits for Hg^{2+} in cosmetics, particularly in whitening creams, at $1000 \mu\text{g g}^{-1}$ and 1 ppm, respectively [3].

Given these health risks, there is a critical need for sensitive, specific, and reliable methods to detect Hg^{2+} in cosmetic products. Conventional techniques, including electrochemistry [6], atomic absorption spectrometry (AAS) [7], atomic fluorescence spectrometry (AFS), inductively coupled plasma mass spectrometry (ICP-MS) [8], direct mercury analysis [9], high-performance liquid chromatography (HPLC) [10], enzyme-linked immunosorbent assay (ELISA) [11], and X-ray fluorescence spectroscopy [12], have been widely employed [2]. However, these methods often face limited sensitivity, reliance on expensive and complex equipment, and time-consuming sample preparation [5], [13]. These drawbacks hinder their use for rapid and in-situ analysis, which is crucial for real-time detection in field settings. To address these issues, colorimetric detection using plasmonic nanoparticles has gained significant attention.

Among these, gold nanoparticles (AuNPs) are particularly appealing for colorimetric detection because they have a high surface volume ratio and selectivity [14]–[16]. AuNPs have gained significant attention for their ability to produce visible color changes detectable by the naked eye based on their localized surface plasmon resonance (LSPR) [13], [17]. These peaks' intensity and position are influenced by particle size, shape, inter-particle distance, and the surrounding dielectric environment [17]. Even minor changes in these parameters can shift the LSPR peak and alter the color of the AuNPs colloidal solution [7]. This unique property enables AuNPs-based colorimetric sensors ideal for colorimetric sensors in detecting heavy metals, including Hg^{2+} in complex matrices [16].

AuNPs can be synthesized using bioreduction derived from plant extracts, which serve as reducing and stabilizing agents [18], [19]. Plants are abundant, and renewable sources can be considered sustainable

for synthesizing AuNPs [20]. Its bioactive compounds, such as alkaloids, flavonoids, and phenolic acids in plant extracts, aid in reducing and stabilizing the nanoparticles, offering a simple and cost-effective synthesis method [21], [22]. For instance, *Eleutherine bulbosa*, known for its anti-inflammatory, antioxidant, and antimicrobial properties, contains bioactive compounds that could be utilized in AuNPs synthesis. However, its application in nanotechnology, particularly for AuNP synthesis, remains underexplored in the literature [23].

Despite the advantages of using AuNPs for colorimetric sensing, one limitation is their tendency to agglomerate, resulting in larger particle sizes. To overcome this, embedding AuNPs within a rigid, hierarchical structure such as metal-organic frameworks (MOFs) can reduce agglomeration. MOFs are porous coordination polymers with mesoporous and hierarchical properties, making them suitable for distributing metal nanoparticles. They also enhance mechanical properties, electrical performance, and biocompatibility [7]. MOFs can be easily modified to stabilize chromogenic reactions through interactions between chromophore groups on organic ligands and metal ions in the MOF framework [24]–[26].

Moreover, MOFs improve detection sensitivity through their porosity, metal active sites, and Lewis acid-base sites, while their uniform and regular pore size enhances selectivity for target analytes [27]. However, some MOFs synthesized using divalent metal ions like Zn^{2+} , Cu^{2+} , and Co^{2+} lack chemical and hydrothermal stability [28]. Metals such as cadmium and nickel also pose environmental risks [29]. In contrast, aluminum-based frameworks offer superior stability, environmental compatibility, and cost-effectiveness, rendering them particularly advantageous for practical applications [29]–[31]. Al-MOF can be synthesized using green solvents like water, unlike other MOFs that require toxic organic solvents. They also exhibit excellent thermal, chemical, and mechanical stability, high selectivity, and large adsorption capacity in aquatic systems [31]–[34]. Furthermore, Al-MOF can function as colorimetric sensors with various chromophore organic ligands to detect heavy metal ions in water.

The development of Al-MOF colorimetric sensors for Hg^{2+} detection has been extensively studied through various functionalization strategies. Shahat *et al.*, (2017) employed amino-functionalized Al-MOF (Al-MOF- NH_2), which exhibited enhanced binding affinity toward Hg^{2+} and achieved a detection

limit of 0.494 ppb [35]. Radwan *et al.*, developed Al-MOF functionalized with chromophoric ligands, which exhibited a distinct yellow-to-green color change upon Hg^{2+} complexation, with a detection threshold of 0.8 ppb [33]. El-Fattah *et al.*, further advanced sensor design by modifying Al-MOF-NH₂ with 5-bromo salicylaldehyde, enabling the specific detection of Hg^{2+} , Co^{2+} , and Al^{3+} ions [36]. While these studies demonstrate Al-MOF versatility as sensing platforms, they predominantly focus on ligand coordination and framework modification without investigating the potential advantages of integrating plasmonic nanomaterials.

Incorporating AuNPs into Al-MOF, particularly via environmentally benign synthesis approaches, remains largely unexplored. Specifically, the use of *E. bulbosa* extracts as a biogenic reducing agent for in situ AuNP formation within MOF structures has not been previously reported. This study aims to address this gap by synthesizing Au@Al-MOF nanocomposite through a green route employing *E. bulbosa*, aiming to produce a sustainable colorimetric platform with enhanced optical sensitivity, chemical selectivity, and long-term stability for Hg^{2+} detection in cosmetic products.

The resulting nanocomposite will be comprehensively characterized using X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), Thermogravimetric analysis (TGA), and advanced electron microscopy techniques (TEM, SEM, and FESEM). Analytical performance, including sensitivity, detection limit, interference resistance, and stability, will be evaluated using UV-Vis spectrophotometry. Validation will be conducted on commercial skin-whitening cream samples, with results compared to those obtained via AAS to assess accuracy and real-sample analysis.

2 Materials and Methods

2.1 Reagents and Chemicals

E. bulbosa and cosmetic products were procured from a traditional market in Palangka Raya, Central Kalimantan, Indonesia. Reagents, including HAuCl_4 , ethanol, methanol, nitric acid (HNO_3), aluminum chloride hexahydrate ($\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$), dimethylformamide (DMF), and terephthalic acid (H_2BDC), were sourced from Merck. Standard solutions of metal ions such as Hg^{2+} , Pb^{2+} , Ca^{2+} , Co^{2+} , Cu^{2+} , Cl^{2+} , and Zn^{2+} were also obtained from Merck.

