

Green-AgNPs Modified Membrane for Monitoring Mercury Ions in Cosmetic Sample using Pre-concentration Assisted Voltammetry Technique

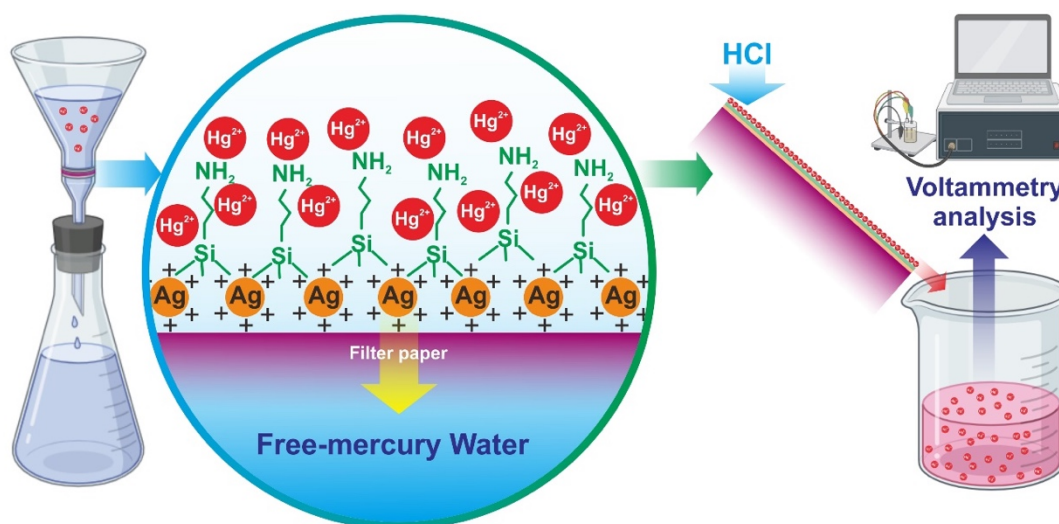
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GRAPHICAL ABSTRACT



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ABSTRACT

The carcinogenic and teratogenic properties of mercury have driven the necessity for the development of highly sensitive methods capable of detecting even trace amounts of the element. In response to this need, an analysis technique has been established for mercury ions, employing preconcentration methods utilizing filter paper modified by silver nanoparticles (AgNPs) and 3-Amino propyl trimethoxy silane (APTMS). This method allows for the detection of mercury ions through the voltammetry technique, ensuring accurate and reliable results. Upon conducting analyses using this method, it was found that the tested cosmetic samples were free from Hg²⁺ ions, indicating the absence of mercury contamination in the cosmetics under investigation. The correlation coefficient derived from the graph of the analysis results stands at an impressive value of 0.9976, affirming the strong relationship between the measured concentrations and the actual mercury content. Additionally, the method demonstrates excellent sensitivity, as evidenced by the low limit of detection (LOD) value of 0.0483 mM and the limit of quantification (LOQ) value of 0.1611 mM.

1. INTRODUCTION

Heavy metals, characterized by their inorganic nature and density surpassing 4 g/cm^3 , are categorized according to their toxicity levels into essential and non-essential variants [1, 2]. Mercury, known for its carcinogenic and teratogenic properties, poses significant health risks, even at reduced concentration [3]. In Indonesia, the misuse of heavy metals is primarily observed in skincare cosmetic products containing hazardous substances, notably mercury (Hg). Given the routine use of cosmetics by people, ensuring their safety from harmful substances like heavy metals is imperative. Consequently, the Head of Food and Drug Supervisory Agency of the Republic of Indonesia (BPOM) enacted Regulation number 17 of 2014, stipulating limits for microbial contamination and heavy metal content in cosmetics, with mercury (Hg) restricted to not exceed 1 mg/L (mg/kg) [4].

