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Article

The potency of $AgNO_3$ nanoparticles combined with sweet potato (Ipomea batatas) starch as a sensor for mercury detection in cosmetic products

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Abstract: Fraudulence in cosmetic ingredients is becoming increasingly prevalent, alongside the rising demand and utilization of cosmetics within the populace. One of the whitening agents still utilized in cosmetics is mercury, present in forms such as mercury chloramide ($HgNH_2Cl_2$) and mercury chloride ($HgCl_2$). Prolonged mercury exposure can have adverse health effects. To address this issue, alternative mercury analysis methods in samples have been developed, including the utilization of silver nanoparticles amalgamated with sweet potato starch as a stabilizing agent. This paper aims to delve into the roles of silver nanoparticle $AgNO_3$ and sweet potato starch (as a stabilizer) as a sensor for mercury detection, which can be applied in cosmetic products. Detection of mercury utilizing nanoparticles is based on the Surface Plasmon Resonance phenomenon, which endows a high level of selectivity and sensitivity toward the presence of mercury metal ions. When interaction occurs between mercury metal and silver nanoparticles, the liquid undergoes a color change from yellowish-brown to transparent. This phenomenon arises from the oxidation of AgO (yellow) to Ag^+ ions (transparent) by the mercury metal. Consequently, a silver nanoparticle sensor utilizing sweet potato starch as a stabilizing agent exhibits the potential to detect mercury metal within a substance with high efficacy.

Keywords: cosmetic; mercury detection; stabilizer; sweet potato starch

1. Introduction

Commercial whitening creams are widely available and easy to use, at affordable prices. In Indonesia, many cosmetic producers engage in fraudulent practices due to the increasing demand and consumption of cosmetics, driven by the high enthusiasm of the Indonesian population for cosmetics. Consequently, cosmetic producers compete to create products that can quickly brighten and whiten skin at affordable prices, leading to fraudulent practices in cosmetics production. According to the Central Statistics Agency, online transactions increased by 480% during the seven-month pandemic period. Unscrupulous e-commerce sellers exploit this trend to distribute unauthorized (TIE) or illegal and hazardous cosmetic products in various markets. Data on crime vulnerability reported by the Center for Drug and Food Control (POM) from 1 January 2018, to 15 September 2020, revealed several cosmetic products containing harmful whitening agents circulating in Indonesia. Mercury is a commonly used whitening agent in cosmetics, present in forms such as mercury chloride ($HgCl_2$) and mercury amino chloride ($HgNH_2Cl_2$). Prolonged mercury exposure can cause skin discoloration, black spots, allergies, skin irritation, and permanent damage to the nervous system, brain, kidneys, and fetal development. Therefore, there is a need for mercury content analysis in various cosmetics available on the market.

According to Azhar [1], there are several methods for measuring mercury metal concentrations in samples, such as inductive coupled plasma mass spectrometry (ICP-MS) and atomic absorption spectroscopy (AAS). However, the equipment costs for these methods are relatively high, necessitating alternative mercury analysis methods, including the use of silver nanoparticles mixed with starch as a stabilizing agent. Previous studies have utilized starch as a new nanocomposite material containing zinc sulfide quantum dots coated with L-cysteine. Nanocomposites were prepared in the form of potato starch gel and foil embedded with spherical quantum dots sized at 1020 nm. Pb^{2+} and Cu^{2+} ions reduced emission intensity in the photoluminescence spectral band. The described quantum dots were obtained using a simple, safe, and inexpensive method. Due to these properties, alternative sensors for Pb^{2+} and Cu^{2+} can be used in biotechnology and food technology.

Sweet potato is a nutritious tuber, containing fiber 6.33%–9.51%, protein 2.14%–2.86%, and b-carotene 18.83 mg/100 g [2]. However, it is still containing antinutrients such as phytate, oxalate, and tannin [2,3]. Additionally, its starch is widely used for thickening or stabilizing, as it contains 95.26%–96.73% of starch with 18.17%–18.56% of amylose [4]. The native starch from sweet potatoes has previously been reported to have a stable viscosity, with a peak viscosity of 3421.5 cP and a final viscosity of 3447.0 cP [5], making it a potential candidate for use as a stabilizer in mercury detection sensors. Innovation in the utilization of sweet potato starch potentially makes sweet potatoes more widely utilized. Furthermore, with sweet potato starch used as a mercury (Hg) detection sensor, which is more affordable and readily available, it can reduce operational costs in the production of mercury (Hg) detection sensors. With affordable prices and ease of use, it is hoped that many cosmetic producers will be more conscientious in their cosmetic selections, as they can easily utilize these mercury (Hg) detection sensors.