2.2 Synthesis of aluminum-based metal-organic framework (Al-MOF)

To synthesize Al-MOF, 0.51 g of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ and 0.56 g of H_2BDC were dissolved in a solvent mixture of DMF and water (30 mL) while stirring continuously for 30 min. The resulting solution was then subjected to hydrothermal synthesis at 160 °C for 24 h. Following the reaction, the product was filtered and washed three times with methanol to remove impurities. The final Al-MOF was obtained by drying the washed material at 60 °C for 12 h (Figure 1).

2.3 Synthesis of Au@Al-MOF nanocomposites using *E. bulbosa* extract

AuNPs were synthesized by reducing HAuCl_4 using *E. bulbosa* extract as a reductant. Specifically, 40 mL of *E. bulbosa* extract (2000 ppm) was added to 25 mL of a HAuCl_4 solution (300 ppm), and the mixture was stirred until homogeneous. The reaction was then heated in a water bath at 90 °C for 5 min to complete the reduction. The resulting AuNPs were used to prepare Au@Al-MOF nanocomposites. For this, 4 mL of AuNPs was mixed with 2 mL of an Al-MOF solution (1 mg/mL) and stirred for 2 h. The nanocomposite was washed with ethanol and dried at 110 °C overnight, and the final sensor material was obtained (Figure 1).

2.4 Characterization of materials

The synthesized materials were characterized using a variety of analytical techniques. Crystallinity was assessed with an XRD PANalytical EMPYREAN X-ray diffractometer, operating in the 2θ range of 5–50° with $\text{Cu-K}\alpha$ radiation ($\lambda = 1.540593 \text{ \AA}$). The functional groups of the materials were identified using a Bruker Tensor II FTIR spectrometer equipped with the attenuated total reflectance (ATR) method, covering a spectral range of 4000–300 cm^{-1} . Ultraviolet-visible (UV-Vis) spectra were recorded on a Shimadzu S-600 spectrophotometer within the 400–800 nm wavelength range. Nanoparticle size distribution was analyzed using HR-TEM (Hitachi H-9500) at varying magnifications, and particle size was determined via image processing software (ImageJ). Morphological analysis was performed using field emission scanning electron microscopes (FESEM Apreo 2S and SEM SU3500). Thermogravimetric analysis (TGA) was conducted on a TG/DTA Hitachi

STA7300, with a temperature range of 20–500 °C and a heating rate of 20 °C/min under a nitrogen atmosphere.

2.5 Colorimetric detection of Mercury (Hg^{2+})

The colorimetric detection of Hg^{2+} was performed using 1 mL of the prepared Au@Al-MOF solution. Various metal ions were introduced into the Au@Al-MOF solution containing Hg^{2+} to evaluate potential interference. Specifically, 1.5 mL of the Au@Al-MOF solution was mixed with 0.5 mL of 50 ppm Hg^{2+} and 0.5 mL of 50 ppm solutions of other metal ions, including Ca^{2+} , Ni^{2+} , Co^{2+} , Zn^{2+} , Cu^{2+} , Pb^{2+} , and Mn^{2+} . For analysis, the Au@Al-MOF solution was combined with Hg^{2+} ions at varying concentrations

(0.0001 to 0.05 mM), and the mixtures were analyzed using a UV-Vis spectrophotometer. Absorption intensity at the characteristic peaks was plotted against Hg^{2+} concentration to assess sensor performance.

2.6 Mercury (Hg^{2+}) detection in cosmetic products

A 0.1 g sample of the cosmetic product was treated with 1 M nitric acid and heated to 80 °C. The resulting solution was then filtered and diluted to a final volume of 100 mL. Subsequently, 1 mL of the solution was mixed with 1.5 mL of Au@Al-MOF, stirred for 5 s, and analyzed visually. The mixtures were then examined using a UV-Vis spectrophotometer, with a wavelength range between 400 and 800 nm.

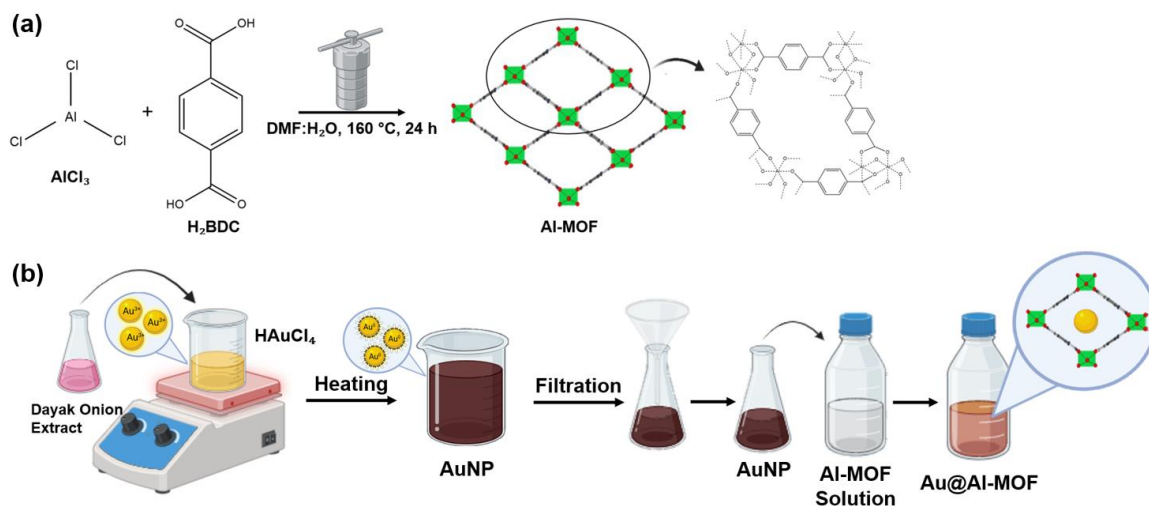


Figure 1: Schematic representation of (a) the synthesis of Al-MOF and (b) the preparation of Au@Al-MOF nanocomposites using *Eleutherine bulbosa* extract.