Typically, when assessing mercury levels in cosmetics, the methods commonly employed include Atomic Absorption Spectrophotometry (AAS) [5], Cold Vapor Atomic Absorption Spectrophotometry (CV-AAS) [6], Cold Vapor Atomic Fluorescence Spectrophotometry (CF-AFS) [7], Direct Mercury Analyzer [8] and ICP-MS [9]. These techniques are favored for their superior analytical capabilities, delivering precise results with high accuracy and sensitivity. Nevertheless, they come with significant drawbacks such as high costs, lengthy analysis periods, and intricate sample preparation procedures [10]. Moreover, given the typically low concentrations of heavy metals like mercury in cosmetic products, there's a pressing need for developing more efficient methods to analyze such minute amounts effectively. One promising approach involves sample preconcentration techniques analyzed via voltammetry. These alternative methods offer advantages like simplicity, affordability, ease of operation, shorter processing times, and heightened selectivity and sensitivity [11].

The pre-concentration method in this approach involves utilizing filter paper, which offers various advantages such as simplicity, minimal operational time, high pre-concentration factors, and excellent retention capabilities [12]. Filter paper can be modified using green and nanotechnology approach. Green technology, biosynthesis method, stands as the most prevalent technique for producing nanoparticles, owing to its straightforwardness, user-friendliness, and environmental benignity, such as silver nanoparticles (AgNPs). In this process, plant agents rich in antioxidants, like Green Tea, serve as reducing agents for AgNPs synthesis [13]. Green tea is widely recognized for its antioxidant properties, attributed to its high polyphenol content [14]. Its primary constituents include epigallocatechin (ECG), epigallocatechin-3-gallate (EGCG), epicatechin-3-gallate (ECG), and epicatechin (EC) [15]. EGCG, which makes up 50-80% of the total catechin content, is the most abundant compound. In addition to these, green tea contains flavonoid aglycones (such as quercetin, kaempferol, myricetin, and glycosides), caffeine, vitamin K, saponins, small amounts of theobromine and theophylline, 6% protein, 8% amino acids, 3% theanine, nucleic acids, and trace minerals, fluoride, and phenophytin [16-18]. However, while AgNP-modified filter paper is effective in adsorbing heavy metal ions, its binding capacity is somewhat limited due to direct binding of AgNP groups to Si atoms in the silica structure, resulting in weak metal ion binding on the silica surface. To address this issue, the modification method involves the addition of the organic compound 3-APTMS to enhance adsorption effectiveness, particularly towards Hg^{2+} ions [19].

The main objective behind modifying the filter paper with APTMS and AgNPs is to boost its ability to concentrate mercury ions (Hg^{2+}) found in cosmetic samples. This modification seeks to enhance the filter paper's adsorption capacity, enabling it to efficiently trap and concentrate even tiny traces of mercury present in cosmetic formulations. By harnessing the unique characteristics of APTMS and AgNPs, such as their large surface area and affinity for heavy metal ions, the modified filter paper is anticipated to significantly enhance the sensitivity and reliability of mercury analysis using voltammetric methods. Ultimately, this improvement in pre-concentration efficiency will lead to more accurate and precise detection of mercury contamination in cosmetic products, thus promoting consumer safety and adherence to regulatory standards within the cosmetics industry.

2. EXPERIMENTAL METHOD

2.1. Materials

The chemicals were purchased from supplier (Merck), such as amino-propyl trimethoxy silane (APTMS) 97%, sodium hydroxide (NaOH) $\geq 97\%$, ethanol 95%, hydrochloride acid (HCl) 37%, potassium iodide (KI) $\geq 99\%$, nitric acid (HNO₃) 65%, potassium nitrate (KNO₃) $\geq 99\%$, sodium chloride (NaCl) $\geq 99\%$, silver nitrate (AgNO₃) $\geq 99\%$, sulphuric acid (H₂SO₄) 95-97%, and mercury (II) chloride (HgCl₂) $\geq 99.5\%$. All of chemical are analytical grade without further purification. In this study also used DI water and cosmetic sample that obtained from commercial market.

2.2. Green-tea extract preparation

Green-tea of 4 g was weighed and solved in 100 mL of DI water. The solution is heated at 60 °C for 20 min. Then, the mixture was filtered for obtaining the filtrate added by NaOH 0.1 M until reach pH of 8 (HCl and NaOH for adjusting the pH).