The innovation of sweet potato starch as a stabilizer in the mixing of silver nanoparticles can be beneficial in reducing the production and distribution of cosmetics containing mercury. This concept is also useful in creating a cheap, fast, and effective tool for detecting mercury. The development of sweet potato starch can also increase the productivity of sweet potatoes. The paper aimed to explore the potency of $AgNO_3$ nanoparticles and sweet potato starch (as stabilizers) as a sensor for mercury detection in cosmetic products.

2. Methods

The method used is an effective literature review following the topic. The method of discussion is based on the research results found by previous researchers, which are then integrated with other researchers to get strong results and conclusions.

3. Results and discussion

3.1. Mercury as heavy metals

Heavy metal ions have become a widely discussed environmental pollution issue. Apart from polluting the environment, these metals pose significant risks to human health. One such example of heavy metal is mercury, which is commonly encountered.

Mercury is identified as a hazardous pollutant due to its high toxicity and strong bioaccumulation potential, capable of causing damage to vital organs and tissues in the human body even at low concentrations [6].

Mercury metal sensors are technologies used to detect the presence of mercury in a substance. These sensors are fabricated using AgNO3 nanoparticles stabilized with sweet potato starch. The detection of mercury metal using these nanoparticles is based on the Surface Plasmon Resonance (SPR) effect, wherein the $AgNO_3$ nanoparticles exhibit high selectivity and sensitivity towards the presence of mercury metal ions (Hg) [1]. According to Wahyudi [7], the production of silver nanoparticles requires a stabilizing agent to prevent the colloidal particles from agglomerating. Agglomeration refers to the formation of particle clusters in a solution, leading to colloidal instability in nanoparticles. Starch derived from sweet potatoes is employed as the stabilizing agent in this sensor due to its environmentally friendly nature and non-hazardous properties.

Typically, the preparation of materials for synthesizing silver nanoparticles involves hazardous chemicals, high energy consumption, and complex purification processes [8]. Innovations in nanoparticle synthesis using starch as a stabilizer offer a non-toxic and environmentally friendly chemical development solution, requiring minimal costs for silver nanoparticle synthesis. This is attributed to the abundance of sweet potatoes in Indonesia and their affordable prices. According to data from the Agricultural Data and Information Center of the Ministry of Agriculture in 2022, sweet potato production in Indonesia showed a slight increase of 4.02% from 2020 to 2022. This rise in sweet potato production presents an opportunity for expanding the utilization of sweet potatoes, particularly in non-food applications.

Detection of mercury metal in cosmetics can be conducted on a laboratory scale or implemented by cosmetic resellers to ascertain whether the products being sold are free from mercury. This testing involves mixing the mercury metal sensor solution with the cosmetics under examination, followed by analyzing their absorbance using a UV-VIS spectrophotometer. During this process, a change in the solution's color occurs, enabling the determination of absorbance values.

3.2. Previous study

Previous research studies related to mercury metal sensors using nanoparticles include the research by Winiari and Kurniawan [9], which focused on mercury detection using direct solutions of gold nanoparticles. The results of this study indicated that the sensor activity was demonstrated by a shift in the wavelength towards higher values with increasing concentrations of mercury and gold nanoparticles without modification, which can be utilized for simple, rapid, and practical mercury detection.

Another study relevant to mercury metal sensors utilizing nanoparticles is by Vasileva [10], which explored the application of silver nanoparticles stabilized with starch as a colorimetric sensor for mercury (II) in 0.005 mol/L Nitric Acid. This study highlighted that the presence of 0.005 mol/L nitric acid utilizing starch-coated AgNPs as an optical sensor based on LSPR (Localized Surface Plasmon Resonance) is effective in mercury detection. The procedures conducted were practical, fast, and cost-effective. The mercury metal sensor using nanoparticles in this optical sensor based on LSPR can be applied for drinking water and wastewater.