3 Results and Discussions

3.1 Characterization of Au@Al-MOF

The synthesis of AuNPs was performed using the Turkevich method, which produces nanoparticles with a small diameter ranging from 10 to 30 nm [37]. This process involved adding *E. bulbosa* extract as a reducing agent to gold salts in the $HAuCl_4$ precursor, where the Au^{3+} ions (in a brownish-yellow oxidation state) were reduced to Au^0 , forming the AuNPs core. These AuNPs were then combined with Al-MOF to fabricate Au@Al-MOF nanocomposites. The characterization of the Au@Al-MOF nanocomposites was carried out using several analytical techniques,

including XRD, FTIR, TGA, and various electron microscopy methods (TEM, SEM, and FESEM).

The XRD patterns for AuNPs, Al-MOF, and Au@Al-MOF are presented in Figure 2. The AuNPs display characteristic peaks corresponding to the face-centered cubic (FCC) structure of gold, with prominent peaks at 38.4°, 44.4°, 64.7°, 77.6°, and 81.7°, aligning with the (111), (200), (220), (311), and (222) planes. These peaks confirm the crystalline purity of the AuNPs, in agreement with JCPDS data (NO: 00-004-0784) [38]. The broadening of peaks, particularly for the (111) plane, indicates the nanoscale size of AuNPs [39].

The XRD pattern of the synthesized Al-MOF exhibits high crystallinity, with characteristic peaks at

9.3°, 10.13°, 12.56°, 14.86°, 17.8°, 25.24°, and 28.33°, corresponding to the (101), (200), (110), (011), (202), (220), and (002) planes. These peaks are in agreement with those reported in the literature and indicate the presence of multiple phases, including large-pore, narrow-pore, and as-synthesized forms (CCDC: 220476 and CCDC: 220477) [40]–[42]. Furthermore, the diffraction peaks of Au@Al-MOF show contributions from both Al-MOF and AuNPs. The broad peaks of the Al-MOF framework remain prominent. In contrast, the distinct peaks of AuNPs, especially the (111) plane at 38.2°, are visible, indicating the successful incorporation of AuNPs into the Al-MOF structure. The coexistence of both phases highlights the retention of the MOF framework along with the crystalline properties of AuNPs, confirming successful hybridization.

The FTIR spectra of H₂BDC (terephthalic acid) and Al-MOF, shown in Figure 3, reveal significant changes that indicate the successful transformation of the organic linker into a MOF. In H₂BDC, a broad O–H stretching band is observed between 2500–3300 cm^{−1} and a C=O stretching peak at 1685 cm^{−1}, typical of carboxylic acid groups. In contrast, the Al-MOF spectrum shows a shift of the C=O peak to 1664 cm^{−1}, accompanied by new peaks at 1601 cm^{−1} and 1412 cm^{−1}, which correspond to carboxylate groups (COO[−]), confirming the deprotonation of H₂BDC during coordination with Al³⁺ [40]. Additionally, the appearance of peaks at 608 cm^{−1} and 990 cm^{−1} in the Al-MOF spectrum corresponds to Al–O bonds in AlO₄(OH)₂μ₂-hydroxo groups [43], confirming the coordination of Al³⁺ with the oxygen atoms of the BDC linker. Despite these structural changes, the aromatic ring vibrations are preserved, and the absence of the 1700 cm^{−1} peak suggests the removal of BDC during calcination. Broad peaks at 3466 cm^{−1} indicate the presence of adsorbed H₂O and hydroxyl groups, confirming the successful transformation of H₂BDC into Al-MOF [40].

FTIR analysis of the AuNPs and *E. bulbosa* extract (Figure 3), reveals the involvement of plant bioactive compounds in reducing Au³⁺ ions and stabilizing nanoparticles. The natural extracts from *E. bulbosa*, rich in flavonoids and phenolic compounds, likely influence the functional properties of the AuNPs [44]. The extract exhibits a broad band at 3375 cm^{−1}, attributed to O–H stretching vibrations in polyphenolic compounds. Peaks at 2920 cm^{−1} and 2856 cm^{−1} correspond to C–H stretching vibrations in aromatic and aliphatic groups, respectively. The

strong peak at 1734 cm^{−1} is assigned to C=O stretching in carboxylic acids, while bands at 1634 cm^{−1} and 1577 cm^{−1} are associated with C=C stretching in aromatic rings and COO[−] symmetric stretching, respectively.

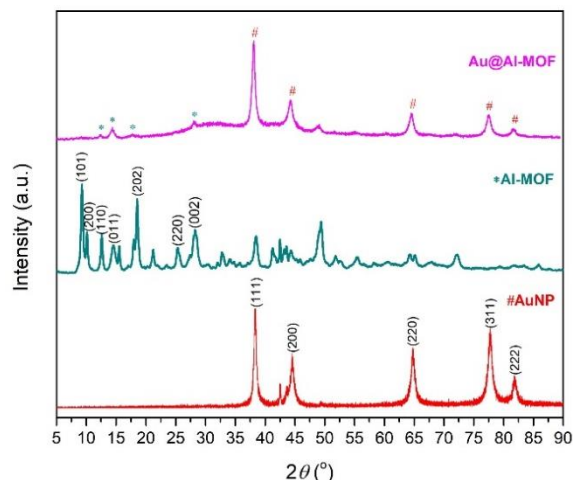


Figure 2: XRD patterns of AuNPs, Al-MOF, and the Au@Al-MOF nanocomposites.