2.3. Filter membrane modification

The modification was initialized by filter paper (Whatman No. 24) that was dipped into 25 mL of 0.02M AgNO₃ solution for 5 minutes. Afterwards, filter membrane was added ethanol dropwisely (10 droplet). The filter membrane was dipped into Green-tea extract (20 mL) solution for 5 minutes then rinsed using DI water. Finally, the filter membrane was dried under room temperature then resulting AgNPs modified membrane. Subsequently, APTMS was prepared with various concentration of 0, 0.5, 1, and 2% v/v. AgNPs modified membrane was drowned and left for 2 minutes. Then, the modified membrane was dried under room temperature to result AgNPs-APTMS modified membrane.

2.4. Characterization

Characterization instruments were utilized for observing the successful of modification on filter membrane. X-Ray diffraction from Rigaku (Cu K α 1.54 nm) was performed to reveal formation AgNPs. FTIR spectrophotometer from Shimadzu showed functional groups on unmodified and modified membrane. SEM microscopy from JEOL was used to image the surface morphology of modified membrane.

2.5. Pre-concentration studies using LoD, LoQ, and linearity parameter

Modified membrane was prepared for filtering the 0.5 mM HgCl₂ solution with volume of 10, 15, 20, and 25 mL. The filtrate was measured using potentiometer for calculating optimum volume of HgCl₂. Then, the pH was variated for optimizing pH condition (2, 4, 6, and 8) using similar steps of volume optimization. The linearity was analyzed to reveal the limit-of-detection (LoD), limit-of-quantification (LoQ), and linearity constant (*r*). Linearity test used 25 mL HgCl₂ solution with concentration of 0.025, 0.05, 0.1, 0.2, 0.3, 0.4, and 0.6 mM. The measurement was observed by potentiometer and calculated using **Equation 2** and **3** for LOD and LOQ estimation, respectively.

$$SD = \sqrt{\frac{\sum(X - \bar{X})^2}{n-1}} \quad (1)$$

$$LOD = \frac{3 \times Sx/y}{slope} \quad (2)$$

$$LOQ = \frac{10 \times Sx/y}{slope} \quad (3)$$

2.6. Mercury determination in cosmetic sample

Cosmetic samples were prepared by grinding 2 grams. The crushed sample was completely dissolved in 15 mL of HNO₃ followed by heating. Next, 5 mL of the filtrate was pipetted and put

into a 25 mL measuring flask until the limit mark. The solution was homogenized and then filtered using filter paper modified for preconcentration. The remaining results were measured using potentiation. The previous step was repeated by adding 5 mL of 0.4 mM standard solution and 0.6 mM HgCl_2 . Subsequently, the filter paper was eluted with 100 mM HCl. The eluent solution was collected and tested with a potentiometer.

3. RESULT AND DISCUSSION

3.1 Modification of membrane using green synthesized AgNPs

The concentration method used is Solid Phase Extraction (SPE), where the concentration process employs adsorbents to enhance adsorption capacity and method selectivity. One of the commonly used adsorbents is nanoparticles. The use of nanoparticles finds widespread application in various fields such as chemical sensors. The nanoparticles utilized in this method are AgNPs, which possess the advantage of observing interactions between metal surfaces, thus leading to high selectivity and sensitivity of AgNPs towards mercury. The formation of AgNPs is conducted via biosynthesis method, chosen for its environmental friendliness and relative simplicity. The bioreducer utilized in this research is Green Tea extract. Green Tea, with a catechin content of 60-80% [20], has the highest antioxidant content among teas. Antioxidants play a crucial role in the formation process of AgNPs. The color change in the filter paper is influenced by the reduction process of silver ions from organic compounds in plants. According to Thirumugran et al. (2010), the colors indicating the formation of silver nanoparticles range from yellowish to brown [21]. The formation process of nanoparticles occurs due to the reaction between the metal salt solution, AgNO_3 , and the reducing agent, Green Tea extract, which leads to the reduction of Ag^+ to Ag^0 in the form of nanoparticles.

