Poly (propylene imine) Coated Gold Nanoparticles Sensor for Cd (II) in Water

Azeez O Idris, Neo K Mogamisi, Fanyana Mtunzi, Omotayo A Arotiba,
Nonhlangabezo Mabuba*

Abstract: The application of gold and dendrimer (poly (propylene imine)) nanoparticles coated glassy carbon electrode (GCE-AuNPs/PPI) in the electrochemical determination of cadmium ion in water is presented. Gold and dendrimer nanoparticles were co-electrodeposited on the exterior of GCE using cyclic voltammetry (CV) at a potential range of -400 mV to 1100 mV for ten cycles. The modification of GCE with gold and dendrimer nanoparticles enhanced the redox current of $[Fe(CN)6]3-/4-$ when compared to results obtained from bare GCE. Cd(II)detection was accomplished using square wave anodic stripping voltammetry (SWASV) at the adjusted conditions: pH 1, deposition potential of -0.200 mV, pre-concentration time of 180s and 0.1 M HCl as supporting electrolyte. The GCE-AuNPs/PPI electrode detected Cd(II)to the limit of 0.34 ppb and was not susceptible to many interfering cations except Pb^{2+}, Hg^{2+} and As^{3+}. The GCE-AuNPs/PPI was practical for the quantitative assessment of Cd(II) in environmental water sample. The results obtained were in concord with Inductively Coupled Plasma-Optical Emission Spectroscopy procedure, thus validating the reported method.

Keywords: Cadmium, Dendrimer, Gold Nanoparticles, Co-Electrodeposition, Square Wave Anodic Stripping Voltammetry.

INTRODUCTION

Heavy metals are found in drinking water, earth crust and in living organisms either in their elemental form, ions or complexes. Although, some metals such as selenium, zinc, iron or cobalt are essential in trace amounts for physiological growth in the body. However, cadmium is the notorious heavy metal that is very lethal even at low concentration [1]. Despite its toxicity, it is employed for various applications such as corrosion resistance in electroplating, photovoltaic cells, fluorescent probe in fluorescence microscopy, combustion of coal, alloy processing, paint industries, smelting and nickel cadmium rechargeable batteries to name a few [1,2, 3].

Unfortunately, some of these applications result in the discharge of cadmium into water bodies, invariably causing different health-related problems, which include cardiovascular disorders, respiratory disease, nervous system disorders and cancer [4,5,6]. Owing to the toxicity of cadmium, a limit of 5 ppb has been set for cadmium in water by international water quality regulating organisations[7]. Arguably, since wastewater discharge is the major pathway or channel by which cadmium enters our environment,

Azeez O Idrisa, Department of Applied Chemistry, University of Johannesburg, Doornfontein, Johannesburg, South Africa.

Neo K Mogamisic, Department of Chemistry, Vaal University of Technology, Andries Potgieter BLV, Vanderbijlpark, South Africa.

Fanyana Mtunzic, Department of Chemistry, Vaal University of Technology, Andries Potgieter BLV, Vanderbijlpark, South Africa.

Omotayo A Arotiba, Department of Applied Chemistry, University of Johannesburg, Doornfontein, Johannesburg, South Africa.

Centre for Nanomaterials Science Research, University of Johannesburg, South Africa.

Nonhlangabezo Mabubaa*, Department of Applied Chemistry, University of Johannesburg, Doornfontein, Johannesburg, South Africa.

Centre for Nanomaterials Science Research, University of Johannesburg, South Africa. E-mail: nmabuba@uj.ac.za

developing, simple, portable, affordable, fast and dependable analytical technique for cadmium(II) quantification in the environment is of utmost importance.

The different analytical methods are absorption spectroscopy [8], mass spectrometry[2], spectro fluorimetry [9], chemiluminiscence [10] and spectrophotometry [11] are functional for the identifying Cd(II) in several matrices. But these procedures have some shortcomings which include long analysis time, complicated sample preparation method, the need for a very skilled operator, high cost of instrument and size which hinders on-site analysis. The problems related to these techniques, demands an urgent need for an alternative analytical method that is affordable, portable, fast and less time-consuming. The analytical technique that has these analytical merits or credentials is an electrochemical technique.