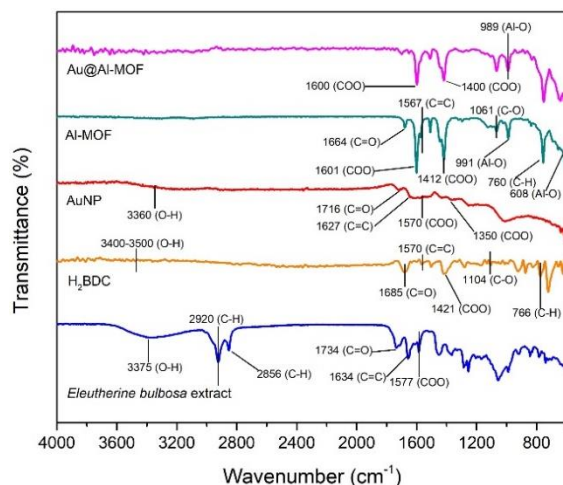


Figure 3: FTIR spectra of *E. bulbosa* extract, H₂BDC, AuNPs, Al-MOF, and Au@Al-MOF.

In the AuNPs spectrum, several key changes are observed. The O–H stretching band weakens and shifts, suggesting that hydroxyl groups from phenols and flavonoids are involved in reducing Au³⁺ [44]. The C=O peak at 1716 cm^{−1} decreases in intensity, indicating that carbonyl groups play a role in the reduction of Au³⁺. The C=C stretching band also shifts

slightly and broadens, suggesting changes in the aromatic structure during nanoparticle formation. Additionally, new peaks at 1570 cm^{-1} and 1350 cm^{-1} appear, pointing to the involvement of carboxylate groups in stabilizing the AuNPs. These changes confirm that flavonoids and phenolics in the extract reduce Au^{3+} and stabilize the nanoparticles through functional groups like hydroxyl, carbonyl, and carboxylate [38], [39], [45].

In the FTIR spectrum of Au@Al-MOF (Figure 3), the broad O–H band weakens and shifts slightly, indicating changes in water adsorption or hydrogen bonding due to AuNPs. The carboxylate vibrations at 1600 cm^{-1} and 1400 cm^{-1} remain prominent, confirming the preservation of the MOF framework. Minor shifts in the Al–O stretching region (989 and 610 cm^{-1}) suggest interactions between AuNPs and the aluminium centers of the MOF. At the same time, the aromatic ring vibrations remain unaffected, indicating that the organic linker structure is intact. These results suggest that the incorporation of AuNPs does not disturb the overall MOF structure, but rather induces subtle interactions within the framework. However, it is important to note that FTIR data alone cannot be used to conclusively determine whether AuNPs incorporation affects the porosity of the Al-MOF, and additional characterization techniques would be required to assess this.

The thermogravimetric analysis (TGA) of AuNPs, Al-MOF, and Au@Al-MOF (Figure 4) reveals distinct thermal behaviors. AuNPs exhibit significant weight loss between 50 – 250°C , primarily due to the evaporation of water and organic compounds. However, this weight loss does not directly reflect the thermal stability of the AuNPs themselves. Above 250°C , the minimal weight loss suggests that the AuNPs retain their structural integrity and thermal stability, with little further decomposition, indicating their high stability [46]. Al-MOF shows weight loss below 150°C , primarily due to the removal of water and solvent molecules, while the thermal decomposition of the BDC organic linker occurs between 150 – 400°C . Above 400°C , minimal weight loss is observed, suggesting the stability of the aluminum oxide framework (Al_2O_3) [43]. Au@Al-MOF exhibits a similar weight loss pattern, but with a reduced loss between 150 – 400°C , suggesting that the incorporation of AuNPs enhances the thermal stability of the framework. This improvement is likely due to AuNPs stabilizing the structure by strengthening interactions between the organic linker and aluminum

centers and reducing the mobility of the framework, making it less prone to decomposition. The higher residual weight of Au@Al-MOF compared to Al-MOF further confirms that AuNPs enhance the framework's thermal stability by strengthening its structural integrity at elevated temperatures.

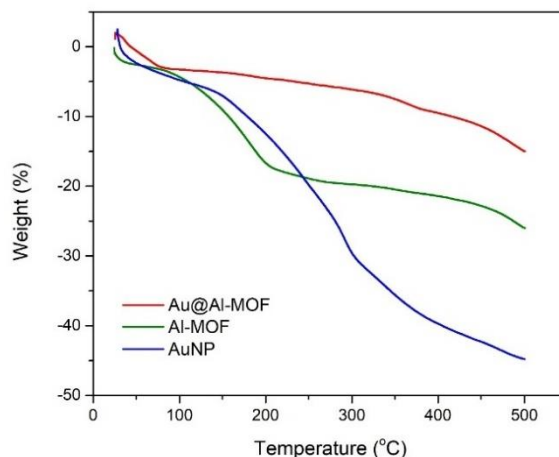


Figure 4: TGA curves of AuNPs, Al-MOF, and Au@Al-MOF.

The surface morphology of the prepared AuNPs, Al-MOF, and Au@Al-MOF was characterized using TEM, SEM, and FESEM. Figure 5 presents TEM images of AuNPs, revealing predominantly spherical particles with sizes ranging from 5 to 35 nm and an average diameter of $8.33 \pm 5.05\text{ nm}$. The nanoparticles are well-dispersed, with minimal aggregation, though some clustering is observed, likely due to sample preparation effects. The Gaussian fit indicates a relatively narrow and symmetric particle size distribution, reflecting reasonable control over nucleation and growth during synthesis. In contrast, TEM analysis of Au@Al-MOF reveals irregular and non-spherical particle morphologies, including triangular shapes and aggregated structures, suggesting strong interactions between AuNPs and the Al-MOF framework. The particle sizes in Au@Al-MOF range from approximately 5 to 60 nm , with noticeable clustering and aggregation, likely due to uneven nucleation or growth within the MOF matrix. The average particle size is $25.96 \pm 11.38\text{ nm}$, with a broad distribution that indicates considerable size variation. This heterogeneity and clustering could influence the material's performance. Smaller particles are expected to enhance surface area and reactivity, while larger particles may reduce stability or compromise

performance in applications such as catalysis. Additionally, the clustering of AuNPs may alter their interaction with the MOF framework, potentially

affecting the overall stability and efficiency of the material in practical applications.

