UMYU Scientifica, Vol. 1 NO. 1, September 2022, Pp 221 – 226
https://doi.org/10.56919/usci.1122.028
ISSN: 2955 – 1145 (print); 2955 – 1153 (online)
A periodical of the Faculty of Natural and Applied Sciences, UMYU, Katsina

ORIGINAL RESEARCH ARTICLE

Modification of Glassy Carbon Electrode Using Microcrystalline Cellulose-Ethylenediaminetetraacetic Acid for the Detection of Lead and Cadmium Ions

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ABSTRACT

There is a greater need for the identification and monitoring of metal contaminants as a result of the growing hazard that heavy metal contamination of water poses to the environment. In this work, microcrystalline cellulose was functionalised with ethylenediaminetetraacetic acid, and the product analysed using scanning electron microscopy and X-ray diffraction techniques. The functionalised microcrystalline cellulose-ethylenediaminetetraacetic acid was employed for the modification of glassy carbon electrode. Detection for Pb^{2+} and Cd^{2+} ions was determined using square wave anodic stripping voltammetric analysis at square wave potential scan of -1.0 V to -0.2 V, and deposition potential of -1.0 V in 0.1M acetate buffer for 240 sec. Higher current response of Pb^{2+} was obtained at -0.6 V and that of Cd^{2+} at -0.8V. Limit of detection for Pb^{2+} was 1.8 ppb (MCC-EDTA GCE) and 5.0 ppb (MCC-GCE) , while that of Cd^{2+} was 7 ppb (MCC-EDTA GCE) and 10 ppb (MCC-GCE), these indicate MCC EDTA GCE has higher sensitivity towards detection of the metal ions and selectivity of modifiers for detection of Pd^{2+} and Cd^{2+} was achieved successfully.

ARTICLE HISTORY

Received September 2, 2022
Accepted September 27, 2022
Published September 30, 2022

KEYWORDS

Electrochemical sensor, Lead, Cadmium, Glassy Carbon electrode, Microcrystalline Cellulose, Microcrystalline Cellulose-Ethylinediamine Tetra acetic Acid.

INTRODUCTION

Increasing heavy metal pollution which is hazardous to the environment and living things has been the subject of considerable interest. Heavy metal pollution is a problem associated not only to intensive industries but also hugely contributed by automobiles. Heavy metals are non-biodegradable chemical species that can exist in various forms for a long time (Proshad *et al.,* 2021). For instance, cadmium has a biological half-life of 10 to 33 years in the human body and is extremely poisonous even at low concentrations. It also bio-accumulates in other organisms and the ecosystem (Genchi *et al.,* 2020). On the other hand, accumulation of lead occurs slowly in the body, over 95% of the lead in an adult's body is found in their bones and teeth. The body can mobilize its lead reserves at stressful times, especially during pregnancy and lactation, which raises the level of lead in the blood. Nonetheless, even low quantity can eventually lead to poisoning which causes renal tubular dysfunctioning and nervous system toxicity, causing irreversible interstitial nephrosis with dynamic renal impairment and hypertension (Kumar *et al.,* 2020).

Developing robust and *in situ* detection of heavy metal ions has become an important overall green strategy. Several methods used to detect these metals, of which atomic absorption spectrometry (AAS) is the most common technique. However, the cost, and maintenance of the instrument as well as the tedious sample preparations calls for an alternative method (Wang *et al.,* 2020). One of the methods explored for the detection of such metals is by using glassy carbon electrode (GCE). Due to its outstanding mechanical and electrical characteristics, wide potential window, chemical inertness (solvent resistance), and generally consistent performance, glassy carbon electrode has been the focus of attention (Hassan *et al.,* 2019). Additional advantageous features of GCE includes minimal porosity, isotropicity, nearly glass tightness, hardness, and high conductivity. Moreover, the absorptivity of

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How to cite: Almustapha S. (2022). Modification of Glassy Carbon Electrode Using Microcrystalline Cellulose-Ethylenediaminetetracetic Acid for the Detection of Lead and Cadmium Ions. UMYU Scientifica, 1(1), 221 – 226. https://doi.org/10.56919/usci.1122.028

GCE is low as compared to other structured graphite materials which results in low sensitivity. In order to address the low sensitivity, the detection limit of electrodes can be reduced by increasing accumulation time, and applying additional measures such as ultrasonic extraction or modifying the surface of the electrodes (Petova *et al.*,2018). In fact, modifiers such as crown ethers and ion exchangers have been successfully used for metal ions detection using stripping voltammetry (Kulpa-Koterwa and Niedziałkowski, 2021).