Nanoparticles formed from the biosynthesis process have relatively low adsorption capacity. This is because the AgNPs groups are directly bound to the Si groups in the silica structure, resulting in weak binding of metal ions on the surface of the filter paper. Therefore, APTMS is added to provide functional groups, enabling the silica material to form stronger complexes with metal ions. Figure 1(a) reveals diffraction pattern of AgNPs that is synthesized through bio-reduction using green tea extract. The diffractogram peaks at 2θ of 38.58° , 44.80° , 64.91° , and 77.80° indicate crystalline plane of (111), (200), (220), and (311), respectively from face-centered cubic (FCC) structure of metallic silver (JCPDS No. 01-071-4613) [22]. The un-availability of silver oxide peaks on diffractogram shows that this green process only produces AgNPs [23].

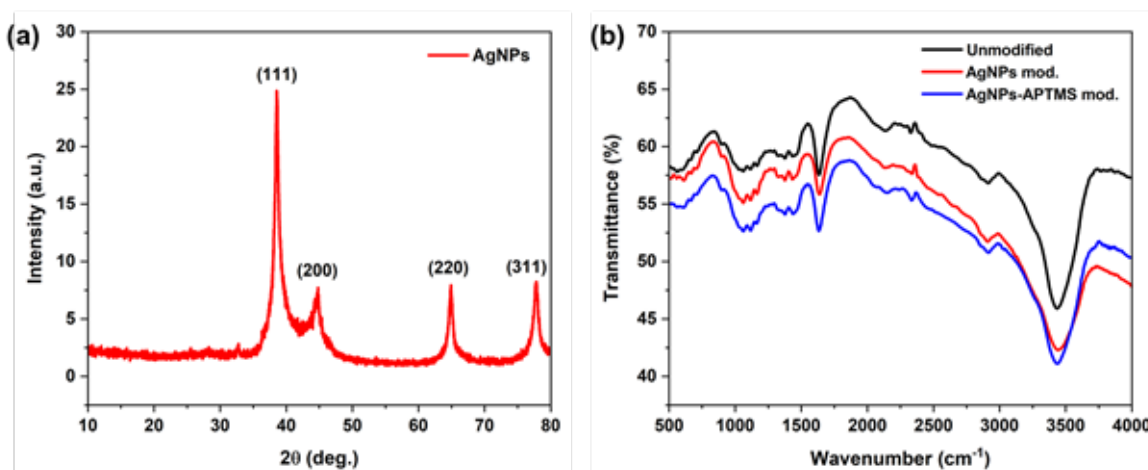


Figure 1. (a) Diffractogram of green-synthesis AgNPs and (b) the FTIR spectra comparison between unmodified, AgNPs modified, then AgNPs-APTMS modified membrane.

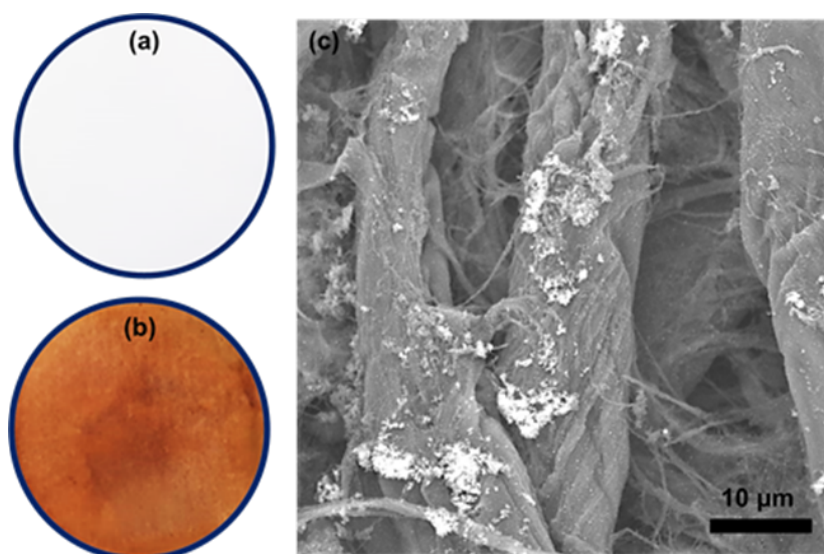


Figure 2. The surface appearance of filter membrane (a) before and (b) after modification, meanwhile (c) SEM image of AgNPs-APTMS modified membrane.