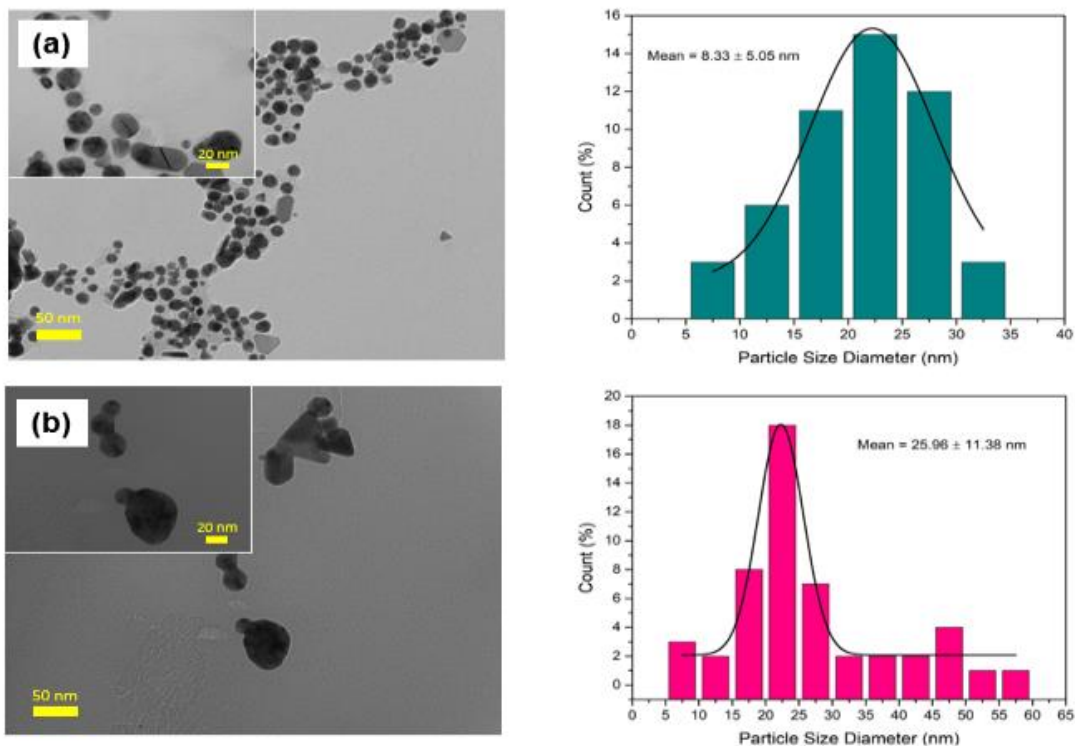


Figure 5: TEM image and size distribution histogram for AuNPs (a) and Au@Al-MOF (b).

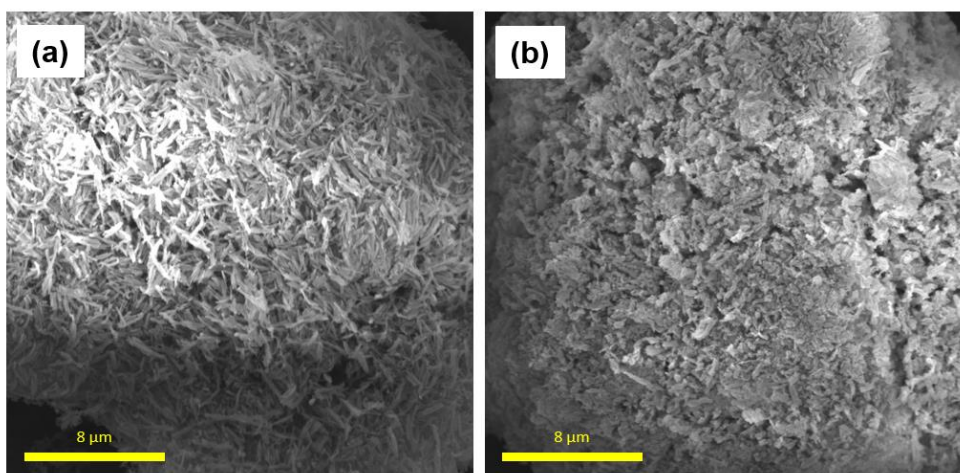


Figure 6: SEM image of (a) Al-MOF and (b) Au@Al-MOF.

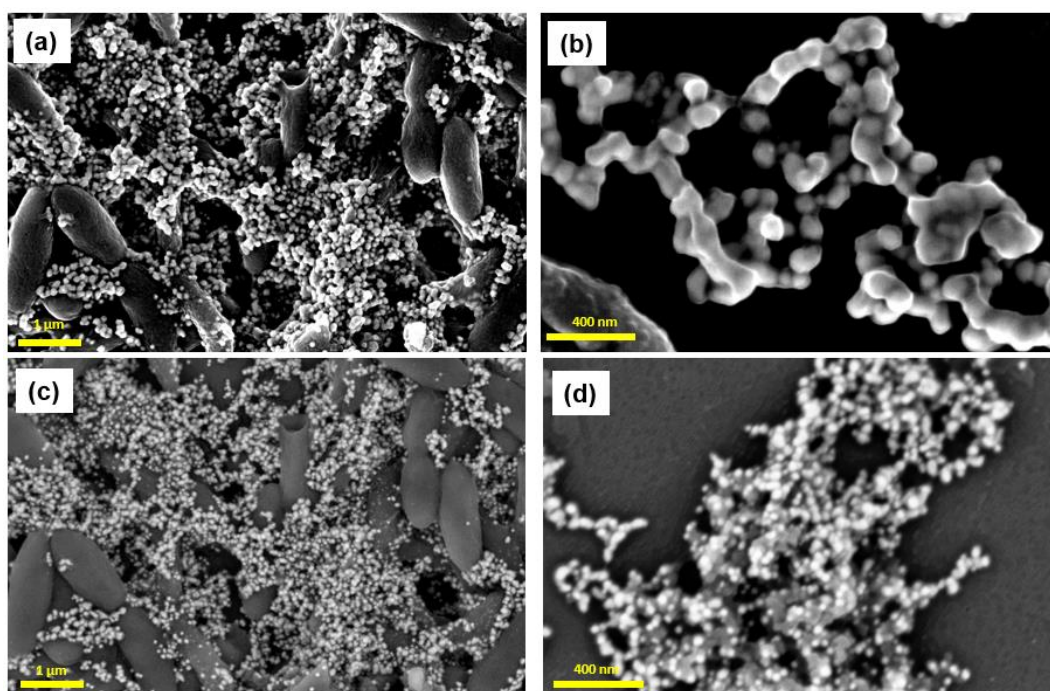


Figure 7: SE-FESEM images (a)-(b) and BSE-FESEM images (c)-(d) of AuNPs.