Cellulose is one of the most prevalent and renewable biopolymers in nature. It is also a very promising raw material that is inexpensive and may be used to create a variety of functional products (Ajab *et al.,* 2020).The cosmetics, culinary, and pharmaceutical industries use microcrystalline cellulose (MCC) which is a thin, white, odourless, crystalline powder that may be separated from cellulose and used as a suspension stabilizer and water-retainer. Due to its advantageous characteristics, including its zero toxicity, hygroscopicity, chemical inactivity, and reversible absorbency, MCC is employed in the pharmaceutical sector as a tablet excipient (Wu and Wang, 2019).

Garba *et al.,* (2020) utilized MCC based materials as emerging adsorbents for the removal of dyes and heavy metal, it performed excellently compared to other adsorbents. MCC-magnesium hydroxide (MH) was also utilized to adsorb Co (II) ion in aqueous solution under different parameters, were the optimal process shows removal rate of Co (II) ion by MCC_MH up to 97.67% and maximum adsorption capacity of MCC-MH reached 153.84mg/g (Wang *et al.*, 2021). A research was also conducted by El-naggar *et al.,* (2018) using MCC base nanogel to removed reactive red 195(RR195) dye and Cd (II) and it proved that both the organic pollutant as well as the Cd (II) were successfully removed at 93% and 97% capacity respectively.

This work aimed at the modification of glassy carbon electrode using a microcrystalline cellulose-ethylenediaminetetraacetic acid (MCC-EDTA) for the detection of lead ions, Pb^{2+} and cadmium ions, Cd^{2+}.

MATERIALS AND METHODS

Chemicals

Analytical grade reagent standard stock solution of Pb (1000 ppm) and Cd (1000ppm) were purchased from E. Merck (Germany) and microcrystalline cellulose powder from Sigma-Aldrich (USA). NaOH (Merck), $(NH_4)_2HPO_4$ (Merck), 25% Ammonia solution (Merck), $Ca(NO_3)_2.4H_2O$ (Merck), EDTA (Merck). Supporting electrolytes (acetate buffer) was prepared from sodium acetate (Merck) and acetic acid (Merck). Metal solutions of lower concentrations from 0-100 ppm were prepared fresh before experiments. Ultrapure de-ionized water (Elga Pure lab Ultra) was used to prepare each solution.

Preparation of Modifiers

Microcrystalline Cellulose Mercerization

The standard mercerization process, ASTM D 1695 was adopted for the mercerization of the microcrystalline cellulose. Thus, the sample was treated with a very concentrated sodium hydroxide which resulted in the significant swelling, changes to the fine structure, size, shape, and mechanical properties of MCC (Ernest, & Peter, 2022). The mercerized MCC (100g) was kept at room temperature for further use.

Microcrystalline Cellulose-Ethylenediaminetetraacetic Acid

In a round bottom flask, 20 g of dried, mercerized microcrystalline cellulose was treated with 0.1M NaOH solution (1L) followed by 200 ml of 0.1M EDTA (10% wt) in the ratio of 1g cellulose: 10ml EDTA. The solution was refluxed with constant stirring (350 rpm) for 6 h. The mixture was then filtered and dried in an oven for 12 hours at 100°C. Once obtained, the powdered microcrystalline cellulose-ethylenediaminetetraacetic acid was kept in a desiccator until use (Nazir, et al., 2013).