Subsequently, other characterization, FTIR spectroscopy is performed for observing the functional groups on filter paper membrane surface. Sun et al. (2014) reported that tea extract synthesized AgNPs has peaks at wavenumber of around 3370 cm^{-1} (N-H, amides), 2925 cm^{-1} (C-H, alkanes), 1695 cm^{-1} (C=C), 1452 (tertiary ammonium ions), 1371 cm^{-1} (hydroxyl), 1241 cm^{-1} (polyphenols), 1044 cm^{-1} (ether groups) and 926 cm^{-1} (alkene groups) [22]. This spectrum confirms that AgNPs contains amides, polyphenols, carboxyl, and amino groups. The organic compounds play role as reduction agent, then stabilizing of AgNPs surface bound [24]. The analytical findings from the modified filter papers containing AgNPs and AgNPs-APTMS do not exhibit substantial variance compared to the FTIR analysis results of the unmodified filter paper depicted in figure 1 (b). This could be attributed to the filter paper comprising over 98% cellulose, thereby displaying O-H, C-H, and C-O groups. The abundance of these groups makes it challenging for the signals from AgNPs and APTMS to be distinctly discernible, resulting in the FTIR outcomes failing to indicate the presence of AgNPs-APTMS on the filter paper. The shift in peak indicates coordination interactions and the addition of oxygen from APTMS and green tea extract. Similar results are observed in the paper modification using silver nanoparticles synthesized with leftover green tea extract [23].

Significant physical changes in the color of the modified filter paper are observed in figures 2 (a) and (b). The modification results in a color change from white to brown. SEM micrograph observations in figure 2 (c) demonstrate the attachment of AgNPs to the surface of the filter paper fibers. Thus, the modification of the filter paper is confirmed by SEM morphology analysis. The distribution of AgNPs on the surface of the filter paper occurs less homogeneously due to some areas being covered by AgNPs compounds.

3.2 Mercury detection

Optimizing the pH parameter of the sample is highly important as it directly influences the stability of Hg ions. The purpose of pH optimization is twofold: firstly, to determine the ideal acidity level of the filtrate within either the acidic or basic pH range to achieve maximum absorption capacity, and secondly, to minimize the reduction of Hg (II) ions on AgNPs, thereby facilitating the formation of Ag-Hg amalgam.

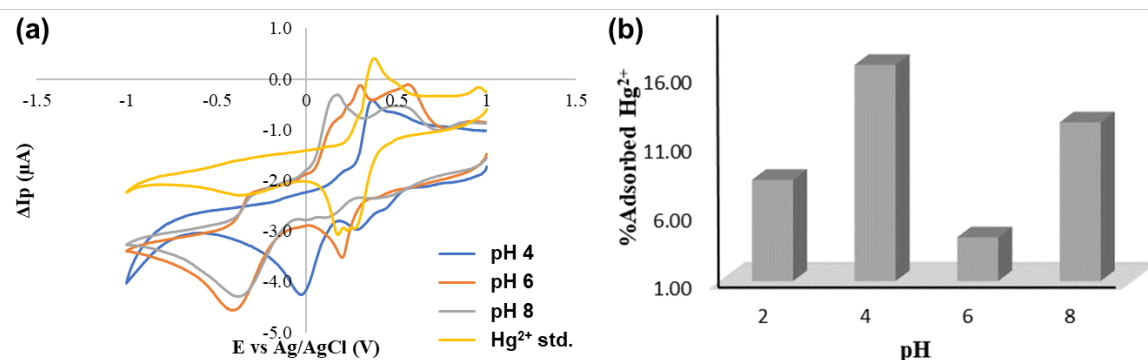


Figure 3. (a) The voltammogram of pH optimization using Au, Pt, Ag/AgCl as working, counter, and reference electrodes, respectively, (HgCl_2 0,5 mM & scan rate 100 mV/s) and (b) the comparison graph among different pH of 2, 4, 6, and 8.

TABLE I. Calculation of adsorbed Hg^{2+} (%) influenced by pH changing.