The SEM images of Al-MOF (Figure 6) exhibit a well-defined flake-like morphology characterized by a layered and interconnected network. This hierarchical structure, with uniformly distributed flakes, reflects a consistent and reproducible synthesis process. The sharp edges and irregular stacking of the flakes indicate high crystallinity and a large surface area. In contrast, the SEM images of Au@Al-MOF display a similar structure but with less well-defined flakes and aggregated clusters. This change suggests that the incorporation of AuNPs modifies the framework's morphology. Such changes may result from interactions between the gold precursors and the MOF during synthesis, leading to localized nucleation and densification in certain areas.

FESEM provides crucial information about the morphology of the AuNPs surface [47]. The images were captured using both SE-FESEM and BSE-FESEM. The SE-FESEM images of AuNPs (Figure 7a-b) reveal a dense distribution of predominantly spherical nanoparticles, with noticeable aggregation in some areas. These nanoparticles are uniformly dispersed on a rough, porous substrate, which likely facilitates anchoring. Individual particles appear smooth and well-defined, indicating good crystallinity. However, some clustering is observed,

likely due to van der Waals forces or incomplete stabilization during the synthesis process. The BSE-FESEM images (Figure 7(c) and (d)) further confirm this observation, with a dense and uniform distribution of nanoparticles on a textured substrate. The high atomic number of gold generates a bright contrast against the darker background, which aids in confirming the composition and presence of the nanoparticles. These images display widespread nanoparticle coverage, with some aggregation, while individual particles maintain a spherical shape and uniform size. The intense brightness contrast in BSE mode effectively highlights the gold particles and distinguishes them from the surrounding matrix.

Figure 8 illustrates the UV-Vis absorption spectra of *E. bulbosa* extract, AuNPs, and the Au@Al-MOF nanocomposite. The spectrum of the *E. bulbosa* extract shows broad absorption across the visible range, typical of organic compounds with complex chromophores, and lacks distinct peaks. In contrast, the AuNPs display a sharp and prominent peak at 541 nm, indicative of AuNPs' localized surface plasmon resonance (LSPR), confirming their successful synthesis and characteristic size-dependent optical properties [48]. Upon incorporation into the Al-MOF framework, the Au@Al-MOF nanocomposite shows a

red-shifted peak at 548 nm, indicating interactions between the AuNPs and the MOF [49]. This shift is attributed to changes in the local refractive index, highlighting the successful integration of the nanoparticles into the MOF structure. Moreover, the enhanced absorbance intensity at 548 nm for the Au@Al-MOF compared to AuNPs indicates improved stabilization or increased particle interaction within the MOF, further emphasizing the composite's potential for Hg^{2+} sensing applications.

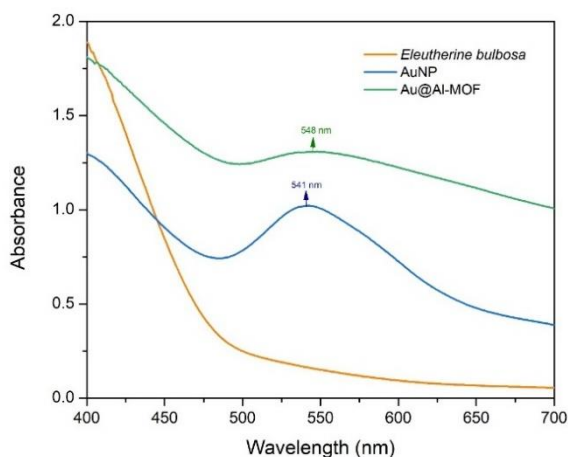


Figure 8: UV-Vis spectrum of *E. bulbosa* extract, AuNPs, and Au@Al-MOF.

The Au@Al-MOF nanocomposites, synthesized using *E. bulbosa* extract, exhibit excellent thermal stability, morphological uniformity, chemical functionality, and enhanced optical properties, as confirmed through various characterization techniques. The incorporation of well-dispersed AuNPs into the Al-MOF matrix not only enhances the sensor's sensitivity but also contributes to its long-term stability and reliability. The use of *E. bulbosa* extract provides an eco-friendly, sustainable approach to synthesizing AuNPs, eliminating the need for toxic chemicals typically used in traditional nanoparticle synthesis. This method ensures that the material is environmentally friendly and aligns with the increasing demand for sustainable materials in scientific applications. The UV-Vis spectra confirm the successful integration of the AuNPs within the Al-MOF, with a red-shift and increased absorbance intensity that highlight the material's potential for

colorimetric sensing applications. These findings suggest that Au@Al-MOF, synthesized with *E. bulbosa* extract, could serve as an effective, eco-friendly material for a variety of applications, offering enhanced stability, functionality, and environmental sustainability, particularly for sensor-based applications.

3.2 Performance evaluation of Au@Al-MOF nanocomposites for Mercury (Hg^{2+}) detection

To estimate the sensitivity and quantitative range of the Au@Al-MOF nanocomposite sensor for mercury ion detection, a UV-Vis spectrum was recorded across a range of Hg^{2+} concentrations (0–1000 ppm). As shown in Figure 9(a), the absorption spectra of the Au@Al-MOF gradually decreased at $\lambda_{\text{max}} = 546$ nm with increasing Hg^{2+} concentration. This decrease in absorbance is primarily attributed to the interaction between Hg^{2+} ions and the AuNPs [50]. The localized surface plasmon resonance (LSPR) of the AuNPs is highly sensitive to changes in the local environment, and the presence of Hg^{2+} ions likely induces a shift in the LSPR frequency or damping of the plasmon resonance, resulting in the observed decrease in absorbance. This interaction between Hg^{2+} ions and AuNPs is a key factor in the sensor's ability to detect Hg^{2+} with high sensitivity, as LSPR is a well-established phenomenon for detecting changes in the local refractive index caused by ion binding.