Electrochemical System Set-up

A glassy carbon electrode (GCE) was used as the working electrode and AgCl/KCl (Metrohom) was used as the reference electrode, and the graphite bar was the auxiliary electrode for all the voltammetric experiments. For the electrochemical measurements, the AUTO LAB type III potentiostat/galvanostat (AutolabEcochemie, Netherlands) was connected to a personal computer and used with the Autolab software NOVA 1.10. At conditioned room temperature (23°C), all electrochemical measurements were conducted in a single compartment voltametric cell. To Analytical curves were created using the standard addition method to reduce matrix interferences. Blank GCE Metrohm was polished with alumina paste to obtain a mirror like surface, followed by washing with de-ionised water and then anhydrous alcohol, and finally with de-ionised water in ultrasonic bath for 5 min. GCE was dried at room temperature. MCC-EDTA solution was prepared by dissolving 5mg MCC-EDTA in 1mL de-ionised water and ultra-sonicated for 15 min. GCE was modified with MCC-EDTA by adding 5µL of MCC-EDTA on the electrode and dried in the open air (Kumary *et al.,* 2013).

Square-wave voltammetry

Under the parameters listed in Table 1, square-wave anodic stripping voltammetry was used for the electrochemical experiments. After transferring the electrolyte solution, lower concentrations of Pb^{2+} and Cd^{2+} solutions were added into the electrochemical cell (1-4 ppm). While 0.1M acetate buffer served as the supporting electrolyte.

Table 1: Experimental Conditions for Cd^{2+} and Pb^{2+} Determination

Parameters	Values
Acetate buffer pH	7.4
Frequency	25 Hz
Amplitude	25 mV
Potential Increment	4 mV
Accumulation Potential	-1V
Accumulation Time	240 Sec
Equilibration Period	30 Sec
SWV Stripping Scan	-1.0- 0.2 V
Conditioning Time	20 Sec
Stirring	200 rpm

Cyclic Voltammetry

Cyclic voltametric , CV studies was conducted at different scan rates (10mV/sec-100mV/sec), and potential scan ranges (-1.0V - 1.0V). Thus, the electrodes were immersed in 5 mM potassium ferricyanide solution, dissolved in 0.1 M KCl (10 ml), at pH 5.5 after elimination of air by nitrogen purges.

X-Ray Diffraction

X-ray diffraction, XRD (D8-Advance Bruker-AXS) was employed to analyse the degree of crystallinity and phase behaviour of MCC and MCC-EDTA. The analysis and instrument conditions were; λ =1.54°A (CuK radiation), 2° per second scan speed, and a 2θ range of 2-80°(Jegatheesan, et al., 2012).

Scanning Electron Microscopy

Morphological studies of MCC and MCC-EDTA were carried out with scanning electron microscopy, SEM (Leo Supra 50 VP, Germany). The surface morphology was observed at magnification 5000x, and fine 'probe' of electrons with energies up to 20keV was focused at the surface of the samples in the microscope and scanned across in a 'raster' or pattern of parallel lines.

Validation

Atomic absorption spectrometer (AAS) was calibrated with standard solutions prior to determination of the detection and quantification limits. 1000 mg/L calibration standard solutions of Cd (II) and Pb (II) in 0.05 M nitric acid were used as standards for AAS analysis. Standard solutions for calibration were prepared by diluting appropriate volume of 1000 mg/L calibration standard solutions with 1% KNO_3, four standard solutions were prepared covering the range from 0.1ppm to 4ppm in 10 ml volumetric flasks.

RESULTS AND DISCUSSION

Scanning Electron Microscopy

The morphological changes between MCC and MCC-EDTA can be seen in Figure 1 (a and b). Figure 1(a) demonstrated the smoothness of the surface of MCC in contrast to the MCC-EDTA which appeared to be aggregated Fig. 1(b). The removal of lignin, cementing wax, and inorganic particles was probably what gave rise to morphology of MCC-EDTA as reported by (Fouad *et al.,* 2020). Furthermore, the swelling effect following grafting with the carboxyl group of EDTA, which causes high electrostatic repulsion in the cellulose polymer's cross-linking network and causes the polymeric network to expand to form porous structure. The active surface area of MCC-EDTA may have been increased by the heterogeneous grafted surface, increasing the likelihood of heavy metal adsorption (Ajab *et al.,* 2018). The EDX analysis (Table 2) shows that Carbon and Oxygen make up the samples' primary chemical compositions. Due to the substitution of COOH for OH in the MCC structure, the weight ratio of Carbon drops while that of Oxygen rises.