Electrochemical techniques are known to be portable, low cost, simple to operate, sensitive to the potential for field application [12]. Interestingly, anodic stripping voltammetry (ASV), a subset of stripping voltammetry techniques, has been utilised for the quantification of different metals and semi-metals such as Hg [13,14], Pb [15,16], As[17], Cr [18] and Se [19] to name a few. ASV has the potential to detect metals at different oxidation states with detection limits at ppb levels [20]. Different types of electrodes such as Hg [21,22], Pt [23,24] and Au [25,26] have been explored in anodic stripping voltammetry. These techniques have undergone different improvements over the years. For example, the focus has shifted from the use of the classical mercury electrode (owing to toxicity) to non-toxicity of GCE, carbon paste electrode (CPE), exfoliated graphite (EG) and screen printed electrode (SPE) [3,4][14,27].

In this work, adjusted GCE is employed as a sharp electrochemical platform for the quantification of metals alloys in environmental water, but it has to be modified with smart nanomaterials like polymers [28] and nanomaterials for it to be sensitive, to obtain high current signals and low detection limit [29–33]. Different nanomaterials were employed to coat GCE for the determination of toxic metal alloys, for instance, an ion imprinted polymer prepared from a sol-gel technique was utilised for the quantitative analysis of cadmium(II) in aqueous samples using CPE. Although, the limit of detection,0.15 μg/L was stated yet the challenge in this report was the reproducibility problem associated with CPE[1]. Similarly, antimony film layered montmorillonite doped CPE was used for a trace quantification of Cd(II) in aqueous samples, a limit of detection, 0.25 μg/L was divulged. In another report, hydrogen peroxide oxidised activated carbon coated electrode was utilised for the analysis of Cd(II) in water samples[6]. Furthermore, Wang et al. described the concurrent sensing of lead and cadmium using bismuth/reduced graphene/ ionic liquid composite layered on SPE[3]. Since electrochemical sensors require a stable platform, it is important to come up with a platform that is not only sensitive but also stable on the electrode interface. For this reason, dendrimer and gold nanoparticles were synergistically used to adjust GCE surface for quantifying Cd(II)in environmental water samples.

More recently, a unique type of polymers known as dendrimers have emerged as electrode modifiers. Dendrimers are nano-sized, hyper branched chain radially symmetric molecule, homogeneous and monodisperse structure with a symmetric core, inner shell and an outer shell [34]. They have the combined properties of polymers and nanomaterials. Interestingly, dendrimers have the potential for rich chemistry owing to their polyvalency, self-assembly capabilities, an intrinsic charge which is suitable for electrostatic attractions and good chemical stability [35]. Furthermore, dendrimers have excellent biological properties such as host-guest chemistry [36], which has made them applicable as drug delivery agents, biometric proteins, gene transfection agents, in vitro and in vivo studies for biomedical applications [9,37-39]. In our previous report, we displayed the function of dendrimer as a platform for the quantification of cholera, HIV and urea [40–42]. The interesting findings from the literature, prompted us towards utilizing dendrimer for the quantification of cadmium in water for this study.

More so, a gold nanoparticle is arguably the most exploited metal nanoparticles probably due to its excellent analytical merits such as high conductivity, high surface area, optical properties, high electron density, strong optical absorption and chemical inertness [43]. These qualities have contributed to its use in the following fields, sensor, quantification of organic, inorganic and biosensor [43–46]. Interestingly, we have employed gold nanoparticle for the quantification of arsenic and also for blocking interferences during the electrochemical quantification of As(III)- by using a complexometric masking approach [17,45]. Furthermore, it is hypothesised, therefore, that a combination of dendrimer (generation 3 poly (propylene imine) (G3-PPI) can be a suitable electrode adjustment for the improved quantification of Cd(II) aqueous samples by anodic stripping voltammetry (ASV). Interestingly, we have reported this platform for the construction of a DNA biosensor [46]. In this work, AuNPs and PPI were electro-co-deposited on GCE in a single step method. This electrodeposition step is straightforward and easily manageable in comparison to drop coating technique, which may be affected by personal errors. It is

foreseen that this novel approach for verification of Cd(II) will assist in the performance of the electrochemical sensor by the synergistic influence of AuNPs and PPI properties.