HgCl_2 conc. (mM)	ΔI_p (mA)	pH	ΔI_p (mA)	Hg_{2+} filtrate (mM)	Adsorbed Hg^{2+} (mM)	% Adsorbed Hg^{2+}
0,5	0,0012	2	0,0010	0,4167	0,0833	8,33
		4	0,0008	0,3333	0,1667	16,67
		6	0,0011	0,4583	0,0417	4,17
		8	0,0009	0,3750	0,1250	12,50

The addition of acid and base, namely 0.1 M HCl and 0.1 N NaOH solutions, serves to maintain the pH value of the solution in accordance with pH variations of 4, 6, and 8. The optimization results of pH can be seen in Figure 3, which displays the voltammograms corresponding to different pH levels. Based on this figure, it is observed that the optimal pH level is acidic at pH 4, as indicated by the purple line. This suggests that the best absorption capacity is achieved at pH 4. Furthermore, a solution with pH 4, or under acidic conditions, results in a 16.67% increase in the absorption capacity of the filter paper compared to solutions with pH 6 and 8 variations. The increase in absorption capacity of the filter paper occurs because fewer free ions are present on the surface of the working electrode, resulting in a lower current response.

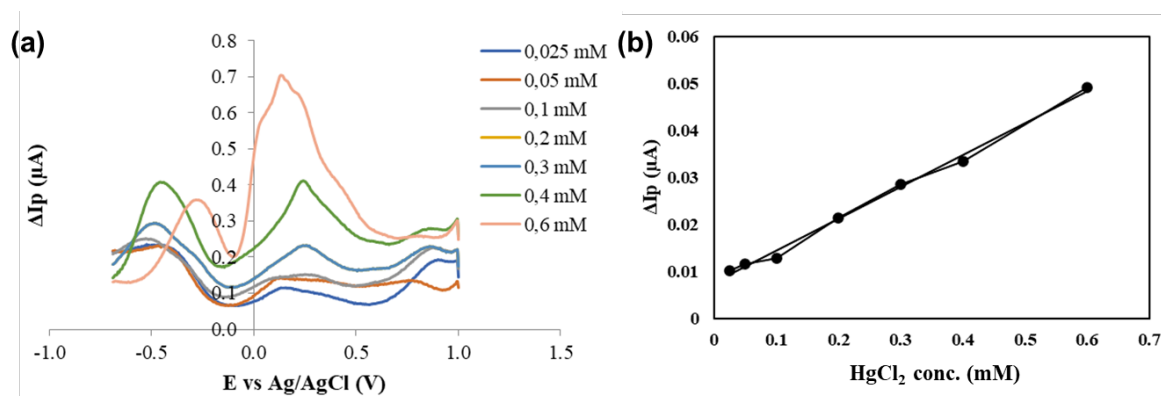


Figure 4. (a) The voltammogram of linearity test using Au, Pt, Ag/AgCl as working, counter, and reference electrodes, respectively, (scan rate 100 mV/s) and (b) correlation graph between concentration of Hg^{2+} and peak current.

Linearity is the response of the analytical method in proportion to the analyte concentration in the sample. The aim of linearity is to establish the linearity relationship or to ascertain the standard's

capability in detecting the analyte present in the test sample. Linearity is determined by measuring the peak current of a series of standard Hg^{2+} solutions at pH 4 that have been prepared. Table 4.5 presents the test data that can be used to determine linearity, resulting in the linear regression equation $y = ax + b$, where a represents the slope, b is the intercept, and x is the concentration. Linearity can be determined using a calibration curve, which illustrates the relationship between the analyte response and the concentration of the standard solution. The x-axis represents the concentration of Hg^{2+} , while the y-axis represents the test response or the peak current generated.

The graph resulting from the determination of linearity is depicted in Figure 4, showing the equation $y = 0.680x + 0.0076$, with $R^2 = 0.9951$ and $r = 0.9975$. The linear relationship can be assessed using the correlation coefficient (r) in linear regression analysis. Linearity is evident when the correlation coefficient value is either +1 or -1, depending on the direction of the linear line. With a correlation coefficient value of 0.9975 obtained from the calculation, it indicates a strong linear relationship in this testing method for assessing Hg^{2+} in cosmetic samples, as the coefficient value approaches 1. This coefficient value signifies the relationship between the two influential data, where the graph resulting from the testing exhibits a direct proportionality; as the concentration of the standard solution increases, so does the obtained current.