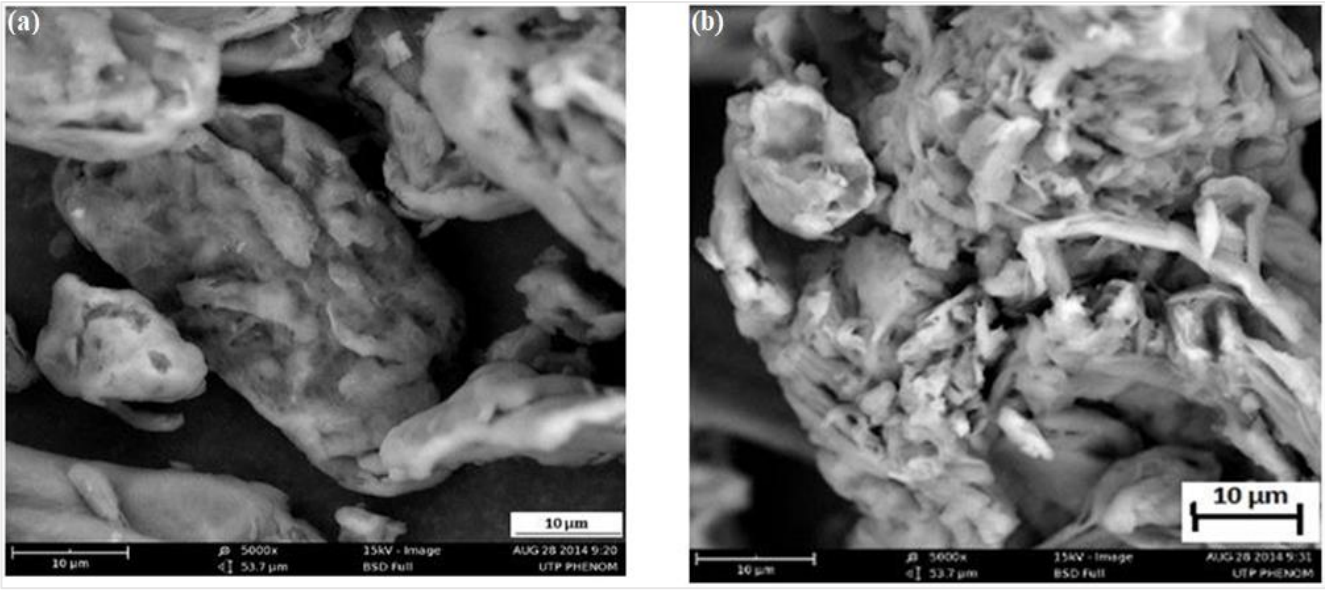

Figure 1: SEM Images at 5000× for (a) MCC and (b) MCC-EDTA

Table 02: Weight percentage of carbon and oxygen in MCC and MCC-EDTA

	Carbon (%)	Oxygen (%)
MCC	44.7	55.3
MCC-EDTA	16.4	83.6

X-Ray Diffraction

Figure 2 displays the X-ray diffraction patterns of MCC and MCC-EDTA (a&b). According to the JCPDS data (03-0289), the diffraction peaks at 2θ = 17.62° and 22.18° for MCC and 17.62° and 22.08° for MCC-EDTA revealed the presence of crystalline cellulose structures (Shao *et al.,* 2020). By applying the Segal formula, the crystallinity index for MCC was found to be 80%. In comparison for MCC-EDTA it was 65%. The crystallinity of MCC-EDTA decreases most likely due to the COOH groups attached. For comparison, the crystallinity index of extracted cellulose from OPEFB in previously published studies was around 70%, and that of cellulose fibers around 63% (Nazir, et al., 2013).