EXPERIMENTAL

Material and Methods

HCl, HNO_3, H_2SO_4, NaOH, KCl and $CdSO_4.8H_2O$ were acquired from Sigma Aldrich (South Africa) and generation 3 poly propylene imine (G3-PPI) was purchased from SyMO-Chem, Eindhoven, Netherlands. All chemicals used for these experiments were of highest analytical grade and deionised water was used for the preparation of solutions. All electrochemical measurements were carried out on an Ivium Technologies Compact-stat potentiostat (Ivium Netherlands) using a three-electrode configuration. The working electrode, counter electrode and reference electrode were glassy carbon electrode, platinum wire and Ag/AgCl (3M KCl) respectively. The bare GCE was refined with alumina powder and rinsed thoroughly with distilled water and ethanol in an ultrasonic bath for a few minutes before use. Inductively coupled plasma-optical emission spectroscopy (ICP-OES) technique was carried out on Icap 6000 ICP spectrometer instrument Thermo Fisher Scientific (USA) and was used to validate the electrochemical results for real water sample experiment.

Electrode Modification

GCE was coated with gold AuNPs and G3-PPI as described by Arotiba et al [46]. Briefly, GCE was simultaneously coated with G3-PPI and AuNPs from a mixture of a solution of 5 mM $HAuCl_4$ and 5 mM G3-PPI by cycling the potential from –400 mV to 1100 mV for 10 cycles at a scan rate of 50 mV s $^{-1}$. The adjusted electrode was referred to as GCE-AuNPs/PPI. The adjusted electrode was electrochemically characterised using cyclic voltammetry (CV) in an equimolar of 1 mM $K_3Fe(CN)_6$ and $K_4Fe(CN)_6.3H_2O$ denoted as $[Fe(CN)_6]^{3-/4-}$ in a supporting electrolyte solution (0.1 M KCl).

RESULTS AND DISCUSSION

Electrode Characterisation

Prior to electrochemical characterisation, the formation of AuNPs and PPI was confirmed by FE-SEM on a screen-printed carbon electrode after the electrodeposition step as depicted in **Fig. 1.** The displayed nanoparticles and distribution are related to prior reports [17][46-47].
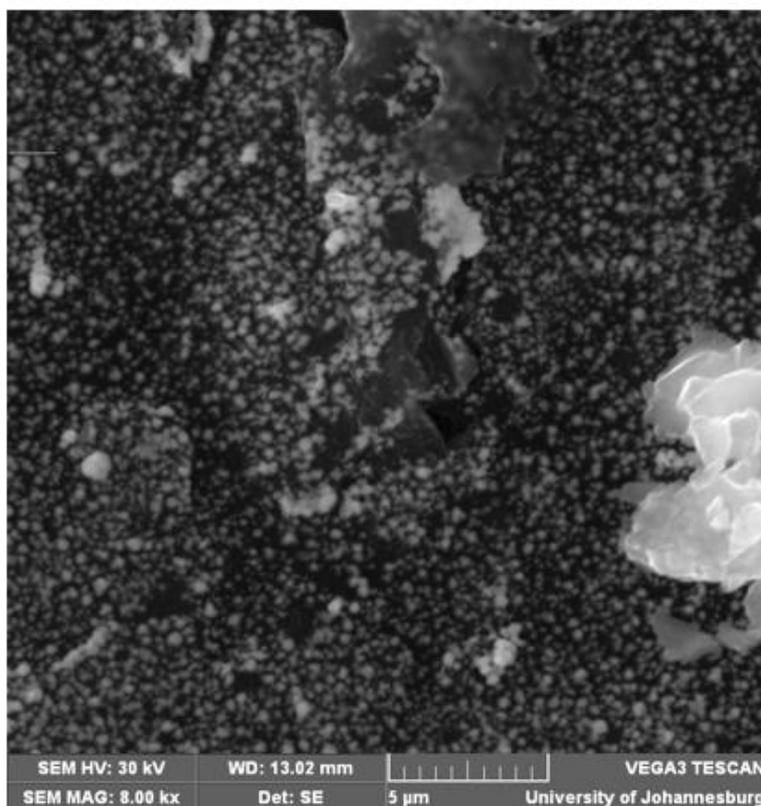

