PAPER-BASED ELECTRODE USING *CLADOPHORA* CELLULOSE-POLYANILINE COMPOSITE FOR ELECTROCHEMICAL QUANTIFICATION OF TOXIC LEAD (II)

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A simple method to accurately detect lead (II) in low concentrations is highly desirable. This study describes the fabrication of a paper-based electrode using *Cladophora rupestris* cellulose coated with polyaniline (PANI) for detection of toxic lead. Polyaniline was polymerized along the fibers of *Cladophora* cellulose, affording thin layers of PANI on cellulose, while preserving its highly crystalline nature. The composite was fabricated into a working electrode and the cyclic voltammetry (CV) profile showed the characteristic double peak of polyaniline. Following the optimization for the anodic stripping voltammetry (ASV) of Pb, the developed electrode had a linear working range of 0.2 ppm to 1.0 ppm and a low limit of detection at 0.348 μM (0.0721 ppm) for Pb^{2+} in a low-cost platform. A comparison using standard atomic absorption spectroscopy (AAS) techniques showed no significant difference in detecting lead, highlighting the potential of paper-based electrochemical sensors for rapid water quality monitoring.

INTRODUCTION

The accumulation of toxic heavy metals, such as lead (Pb), in the environment is a major issue affecting the health of humans and animals. Lead pollutants are derived from industrial processes, such as lead smelting, lead-based paints, lead-containing solders and pipes, coal combustion and battery recycling, among others.[1] Lead is known to affect the central nervous system, the hematopoietic, hepatic and renal systems, producing serious irreversible disorders.[2] Unfortunately, the environmental detection and quantification of toxic lead are costly, requiring certified personnel and sophisticated instrumentation. Thus, analysis of toxic metals becomes prohibitive, especially for occupational exposure evaluation and environmental monitoring. One of the efficient methods of detecting metals is through electrochemical detection, where the critical component is the working electrode. This is because all the electrochemical reactions occur on its surface. The working electrode, therefore, is a very delicate component, which requires frequent cleaning to remove contaminants to maintain the reliability of the electrochemical analysis. This electrode cleaning technique is a labor-intensive and time-consuming operation that limits the practicality of the electrochemical detection. Thus, it is highly desirable to develop efficient but low-cost working electrodes for one-time use.[3-5] We report herein a simple and economical technology that can potentially make the quantification of toxic metals more accessible.

Disposable working electrodes have been reported for various purposes.[6-9] The most common are screen printed electrodes[10-11] and those involving nanomaterials.[12-14] However, they still have shortcomings, such as the need for

expensive substrates and unsatisfactory reproducibility. Cheap and disposable electrodes require a reliable and sensitive substrate. Paper is an ideal substrate for electronics due to its abundance, biodegradability, bendability, light-weight property and recyclability.[15-16] Demonstrations on the utility of paper as a substrate for electronics[17] include sensors,[18-20] biodetection[21-23] displays,[20] transistors,[24] radiofrequency identification devices,[25] generators,[26] light-emitting diodes and energy storage devices.[27] Since paper possesses an inherent poor electrical conductivity in the order of 10^{11}-10^{15} Ω sq^{-1},[17] paper-based electronics are typically fabricated by depositing or growing electro-active components onto the cellulose fibers by chemical modification or coating.[28-30] Another approach is by assembling electrically conductive materials, such as carbon nanotubes, graphene and carbon fibers into paper-like films.[31-32] In these approaches, paper-based electronics exhibit very good electrochemical performance, while retaining its excellent flexibility. These paper-based electronics can potentially achieve ultra-high power density and energy density due to the ultra-small electrical resistance and volume of the cellulosic material.