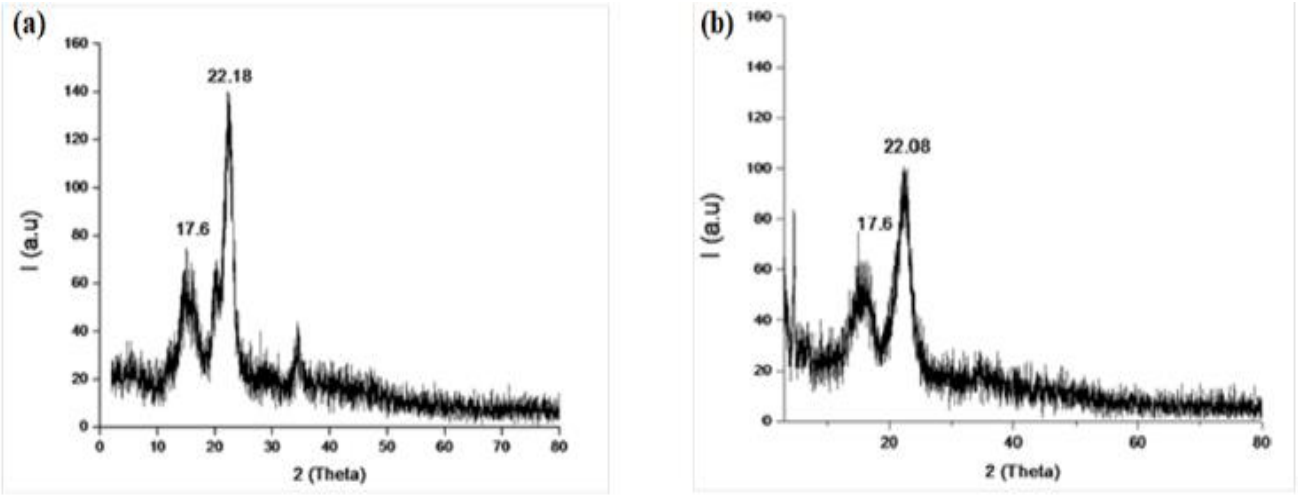

Figure 02: XRD of a) MCC, b) MCC-EDTA

Cyclic Voltammetry

Modification of GCE using MCC-EDTA was expected to improve the performance of the electrode. Thus, the MCC-EDTA-GCE and MCC-GCE, $Fe(CN)_6^{3/4}$ redox couple was chosen as a standard redox. The electron transfer behaviour of $Fe(CN)_6^{3/4}$ is usually influenced by the surface chemistry, microstructure and density of electronic states of the materials (Randviir, 2018). Figure 3(a & b) showed the CV of MCC-EDTA-GCE and MCC-GCE using 5.0 mM $K_3Fe(CN)_6$ as a test probe in 0.1M KCl at various scan rates. An increase in scan rate gives rise to increase in electron transfer as proven by increase in ΔE_p between anodic and cathodic potential. MCC-EDTA-GCE showed higher electron transfer rate than MCC-GCE as indicative of peak-to-peak separation value, suggesting higher sensitivity of MCC-EDTA-GCE for detecting heavy metal ions.