The UV-Vis absorbance intensity at 546 nm demonstrated a linear response to Hg^{2+} concentration in the range of 5–1000 ppm, exhibiting a strong positive correlation ($R^2 = 0.9978$) (Figure 9(b)). The linearity of this response suggests a stable and reproducible interaction between the AuNPs and Hg^{2+} ions within this concentration range, making the sensor highly suitable for quantitative analysis. The limit of detection (LOD) was estimated to be 3.46 ppm, which is relatively low for a colorimetric sensor. This LOD was calculated using the standard formula $\text{LOD} = 3S/N$, where S is the standard deviation of the blank and N is the slope of the calibration curve. The low LOD indicates that the Au@Al-MOF nanocomposite sensor is highly sensitive, enabling it to detect trace levels of Hg^{2+} in complex samples such as cosmetics, which may contain low concentrations of mercury.

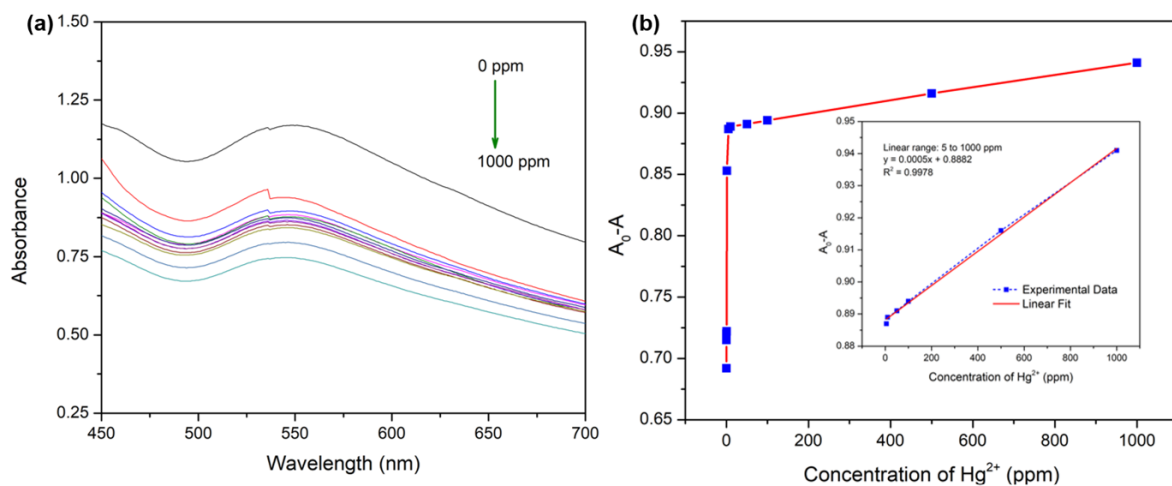


Figure 9: UV-Vis spectrum of Au@Al-MOF in response to different Hg^{2+} concentrations (a); and calibration curve of $(A_0 - A)$ vs. Hg^{2+} Concentration (5–1000 ppm) (b). A_0 is the absorbance of Au@Al-MOF without Hg^{2+} at 546 nm, and A is the absorbance after adding various Hg^{2+} concentrations.

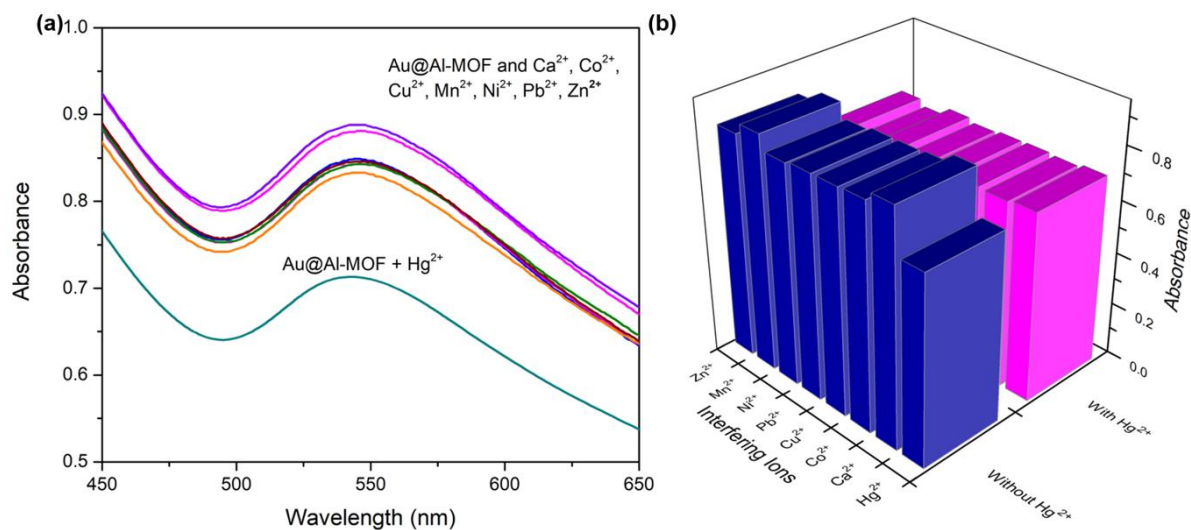


Figure 10: Effect of common interfering cations on absorbance spectra. (a) UV-Vis spectrum of the sensing system in response to various metal ions and (b) UV-Vis absorbance of the sensing system at 546 nm towards various metal ions in the presence and absence of Hg^{2+} .

An interference test was conducted to assess the effect of other metal ions on the selectivity of the Au@Al-MOF sensor for Hg^{2+} detection. This test monitored the UV-Vis absorption response to various metal ions, including Zn^{2+} , Mn^{2+} , Ni^{2+} , Pb^{2+} , Cu^{2+} , Co^{2+} , and Ca^{2+} , using a 1:1 volume ratio. As shown in Figure 10(a), the UV-Vis absorbance at 546 nm remained unchanged after the addition of these interference ions, indicating that they do not affect the sensor's performance. This confirms that the sensor is

selective for Hg^{2+} , which is crucial for mercury detection in environments containing other metal ions, such as in cosmetic products. In contrast, the addition of Hg^{2+} caused a significant decrease in absorbance, further confirming the sensor's specificity for Hg^{2+} ions. Figure 10b compares the UV-Vis spectra of the sensing system in the absence and presence of 50 ppm Hg^{2+} . In the presence of Hg^{2+} , there were no significant changes in the solution color or the UV-Vis spectrum.