The common choice of cellulosic material in the development of paper-based electronics is mostly based on filter paper due to its wicking ability, porosity, particle retention and flow rate.[33-34] An interesting cellulosic material is a cellulose derived from the environmentally polluting green algae (*Cladophora* sp.). The excessive blooming of these algae in bodies of water as triggered by water chemistry leads to serious ecological imbalance. The utilization of these abundant, yet unwanted materials is highly desirable, which motivated this study. The unique feature of the cellulose extracted from *Cladophora* sp. is that it exhibits a higher degree of crystallinity, as compared to plant-derived cellulose (95% *vs*. 82%; X-ray diffraction).[35] It also possesses a larger surface area (63-95 m^2/g *vs*. 1 m^2/g *via* N$_2$ gas adsorption) and higher pore volume (0.554 cm^3/g *vs*. 0.003 cm^3/g; BET N$_2$ adsorption), as compared to wood cellulose.[36-37] These characteristic features of *Cladophora* cellulose make it a good renewable source for highly crystalline material, which has found applications as reinforcement fibers,[38] filter medium, drug carriers and rheology enhancers.[39] Recently, we reported the distinguishable characteristics of the *Cladophora rupestris*

cellulose collected in a freshwater volcanic lake, compared to seawater algae. Coating conducting polyaniline (PANI) on *Cladophora* cellulose revealed that the nano-layer of PANI preserved the high surface area of the cellulose, allowing efficient remediation of toxic chromium (VI).[40]

The paper-based protocol for the detection of toxic heavy metals is highly desirable towards cheap, renewable, disposable and portable environmental monitoring. Current paper-based heavy metal sensors are based on microfluidic systems, where continuous wicking of the analyte solution across the electrodes increases the efficiency and sensitivity of Pb (II) detection.[41] More advanced designs utilize the same microfluidic principles involving 3D geometries.[42] Paper-based electrodes, incorporating silver or carbon inks on paper towards analysis of Pb (II), highlight the potential of paper-based sensors for the detection of heavy metals.[43-44] However, despite their potential, they still present limitations with regard to accuracy and sensitivity.

An efficient approach to the electrochemical detection of heavy metals is through anodic stripping voltammetry (ASV) because metal pre-concentration on the electrode surface generally occur.[45] Moreover, ASV has the potential for portability due to its short response time, lower cost and remarkable sensitivity, compared to other techniques. However, paper-based substrates were shown to be inferior to plastic substrates towards anodic stripping of heavy metals, including lead (II).[46-47] The objective of this work is to demonstrate the potential of *Cladophora* cellulose as a material for the paper-based electrode. We report herein the fabrication of a highly sensitive *Cladophora* cellulose-based electrode for the detection and analysis of toxic Pb (II) by anodic stripping voltammetry (ASV).

EXPERIMENTAL
Materials
The aniline (Techno Pharmchem), ammonium peroxodisulfate (Merck), Polysorbate 20 (Asia Pacific Specialty Chemicals Limited), NaOCl$_2$, acetic buffer, HCl, NaOH, potassium dichromate (UNIVAR Ajax Chemicals) were used as received. Unless otherwise specified, deionized (0.006 μS) water was used. The green *Cladophora rupestris* algae were collected from the shores of Taal Lake in Barangay Balas, Talisay, Batangas, (14.08°N, 121°E), Philippines. Infrared (IR) spectrometry was done on a Nicolet Nexus 6700 FTIR. Energy dispersion X-ray spectroscopy (EDX) and scanning electron microscopy (SEM) were done using

a JSM-5310 Scanning Microscope. Electrochemical impedance spectroscopy (EIS) was done using a Metrohm Autolab Potentiostat PGSTAT 128N with Nova 2.0 software.