Moreover, the Limit of Detection (LOD) is the lowest concentration of an analyte that can be detected and identified without requiring quantification, while the Limit of Quantitation (LOQ) is the smallest concentration or amount of the analyte that can be determined with a certain level of precision and accuracy. Determination of the LOD and LOQ can be performed using three methods, including signal-to-noise ratio, blank determination, and calibration curve. In this testing, the LOD and LOQ are determined using a linear calibration curve method, where the response of the instrument on the y-axis has a linear relationship with the standard concentration on the x-axis, expressed through the equation $y = ax + b$.

The limit of detection is obtained by dividing three times the standard deviation of the intercept by the slope (the slope of the line). The standard deviation of the intercept obtained is 0.0076 with the equation $y = 0.068x + 0.0076$. Meanwhile, the limit of quantitation is obtained by dividing ten times the standard deviation of the intercept by the slope. The value of the limit of detection obtained is 0.0483 mM, which is the smallest amount that can be detected by the instrument, and the limit of quantitation is 0.1611 mM. This quantitation value indicates the smallest amount that meets the criteria of accuracy and precision.

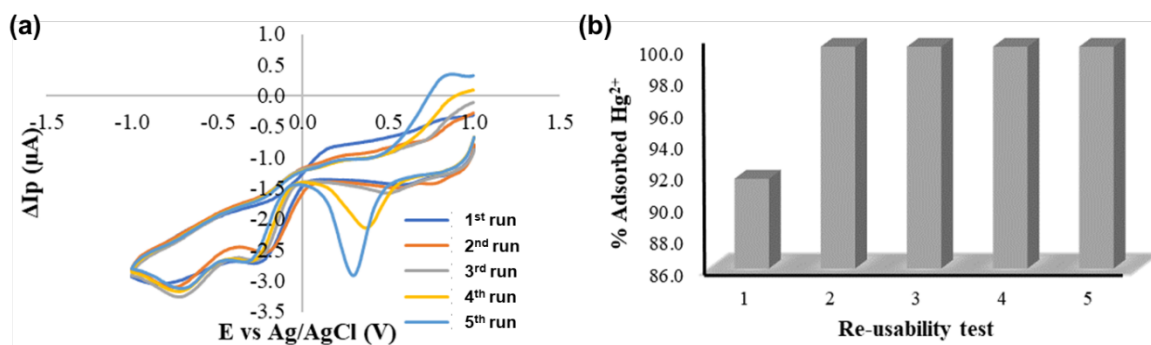


Figure 5. Stability test of modified membrane for Hg^{2+} adsorption.

Testing the effectiveness of the modified filter paper is conducted to assess the stability of the modification, aiming for a more economical method with reduced waste production. The effectiveness of the filter paper modified with AgNPs is evaluated by measuring the current against standard Hg^{2+} solutions filtered using this modified paper. The voltammogram results, depicted in Figure 5(a), show nearly identical peak currents across five repetitions. Then, figure 5(b) shows the measurement diagram of the filter paper modified with AgNPs, indicating that the filter paper used in five repetitions exhibits excellent absorption capacity and durability against the cosmetic samples tested when repeated testing is conducted. The current values show no significant differences among the filter papers used. The filter paper utilized demonstrates excellent adsorption capability even after five rounds of sample testing.

4. CONCLUSION

The pre-concentration technique can be performed using the adsorption method on filter paper, utilizing AgNPs material with Green Tea extract as the modifying agent, reduced by APTMS. Characterization results confirm the presence of AgNPs and APTMS on the surface of the filter paper membrane. The modified membrane demonstrates a good ability to reject Hg^{2+} ions, with optimization measurement results yielding a correlation coefficient of 0.9975 and LOD and LOQ values of 0.0483 mM and 0.1611 mM, respectively.

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