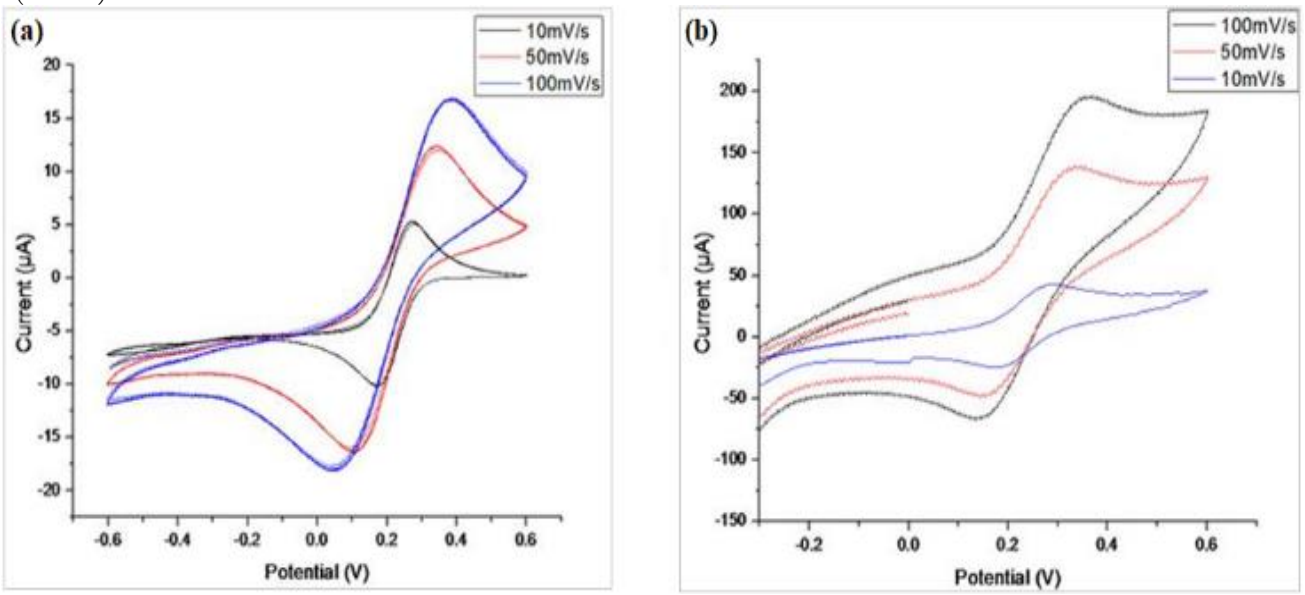

Figure 3: CV for 5 mM $Fe(CN)_6^{-3/-4}$ in 0.1 M KCl at various scan rate using a) MCC-GCE, b) MCC-EDTA-GCE

Single Pb^{2+} and Cd^{2+} Detection

Figure 4(a – d) showed sharp peak currents for Pb^{2+} and Cd^{2+} at 4ppm concentration using GCE, MCC-GCE and MCC-EDTA-GCE. Modification of GCE with MCC and MCC-EDTA increased the peak current and reduced the back ground ratio. The electrode surface has therefore been successfully modified with MCC and MCC-EDTA. Square wave voltammetry, SWV with MCC-EDTA-GCE was selected as a reliable and sensitive technique for these heavy metal ions, due to its low background current and high sensitivity. Validation of MCC-EDTA was carried out using AAS for lake water analysis and the calibration curve was compared with the Calibration of MCC-EDTA-GCE and MCC-GCE (result not shown) using Square Wave Voltametric analysis which was carried out with successive addition of 50µL each of Cd^{2+} and Pb^{2+} in the electrochemical cell which contained 10ml of 0.1M acetate buffer under optimized experimental conditions. The linear regression equations are shown in Table 3.

Table 3: Linear Regression Equation and R^2

Sensor	Pb^{2+}		Cd^{2+}	
	Slope Intercept	R^2	Slope Intercept	R^2
MCC-GCE(SWV)	0.0312 6.82	0.9496	0.1131 6.79	0.9943
MCC-EDTA-GCE(SWV)	0.0093 0.03	0.9993	0.0144 0.03	0.9929
MCC-EDTA (AAS)	0.0025 0.0058	0.9917	0.0023 0.0078	0.9402