Extraction of cellulose and preparation of Clad-PANI composite

The extraction of cellulose from *Cladophora* was done following the previously described protocol.[40] The coating of PANI onto the *Cladophora* cellulose was achieved by first soaking the *Cladophora* cellulose (300 mg) in 150 mL deionized water overnight, followed by sonication (KLN Ultraschall-GMBH 6148 at a frequency of 39 KHz) for 20 min at 45 °C to loosen the fibers. The cellulose was collected through filtration and then added to the aniline-HCl solution (2.60 g of aniline-HCl dissolved in 50 mL deionized water stabilized with a drop of polysorbate-20) and dispersed again through sonication for 10 minutes at 45 °C to allow the anilinium chloride to adsorb onto the cellulose fibers. The mixture was filtered through suction filtration. To induce polymerization of aniline, 50 mL of ammonium peroxodisulfate was added dropwise and allowed to pass through the filter cake. The formation of polyaniline was observable through a blue-green coloration of the filter cake. The composite was filtered through suction filtration and the collected sample was subjected again to sonication with 25 mL aniline-HCl solution for 10 minutes. The polyaniline-coated cellulose was then filtered in a Buchner funnel and was rinsed thoroughly with HCl (0.2 M, 1 L). The treatment by HCl ensures the formation of the emeraldine salt (ES) form of PANI. After washing with deionized water until it becomes neutral, the filtered composite was then subjected to sonication with acetone for 20 minutes to remove free PANI, and then rinsed with acetone through a filter paper until the acetone washing becomes clear. It was then air dried and stored in a desiccator.

Characterization of Clad-PANI composite

The composite was characterized for its functional groups by FT-IR using the KBr pellet method. For elemental analysis by EDX, the samples were sprayed with gold shots and mounted onto the sample holder using double-sided carbon tapes. The morphology of the gold-sprayed samples was analyzed by SEM; the surfaces were scanned and viewed at different magnifications. Electrochemical impedance spectroscopy (EIS) was carried out in a two-electrode set-up. The Clad-PANI composite (50 mg) was first pelletized using a pellet press (¼ inch in diameter). The pellet was then sandwiched between two stainless steel plates using a clip and connected to the potentiostat *via* alligator clips. Measurements were performed in the 10^6-10^{-2} Hz frequency range. The amplitude of the sinusoidal voltage was 10 mV.

Fabrication of Clad-PANI electrode

A working electrode was fabricated using a pelletized *Cladophora* cellulose-polyaniline composite, clear epoxy (Pioneer), silver paste (Electron Microscopy Sciences) and copper wire (PhilFlex). The control electrodes were prepared similarly: epoxy molded copper wire and silver paste (positive control), epoxy-molded *Cladophora* cellulose and pure epoxy electrode (negative controls). All electrodes were connected to an insulated copper wire.

Electrochemical investigations

The working electrode was tested and optimized using the cyclic voltammetry technique in a three-electrode system (reference electrode: Ag/AgCl; and counter electrode: Pt) connected to a potentiostat (Metrohm Autolab Potentiostat PGSTAT 128N with Nova 2.0 software). Every cycle was performed at room temperature for five minutes of purging with nitrogen gas before scanning using 0.5M sulfuric acid (H_2SO_4) as the electrolyte solution. Cyclic voltammetry scans (-1 to 1 V) were performed at increasing scan rates (60-140 mV/s) and three cycles were done at each scan rate. The redox behavior for polyaniline is well documented and peaks were observed through the voltammetric curves.

Anodic stripping voltammetry (ASV) was performed using the linear sweep stripping voltammetry technique in a three-electrode system (working electrode: Clad-PANI; reference electrode: Ag/AgCl; and counter electrode: Pt). The parameters for pH, deposition time and deposition potential were optimized first using 1 ppm Pb in acetate buffer solution. The optimized parameters were: deposition potential = -1V, deposition time = 180 s, resting time = 30 s, ramp range = -1 V to 0 V at a rate of 0.05 V/s, pH of acetate buffer = 4.0. Using the optimized parameters, ASV was used to detect different concentrations of lead standards (0.2, 0.4, 0.6, 0.8 and 1.0 ppm). All measurements were done under continuous stirring and nitrogen conditions. A calibration curve was established and the analytical sensitivity, limit of detection (LOD) and limit of quantification (LOQ) of the paper-based working electrode were calculated. LOD was determined by multiplying the standard deviation of the blank with 3.3 and dividing by the slope (m) of the calibration curve. LOQ was determined by multiplying the standard deviation of the blank by 10 and dividing this by the slope of the calibration curve.[48] The same set of lead standard solutions was analyzed using atomic absorption spectroscopy (AAS) (Shimadzu AA 6300) for comparison. AAS experimental conditions: 283 nm wavelength, 0.5 nm slit, lead halo cathode lamp, 10 mA current, 2.0 L/min acetylene flow rate, 15.0 L/min air flow rate. The ASV readings (triplicate) of the fabricated paper-based electrode were compared with AAS results to test for accuracy.