Figure 1: SEM Image of AuNPs/PPI

The uncoated and coated GCE were electrochemically characterised using cyclic voltammetry (CV) as presented in **Fig. 2a.** CV of uncoated GCE showed a quasi-reversible peak. The modification of GCE by AuNPs/PPI resulted in a 99% peak current improvement compared to uncoated GCE. The current enhancement was ascribed to an increase in electroactive surface area, conductivity and high surface area of the GCE/AuNPs/PPI which facilitated electron transfer on the electrode surface. Similarly, the bare and GCE/AuNPs/PPI were characterised using electrochemical impedance spectroscopy (EIS) in 1 mM $[Fe(CN)_6]^{3-/4-}$ redox probe as shown in **Fig. 2b**. EIS is an electrochemical technique employed in investigating interfacial electron transfer as a result of electrochemical changes that occur on the electrode surface when modified. The semi-circle diameter at higher frequency represents the electron transfer resistance (R_{ct}) and the linear part at a lower frequency is the diffusion process. A well-defined semi-circle was shown by the bare GCE (**Fig. 2b**), the semicircle diameter reduced dramatically (reduction in charge transfer resistance R_{ct}) on modifying GCE with AuNPs/PPI as depicted in (**Fig. 2b**), implying that AuNPs/PPI are excellent conductive smart nanomaterials that can facilitate electron transfer.
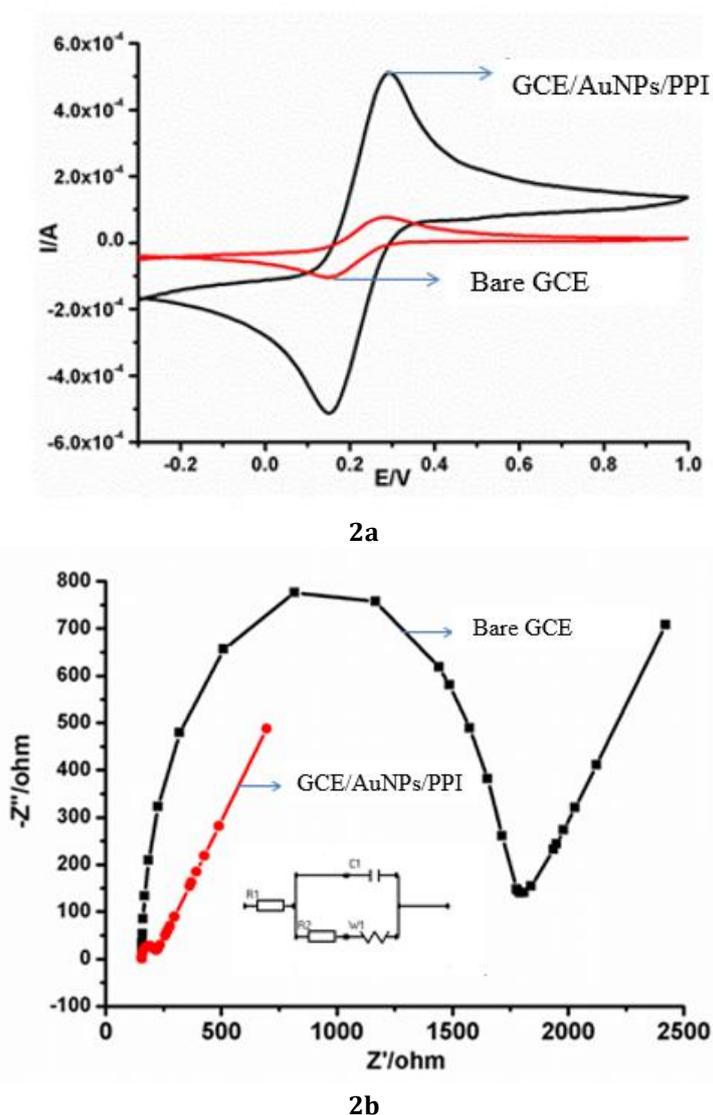