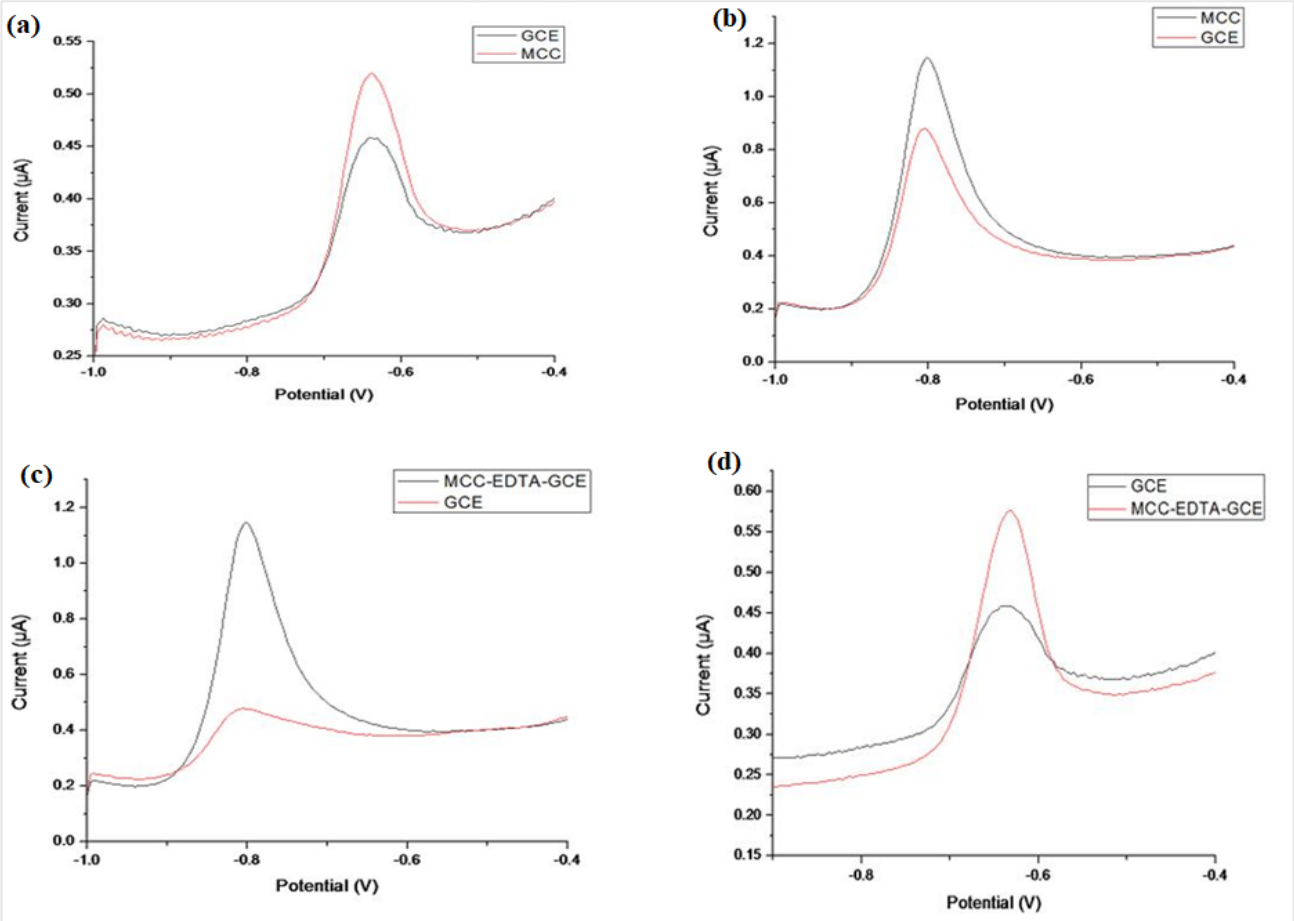

Figure 4:SWV of 4 ppm Pb^{2+} using a) GCE and MCC-GCE, b) GCE and MCC-EDTA-GCE, and 4 ppm Cd^{2+} using c) GCE and MCC-GCE d) GCE and MCC-EDTA-GCE at 240s deposition time in 0.1 M acetate buffer, pH 7.4

CONCLUSION

In this work, MCC and MCC-EDTA were successfully employed as modifiers for GCE. The purity and crystallinity of MCC and MCC-EDTA were analysed using SEM and XRD techniques, and suitability for lead and cadmium ions absorption was checked. By employing square wave voltametry, it was found that the modified electrode gives limit of detection of 1.8 ppb (MCC-EDTA GCE) and 5.0 ppb (MCC-GCE) for Pb^{2+}, while 7 ppb (MCC-EDTA GCE) and 10 ppb (MCC-GCE) were obtained for Cd^{2+}. AAS was used to validate the modifier, while accuracy and precision, accuracy and repeatability was checked using analyte analysis with different media (acetate buffer, $Fe(CN)_6^{3/4}$ and HNo_3),

different concentration of the analyte (10-60ppm) and the experiment was repeated all the times.

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