RESULTS AND DISCUSSION
Synthesis and characterization of *Cladophora* cellulose-polyaniline composite

The as-prepared cellulose-PANI composite is emerald green in color, characteristic of the emeraldine salt, which is the conductive form of polyaniline.[49] A thin coating of PANI on the cellulose fibers was achieved by controlling the polymerization of aniline to prevent bulk formation. This was done by allowing the aniline monomers to first adsorb onto the surface of the crystalline cellulose fibers through H-bonding, after which, the polymerization agent was simply passed through the cake. This technique allows short contact between the monomers and the polymerization agent. As a result, the aniline monomer adsorbed in cellulose polymerizes as it gets in contact with the polymerization agent and the formed PANI becomes coated onto the cellulose fibers. This technique allows the formation of a nano-layer (~50 nm) of polyaniline (PANI) on the cellulose fibers, as compared to the micro- and milli-layers that can be formed by the one-pot bulk polymerization technique.

Cellulose fibers are known to be well-wetted by polymers, like polypyrrole, making the homogeneous coating of individual cellulose fibers possible.[50-51] SEM morphology of *Cladophora* cellulose (Fig. 1 (C)) is smooth, whereas the Clad-PANI composite (Fig. 1 (D)) shows fiber surfaces coated with amorphous coating, indicating uniform morphological attachment of polyaniline on the cellulose surface. A nano-layer of PANI coating on cellulose fibers maintains the characteristic high surface area of *Cladophora* cellulose. EDX elemental analysis confirms the polyaniline coating, as indicated by the presence of nitrogen (29.7) and chlorine (1.4%) (other elements are carbon 30.6% and oxygen 38.3%), which are absent in raw cellulose. FTIR spectra further confirm the presence of polyaniline in the composite (Fig. 2).
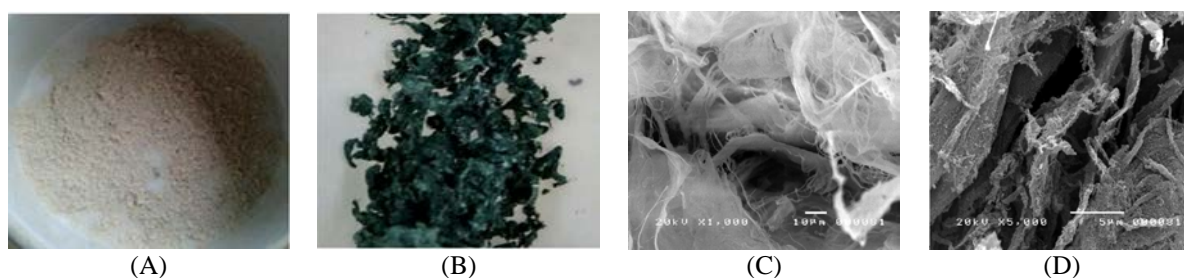

(A)   (B)   (C)   (D)

Figure 1: (A) *Cladophora* cellulose; (B) *Clad*-PANI composite; (C) SEM surface morphology of *Clad* cellulose; (D) SEM surface morphology of *Clad*-PANI composite
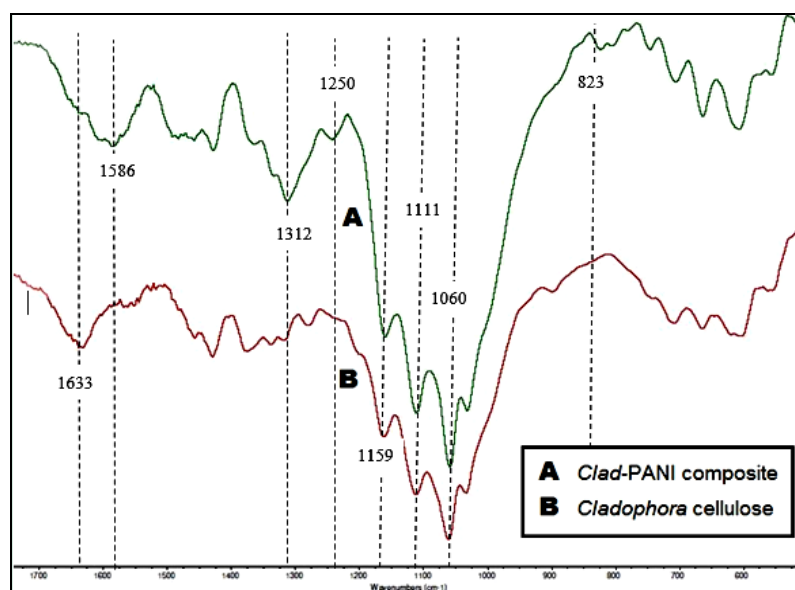