2a

2b

Figure 2: (a)CV of uncoated GCE and GCE-AuNPs/PPI in 1 mM $[Fe(CN)_6]^{3-/4-}$ redox probe(b) EIS of bare GCE and GCE-AuNPs/PPI in 1 mM $[Fe(CN)_6]^{3-/4-}$ redox probe. The EIS measurement was carried out using a bias potential of 0.22 V and a frequency range of 100 kHz to 100 mHz, inset (Randle Sevcik circuit).

Effect of Deposition Potential, Deposition Time, pH and Supporting Electrolyte on Detection of Cd(II) in Real Aqueous samples

The electrochemical responses of different supporting electrolytes are shown in **Fig. 3a.** Neutral and alkaline electrolytes did not give any noticeable Cd(II) stripping current while acidic electrolytes showed higher currents, owing to the magnitude of the stripping current, working supporting electrolyte (0.1 M HCl) for this electroanalytical experiment. Furthermore, it is important to carry out pH studies in a metal

analysis because the ionic states of the analytes are influenced by the proton environment in which they exist. In this study, a pH of 1, which has the highest current was chosen as optimum working pH (**Fig. 3b**). In addition to this, the pre-concentration time was optimised from 30 s to 360 s. The results obtained in **Fig. 3 c**exhibited a rise in the peak current signal from 100 s to 180 s, after which a reduction in the peak current signalwas experienced. Hence, 180 s was used as the electrodeposition time for this experiment. More so, the effect of electrodeposition potential for Cd(II) oxidation to Cd(0) in the presence of GCE/AuNP/PPI was investigated by varying the potential (– 0.1 V to 0.9 V), during the sensingof Cd(II). The corresponding stripping potential of Cd(0) to Cd(II) is shown in **Fig. 3d.** A cathodic potential of –0.2 V was optimal owing to the highest peak current observed.
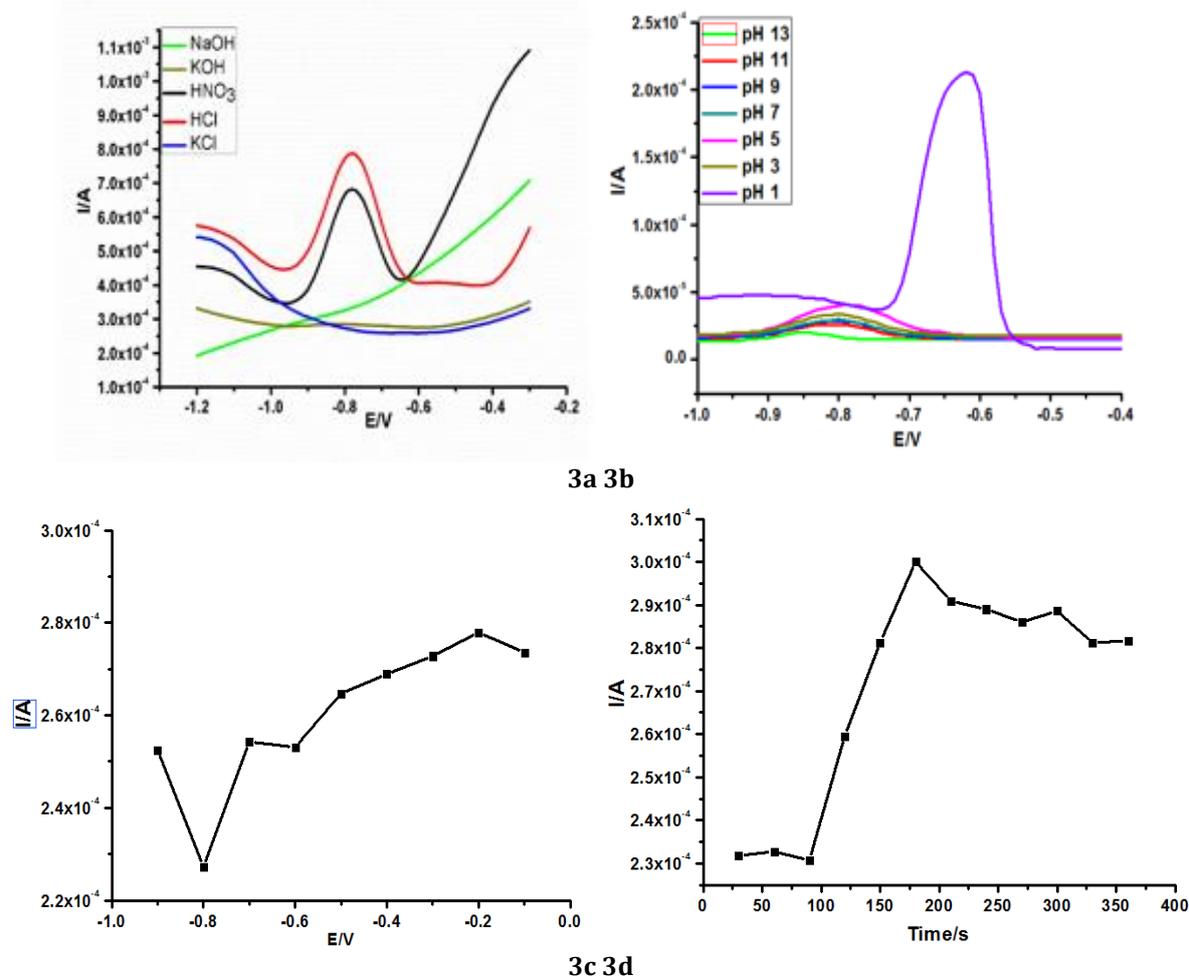