In the study by Vasileva [8], it was reported that they successfully synthesized silver nanoparticles using environmentally friendly starch as a stabilizing agent. The research revealed that the nanoparticle sensor developed to test hydrogen peroxide exhibited excellent sensitivity and a high response to the presence of hydrogen peroxide in the sample.

3.3. Mercury detection

The detection of mercury has been extensively developed using various methods such as Cold Vapor Atomic Absorption Spectroscopy (CV-AAS), Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES), gas chromatography, and others. According to Wang [11], these methods exhibit excellent performance in detecting metals; however, their application requires expensive and sophisticated instruments, complex sample processing, and high analysis costs, hindering their routine application in mercury detection. The increasing mercury metal pollution, particularly in cosmetic products, necessitates routine testing of these products. To reduce the operational costs of mercury detection, cheaper, practical, easy-to-implement, and environmentally friendly technologies are needed. Mercury metal sensors using $AgNO_3$ nanoparticles with sweet potato starch as a stabilizing agent represent an innovative heavy metal detection technology.

In previous research conducted by Wahyudi [7], polyacrylic acid (PAA) was used as the stabilizing agent in the production of silver nanoparticles, while in the study by Khachatryan and Khachatryan [12], potato starch was utilized as the stabilizer in nanocomposites. In this mercury metal sensor, we employ sweet potato starch as an innovation in the use of $AgNO_3$ nanoparticle stabilizers (silver). This innovation is based on the research by Vasileva [10] on the application of nanoparticle particles stabilized with starch for mercury metal detection. **Figure 1** illustrates the reaction that occurs between $AgNO_3$ nanoparticles when reacted with mercury metal (Hg).

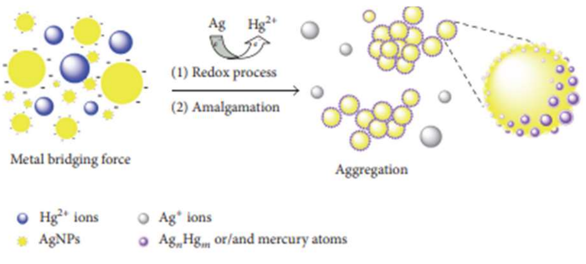

Figure 1. Schematic representation of the interaction mechanism between sweet potato starch-stabilized $AgNO_3$ nanoparticles and mercury.
Source: Vasileva [10].

The interaction between Hg^{2+} and nanoparticles involves electrostatic attraction between negatively charged silver nanoparticles and positively charged Hg^{2+}. This leads to a reduction in the distance between nanoparticles, resulting in aggregation. Hg^{2+} is adsorbed on the surface of AgNPs and reduced to Hg by surface Ag atoms, while simultaneous diffusion of Ag^+ into the solution occurs. The reaction leads to the formation of new mercury atoms combined with surface Ag atoms. This interaction may alter the surface charge of nanoparticles, leading to destabilization and agglomeration.

3.4. Role of $AgNO_3$ nanoparticles with sweet potato starch

The mercury metal sensor is formulated in liquid form, allowing direct application to cosmetics suspected of containing mercury. The production of nanoparticles entails the reduction of AgNO using D-glucose as the reducing agent. A starch solution serves as the capping and stabilizing agent, with the addition of NaOH as a catalyst in the reaction to produce an aqueous dispersion of silver nanoparticles. The schematic diagram of the silver nanoparticle synthesis process with sweet potato starch as the stabilizing agent is illustrated in **Figure 2**.

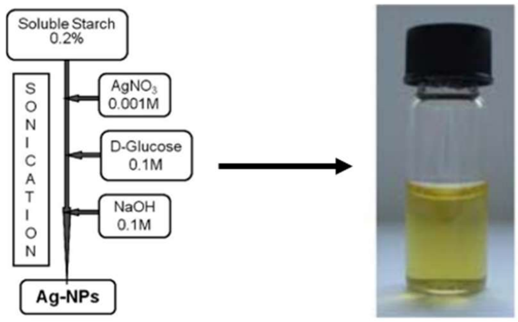

Figure 2. Schematic diagram of the silver nanoparticle synthesis process with sweet potato starch as the stabilizing agent.