Figure 2: Overlay of infrared spectroscopy spectrum of Clad-PANI composite and pure *Cladophora* cellulose
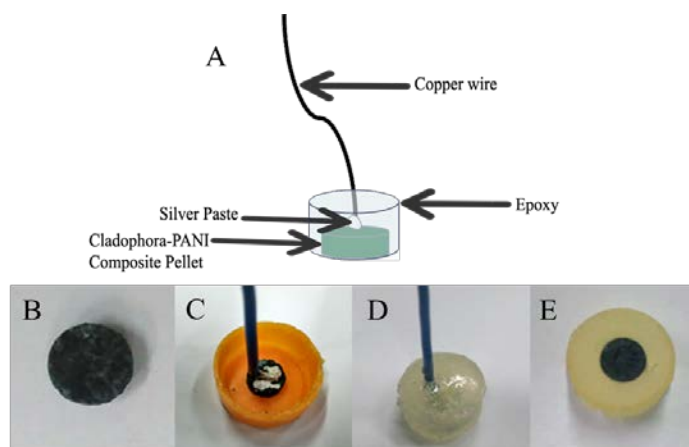
Figure 3: Pelletized composite developed into a working electrode; A) the electrode composition, B) pelletized Clad-PANI, C) silver paste connecting the composite to the copper wire in the mold, D) epoxy-molded electrode top view, E) epoxy-molded electrode bottom view

The characteristic absorptions of PANI, such as the C-H out-of-plane deformation in 1,4-disubstituted benzene (823 cm^{-1}), the C-N-C bond (1250 cm^{-1}), the secondary aromatic amine (1312 cm^{-1}) and benzenic-quinonic nitrogen (1586 cm^{-1}), are observed in the composite, but were absent in the raw cellulose.[52-53] Conductivity was measured through electrochemical impedance spectroscopy (EIS) by modeling an electrical circuit that represents the electrochemical behavior of the material. The experimental conductivity value of the composite was 1.10×10^{-3} ($\pm 7.8 \times 10^{-4}$) S/cm, which is within the 10^{-5} to 10^{-1} S/cm theoretical range of conductivity of PANI.[54] Thus, it can be deduced that PANI in the composite is in its conductive form and can conduct electrical signals.[55]

Fabrication and characterization of the Clad-PANI electrode

The *Clad*-PANI composite was compressed into pellets of ¼ inch in diameter. Silver paste connects the composite with the copper wire ensuring connectivity and the epoxy molds the electrode sealing the connection (Fig. 3). This stabilized the connection and ensured the electrochemical readings of the electrode are through the *Clad*-PANI composite and not through the other components.

Comparing the voltammogram of the Clad-PANI electrode (Fig. 4 (A)) with that of the positive control (epoxy-molded copper wire with silver paste electrode) showed the latter having a significantly higher peak current, which was expected for copper as it is a highly conductive metal.[56] Moreover, the CV profile of the copper wire/silver paste electrode showed only one peak, whereas the *Clad*-PANI electrode has a distinct double peak. On the other hand, when the Clad-PANI electrode (Fig. 4 (B)) was compared to the negative controls (epoxy-molded *Cladophora* cellulose electrode and pure epoxy electrode), a considerably higher peak current was observed for the PANI-coated electrode, compared to the negative controls. Very small peaks were observed for the pure cellulose electrode, while no peak readings were observed for the pure epoxy electrode, proving its inertness.