It confirms that the Au@Al-MOF sensor exhibits excellent selectivity for Hg^{2+} ions.

A stability test was conducted to evaluate the durability of Au@Al-MOF after storage. The samples were stored in a refrigerator to extend their shelf life. Stability was assessed by monitoring the decrease in absorbance intensity of Au@Al-MOF. The study lasted for 80 days, with a slight decrease in absorbance observed on the 54th day, although insignificant. By the 72nd day, the decrease in absorbance intensity became more pronounced (Figure 11). Between the 72nd and 80th days, the absorbance intensity of Au@Al-MOF decreased significantly, indicating a marked loss in stability. This decline could affect its real-world applications, particularly in fields like sensing, where long-term durability is essential. If Au@Al-MOF continues to lose stability over time, its performance in such applications may be compromised. As a result, additional improvements may be required to enhance its long-term stability for practical use.

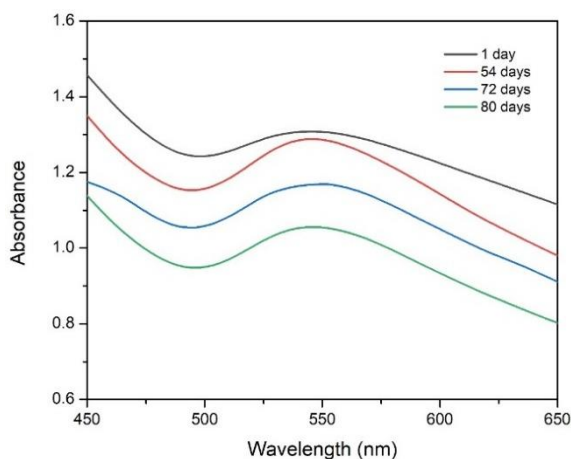


Figure 11: Stability test of Au@Al-MOF.

3.3 Real sample analysis using Au@Al-MOF Nanocomposites

The application of Au@Al-MOF nanocomposites for Hg^{2+} detection was evaluated using cosmetic products, specifically whitening face creams purchased from a traditional market in Palangka Raya. Before analysis, the samples were pretreated with HNO_3 to digest organic matrices and filtered to remove particulates [50]. For the detection process, 1 mL of each sample was mixed with 1.5 mL of Au@Al-MOF solution, followed by brief agitation for 5 seconds to ensure proper interaction. The mixtures were then subjected

to visual inspection and further analyzed using a UV-Vis spectrophotometer. The UV-Vis spectra revealed that adding the cosmetic products decreased the absorbance intensity of Au@Al-MOF, suggesting the presence of Hg^{2+} ions in the samples (Figure 12).

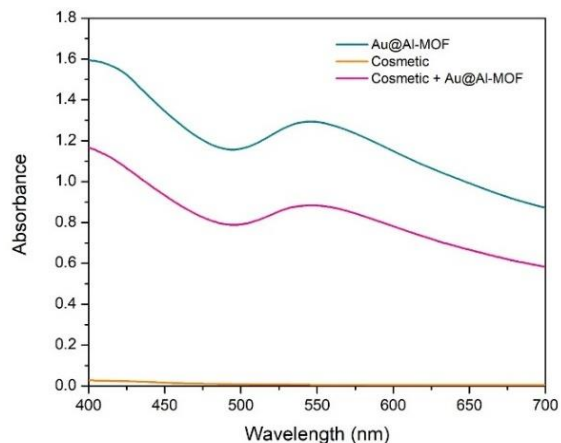


Figure 12: Detection test of Hg^{2+} in cosmetics using Au@Al-MOF.

To validate the accuracy and reliability of the Au@Al-MOF-based detection method, the Hg^{2+} content in the cosmetic samples was also quantified using AAS, a well-established technique for heavy metal analysis. The AAS results were consistent with the UV-Vis spectrophotometric data, confirming the presence of Hg^{2+} ions in the whitening face creams. This agreement between the two methods underscores the effectiveness of the Au@Al-MOF nanocomposites as a sensitive and reliable tool for Hg^{2+} detection. Furthermore, the performance of the Au@Al-MOF-based protocol was compared with other conventional methods, as summarized in Table 1. The results demonstrate that the proposed method is competitive in terms of sensitivity and accuracy and offers advantages such as simplicity, rapidity, and cost-effectiveness, making it a promising alternative for on-site mercury detection in cosmetic products.

Table 1: Determination of Hg^{2+} in cosmetic products.

Sample	Au@Al-MOF (ppm)	AAS (ppm)
Face cream	4.53	4.59

4 Conclusions

The Au@Al-MOF nanocomposite sensor developed in this study offers a practical and eco-friendly solution for detecting Hg^{2+} contamination in cosmetic

products. The flake-like morphology of Al-MOF, with its high thermal stability, enhances the sensor's sensitivity and selectivity by efficiently capturing Hg^{2+} . The sensor demonstrates excellent performance, with a broad linear detection range, low detection limits, and strong stability over time. Its high selectivity for Hg^{2+} , even in the presence of other metal ions, confirms its reliability for real-sample applications. The successful detection of Hg^{2+} in cosmetic samples underscores the practical utility of this sensor. The Au@Al-MOF nanocomposite shows excellent potential for addressing Hg^{2+} contamination and contributing to public health safety.

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Author Contributions

L.R.: conceptualization, investigation, formal analysis, and drafting; M.R.K.: conceptualization, formal analysis, and resource management; S.U.M.B.: conceptualization, validation, manuscript review, supervision, and project administration; A.S.A.: formal analysis and visualization of the data; N.A.: validation, and review and editing of the manuscript. All authors have read and agreed to the published version of the manuscript.

Conflicts of Interest

The authors declare no conflict of interest.

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