The molar ratio of metal to reducer is 1:3, ensuring the complete reduction of Ag^+ ions in the solution into silver metal nanoparticles [10]. As depicted in **Figure 2**, the synthesis process involves stirring a starch solution (0.2% w/v) in a sonication bath for 15 minutes, followed by the addition of 16 mL of 0.0001 mol/L $AgNO_3$ solution. The mixture is stirred for 10 minutes to facilitate the diffusion of metal ions into the starch capping/stabilizing agent. Subsequently, the reducing solution containing D-glucose (0.01 M) is injected under sonication, followed by the addition of 2.4 mL of NaOH solution at 30 °C temperature maintained constant in an ultrasound bath. The reaction is completed within 60 minutes after the color change occurs.

The mercury metal sensor, in the form of silver nanoparticle liquid with starch stabilizer, will react with the tested cosmetic samples. The kinetics of interaction between sweet potato starch-stabilized silver nanoparticles and mercury metal (Hg) are reflected in the color change. According to research by Azhar [1], silver nanoparticles extracted from starfruit are selectively reactive towards mercury metal, indicated by a color change from yellowish-brown to clear. This occurs because mercury metal oxidizes AgO in the yellowish-brown silver nanoparticles to form clear Ag^+ ions. Further characterization of the sensor solution involves measuring the absorbance of the solution via UV-VIS spectrophotometer to determine the effect of mercury on sweet potato starch-stabilized silver nanoparticles. The predicted UV-VIS absorbance graph and color change of the sweet potato starch-stabilized silver nanoparticle liquid with added mercury are illustrated in **Figures 4** and **3**, respectively.

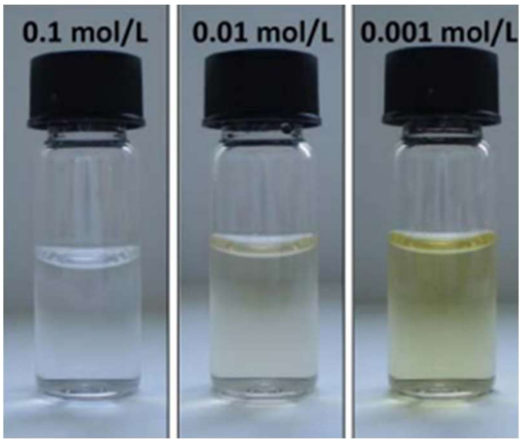

Figure 3. Prediction of mercury metal sensor results using silver nanoparticles with sweet potato starch as the stabilizing agent. Numbers indicated the concentration of mercury.

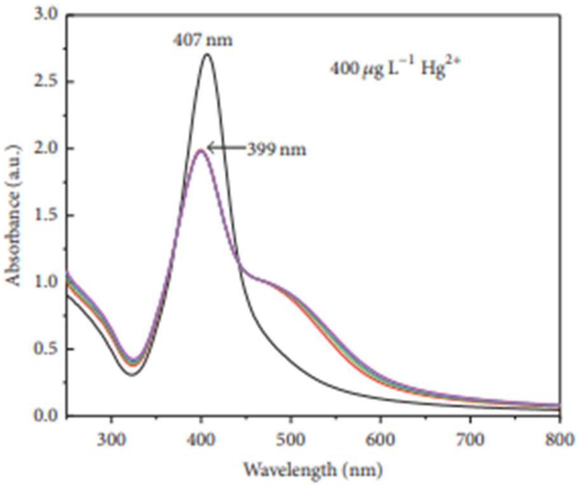

Figure 4. Predicted schematic of UV-VIS absorbance graph for mercury metal sensor using nanoparticles with sweet potato starch as the stabilizing agent.
Source: Vasileva [6].

4. Conclusion

In conclusion, the silver nanoparticle sensor with sweet potato starch as the stabilizing agent shows potential for detecting mercury metal in a substance. This sensor is formulated in liquid form, allowing direct testing on samples suspected of containing mercury, with a color change from yellowish-brown to clear indicating the presence of mercury. The utilization of sweet potato starch for mercury sensor production is expected to enhance the productivity and utilization of sweet potatoes in Indonesia.

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