The CV profile of the Clad-PANI electrode shows a smooth redox curve with two pairs of peak currents, characteristic of PANI cyclic voltammograms.[57-59] This indicates that the electrochemical readings are due to the Clad-PANI composite and not to other components. Polyaniline has two distinct peaks in cyclic voltammetry (Fig. 5). Each peak corresponds to a redox reaction from one oxidation state of PANI to another. The first pair of peak currents ($E_{red} = -0.60$ V; $E_{ox} = -0.41$ V) corresponds to the leucoemeraldine (fully reduced)/emeraldine (half oxidized) couple. The higher intensity is due to the conductivity of the emeraldine form. The second pair ($E_{red} = 0.30$V; $E_{ox} = 0.8$V) corresponds to the further oxidation into the pernigraniline (fully oxidized) form.[57,58,60] The second peak current exhibits a broader oxidation wave compared to the first peak, indicating that the charge transfer that takes place is more difficult for the second oxidation of PANI.[58]

Using the sulfuric acid electrolyte, which is the standard electrolyte in the characterization of PANI modified electrodes,[57,61,62] the CV profile of

the Clad-PANI electrode (Fig. 5) shows a quasi-reversible system with the peak current ratio (I_{pa}/I_{pc}) of 0.785 and the peak potential separation (ΔE_p) > 0.2V. There is a very small decrease in peak current upon cycles (%RSD I_{pa} = 1.782; %RSD I_{pc}= 1.394), indicating the composite is relatively stable and remains redox active upon cycles.[57,59]
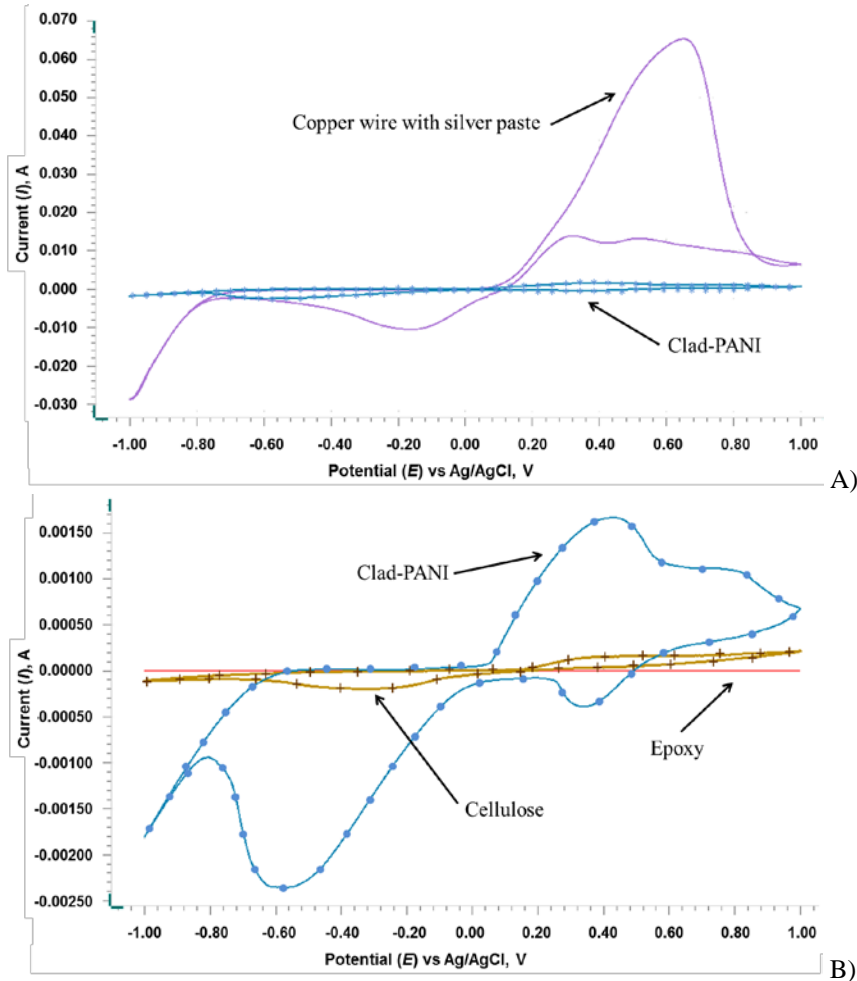

