



# Development of a Modified Screen Printed Electrode for the Determination of Heavy Metals in Water Before and After Remediation With Food Grade Pectin and Citrofortunella Microcarpa Rinds

## Introduction

The rapid increase in population, urbanization, and industrialization, along with inadequate water quality monitoring and wastewater management, contribute heavily to the pollution of water resources. Among the water contaminants of major concern, heavy metals are particularly considered as the most worrisome. Heavy metals tend to accumulate in the tissues of aquatic organisms (Ahmed et al., 2019; Rajeshkumar & Li, 2018; Tabrez et al., 2021) and thus increase in concentration upon moving higher up the food chain. This indicates that once humans ingest these organisms, they have a high risk of experiencing health problems as heavy metals are absorbed into their bodies, leading to the formation of diseases that can be life-threatening. Lead, for instance, can cause kidney and nervous system damage, mental retardation, and cancer (Carolin et al., 2017; Pratush et al., 2018; Vareda et al., 2019; Wani et al., 2020; Zamora-Ledesma et al., 2021). These harmful effects of heavy metals on the human body and the environment require the development of cost-effective technologies to efficiently detect and remove them from water.

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Traditional detection techniques for heavy metals, such as atomic absorption spectroscopy and inductively coupled plasma mass spectroscopy, are expensive, not well suited for in situ measurements, and require complicated instrumentation. Electroanalytical techniques, such as anodic stripping voltammetry (ASV), cyclic voltammetry, differential pulse voltammetry (DPV), and square wave voltammetry (SWV), are more promising alternatives due to their rapid response, ease of operation, cost efficiency, and on-site application, providing high sensitivity, specificity, and accuracy (Lu et al., 2018; Mei & Ahmad, 2021).

Several methods have been used to remove heavy metals from water. Many of these methods have inherent limitations, such as the generation of a large amount of sludge, low efficiency, sensitive operating conditions, and costly disposal (Renu et al., 2017). A potentially preferred alternative for the removal of heavy metals in water is biosorption due to its high efficiency, low cost, and ease of operation (Gomez-Aguilar et al., 2022). Natural sorbent materials employed in biosorption include those derived from biomass, fungi, fruits, algae, humic substances, and by-products from food, agriculture, fisheries, wood, and textile manufacturing. Using by-products not only reduces the cost of removing heavy metals from water but also decreases the amount of residuals that are accumulated in the environment (Wołowiec et al., 2019). Pectin, the main component of some fruit peels and pulps, is found to be capable of absorbing heavy metals (Deshmukh et al., 2017; Lessa et al., 2020; Wang et al., 2016).

In this study, a highly sensitive bismuth/silver nanoparticles/Nafion (Bi/AgNP/Nafion)-modified screen-printed graphene electrode (SPGE) was fabricated and was utilized in ASV for the detection of trace lead (Pb) concentrations in river water samples prior to and after remediation using calamansi (*Citrofortunella Microcarpa*) rinds in different forms, that is, ground sun-dried, dry-ashed, food-grade pectin, fractionated pectin, and alcohol insoluble solids (AIS)-extracted pectin.

## Results and Discussion

The fabricated Bi/AgNP/Nafion-modified SPGE was characterized using scanning electron microscopy and energy dispersive x-ray spectrometry, which confirmed the presence of the modifiers on the electrode surface. The optimum amount of silver nanoparticles was found to be 1.0 mg, and the optimal deposition time and potential were found to be 110 s and  $-9.0$  V, respectively. Under these optimized conditions, the limit of detection of the modified SPGE was found to be 267.6 ppt, and a strong linear correlation ( $R^2 = 0.999$ ) between the Pb concentration and the anodic current response was obtained. Stability test showed insignificant depreciation even after 30 cycles. The optimized electrode was then used to detect lead in river water samples prior to and after a novel method of water remediation using calamansi rinds in different forms, namely, ground sun-dried, dry-ashed, food-grade pectin, fractionated pectin, and AIS-extracted pectin. All these forms of pectin remediated trace Pb concentration in varying amounts. The ground sun-dried calamansi rinds removed a Pb concentration of up to 19%, whereas the AIS-extracted pectin yielded the highest attenuation of up to 70%. Hence, this novel method of using calamansi rinds in different forms is an effective method for the removal of lead in water (Palisoc et al., 2021).

## Policy Recommendation

To minimize heavy metal pollution and its associated health hazards, policies that would translate to excellent water quality monitoring and wastewater treatment must be implemented and strictly enforced. Remediation using cost-effective and eco-friendly techniques, such as the use of food-grade pectin and calamansi rinds, should be carried out to remove heavy metals from contaminated water resources. Routine analysis using the modified SPGE developed in this study must be done prior to and after the remediation process. Moreover, people should be made aware of the health risks caused by exposure to heavy metals through public education and awareness campaigns. Determination of heavy metals in fish and seafood is also recommended to provide possible evidence of bioaccumulation of heavy metals in human food derived from contaminated aquatic systems.

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