3a 3b

3c 3d

Figure 3: a) The influence of different supporting electrolytes on the ASV of 100 ppm Cd(II) b) Effect of 50 ppm Cd(II) solution on different pH c) Effect of electrodeposition time on 50 ppm Cd(II) d) Effect of electrodeposition potential on 50 ppm Cd(II).

Electrochemical Detection of Cadmium (II)

A stripping experiment based on the optimised conditions in section 3.2 was carried out with a Cd(II) concentration of 100 ppb (**Fig. 4a**). The GCE/AuNPs/PPI resulted in current amplification which can be ascribed to the existence of the AuNPs/PPI modifier which enlarged the electroactive exterior area of the electrode.

A calibration curve was constructed from the ASV of numerous concentrations of Cd(II)from 0.001 to 50 ppm (**Fig. 4b**). A direct proportionality was pronounced between the peak current and Cd(II) concentrations. The blank measurement (i.e. absence of Cd(II)) did not show any current suggesting that the recorded peak currents were solely due to Cd(II). A rectilinear regression equation of Y=3727X10^{-6}X + 4388X10^{-6} and a correlation coefficient (R^2) of 0.9857 was obtained. The formula $CL = 3*SB/m$ was utilized to achieve a limit of detection of 0.34 ppb[48], where CL, SB and m are the limits of detection, standard deviation of the blank and the slope of the calibration graph, respectively. The experiments were conducted in triplicates with a good reproducibility as indicated by a 3.5% relative standard deviation (RSD). The small value of the detection limit obtained in credited to an increase in active exterior area,