Figure 4: Cyclic voltammograms of A) *Clad*-PANI electrode as compared to the positive control – copper wire with silver paste electrode, B) *Clad*-PANI electrode as compared to the negative controls – pure *Cladophora* and pure epoxy electrodes
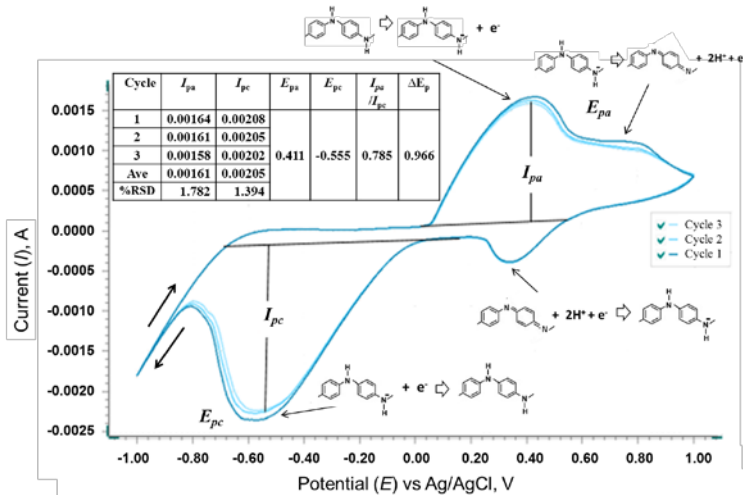

Figure 5: Cyclic voltammogram of *Clad*-PANI working electrode, scanned from -1 V to 1 V (*vs*. Ag/AgCl reference and Pt counter electrodes) with a scan rate of 100 mV/s in 0.5 M H_2SO_4 electrolyte solution
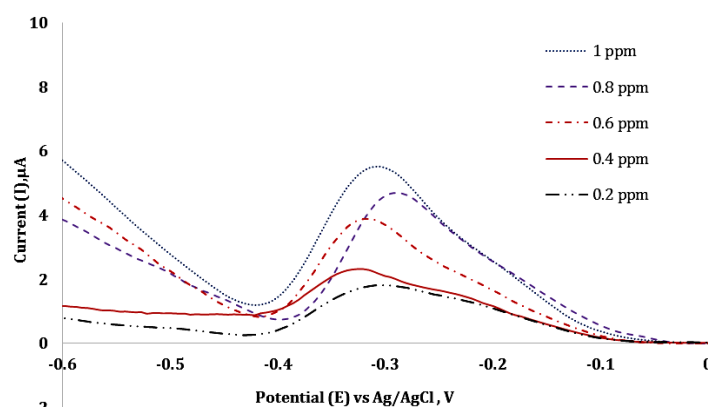
Figure 6: ASV voltammogram for the detection of lead

Table 1
Calculated analytical sensitivity for lead

Concentration (ppm)	Slope	Standard deviation	Analytical sensitivity (ppm^{-1})
0.2		0.0435	95.84
0.4		0.0408	102.24
0.6	4.1679	0.3225	12.92
0.8		0.2519	16.55
1.0		0.4932	8.45

The CV recorded at different scan rates (from 60 to 140 mV/s) showed a linear increase in peak current as the scan rates increased (not shown), indicating that the system is diffusion controlled. This means that the reaction happens instantaneously, as opposed to being activation controlled, which would require a minimum concentration to initialize. This is desirable because diffusion controlled systems allow the easy detection of analytes

Detection of lead using the electrode and anodic stripping voltammetry

The window potential test for anodic stripping voltammetry (not shown) showed the absence of prominent peaks, indicating the lack of reactions between the paper-based Clad-PANI electrode and the acetate buffer electrolyte. This signifies the suitability of the acetate buffer as electrolyte solution because it does not interfere with the electrochemical activity.

The ASV parameters were optimized to obtain the most efficient overall parameters for the specific electrolyte solution, electrode surface and electrochemical set-up. The highest peak current readings were found at a deposition time of 180 s, deposition potential of -1 V and acetate buffer pH of 4.0. Standard lead solutions of 0.2, 0.4, 0.6, 0.8 and 1.0 ppm were read through ASV, using the Clad-PANI electrode as the working electrode (Fig 6). The obtained calibration curve gave an acceptable $R^2 = 0.9707$. The analytical sensitivity (γ) was measured to determine the ability of the Clad-PANI electrode to distinguish between small differences in concentration in different samples. The analytical sensitivity (Table 1) was seen to decrease with increasing concentration. This trend indicates that the electrode is more sensitive to changes at lower concentrations of lead. The calculated limit of detection (LOD), which is the lowest analyte concentration that can be reliably distinguished from a blank sample, and the limit of quantification (LOQ), which is the lowest concentration that can be determined with an acceptable level of repeatability, precision and trueness,[63] for the detection of lead were 0.0721 ppm (0.348 μM) and 0.2184 ppm (1.052 μM), respectively. This indicates that the Clad-PANI electrode can detect low concentrations of lead. Mercury electrodes or bismuth film electrodes are

usually the standards in enhancing sensitivity in stripping voltammetry,[64,65] yet the paper-based electrode showed promise as a sensitive electrode for the detection of lead. Among the non-mercury and non-bismuth low-cost electrodes, the limit of detection at 0.348 µM is better than the 1.65 µM (342 ppb) LOD for the EDTA-PANI/SWCNT system in stainless steel substrate, developed by Deshmukh *et al.*,[66] despite the chelating effect of EDTA to enhance detection.

Table 2
Comparison of concentration readings from AAS *versus* the fabricated working electrode

Sample	AAS		ASV using *Clad*-PANI electrode			% Difference	% Error
	Conc. (ppm)	%RSD*	Ave I (µA)	Conc. (ppm)	%RSD*		
1	0.5106	2.57	3.237	0.5108	5.23	9.30	8.89
2	0.4704	0.93	3.092	0.4787	2.39	8.27	7.95
3	0.5077	2.04	3.088	0.4777	3.20	17.54	16.13

*%RSD = Relative standard deviation

The accuracy of the fabricated working electrode was tested by comparing the ASV data with the standard method of toxic metal detection through AAS (Table 2). The obtained concentrations for the sample solutions determined using the Clad-PANI electrode are close to that obtained from AAS. The precision of readings for AAS *vs*. ASV, evaluated using the percent relative standard deviations (%RSD), are both within the acceptable deviation of 15%. The percent difference and percent errors calculated were all within the acceptable 10% margin of error and t-test analysis (p-value of 0.6030) showed no significant difference. Consequently, it can be concluded that the detection of lead using ASV with the Clad-PANI electrode is a relatively good method to estimate the concentrations of lead in comparison to AAS.

CONCLUSION

The Clad-PANI composite was prepared by polymerizing the aniline adsorbed on the cellulose chains. Characterization indicates that coating PANI onto cellulose fibers affords a conductive composite. The conducting paper composite was fabricated into a working electrode and the cyclic voltammetry profile revealed quasi-reversibility, showing the characteristic double peaks of PANI. Anodic stripping voltammetry (ASV) showed that the analytical sensitivity of the electrode (LOD = 0.0721 ppm (0.348 µM) and LOQ = 0.2184 ppm (1.052 µM)) is better at detecting lower concentrations of lead. The ASV detection of lead using the Clad-PANI electrode was compared with the standard AAS technique and the results were found to be within the acceptable 10% margin of error, revealing no significant difference (p-value of 0.6030) between the two

techniques. Thus, the simple and cheap fabricated Clad-PANI electrode can detect lower amounts of lead accurately, making it highly promising for portable lead detector applications using ASV.

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