conductivity, the electrodeposition techniques used for the modification of the bare electrode which make the sensor to be stable, reproducible and the synergistic analytical properties of gold nanoparticles/poly (propylene imine), which help to facilitate the transport of Cd(II) ion on the electrode surface. The limit of detection acquired was compared with the literature as shown in Table 1. The proposed sensor has added merits such as wide linear range of concentration and ease of fabrication.
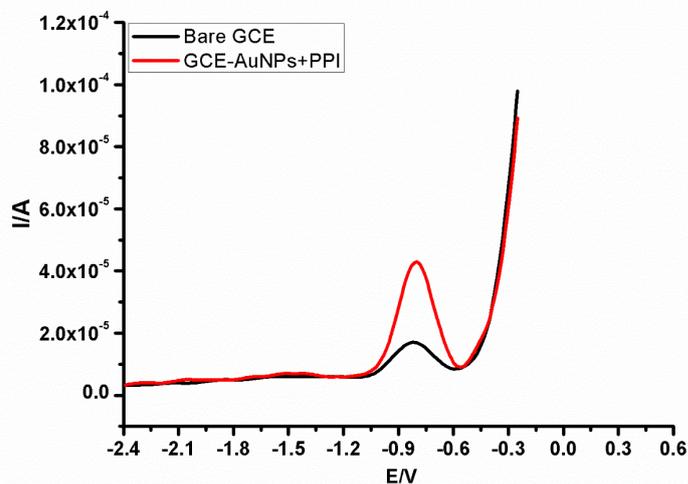
4a
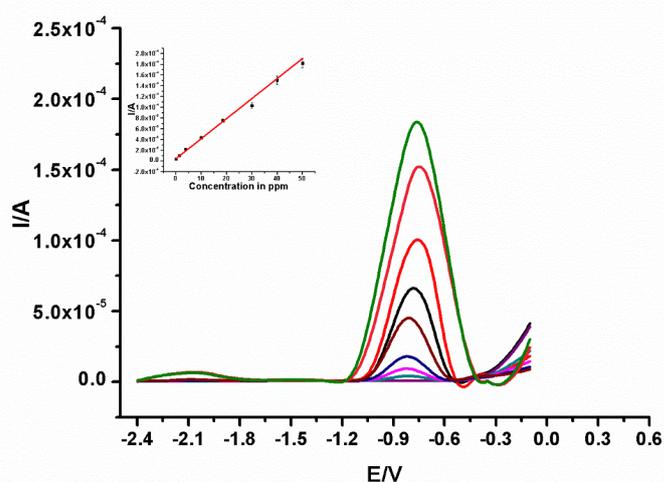
4b

Figure 4: (a) SWASV overlay of 100 ppb solution Cd(II) on uncoated GCE and GCE-AuNPs/PPI b) SWASV responses of various concentrations (0.001 to 50 ppm) using GCE-AuNPs/PPI, the calibration graph (inset) where n = 3, All Ep vs Ag/AgCl (3 M KCl).

Table 1: Electrochemical methods for sensing Cd(II)

Electrode Substrates	Electrochemical Techniques	Linear concentration (ppb)	Limit of Detection (ppb)	Reference
Bi/CNT/GCE	SWASV	20-10	0.70	[49]
SbF/GCE	SWASV	200-140	0.70	[50]
Sb/CPE	SWASV	50-50	0.80	[51]
Nafion-Graphene	DPV	15-30	0.02	[52]
Macroporous Sb	DPV	200-120	0.70	[53]
GCE-AuNPs/PPI	SWASV	1-50000	0.35	**Present work**

Bi/CNT/GCE-bismuth/carbon nanotubes/glassy carbon electrode, SbF/CPE- Antimony film carbon paste electrode.

Interference Studies and Real Water Analysis

The GCE-AuNPs/PPI does not permit interference from common ions such as Ca^{2+}, Na^+, K^+ and Mg^{2+} but was found to be affected by Hg^{2+}, Pb^{2+} and As^{3+} as portrayed in **Fig. 5a,** where all the interfering ions gave an obvious decrease in the peak current signal but arsenic and lead ions gave more reduction in peak current signal on Cd(II).

The applicability of the developed sensor for environmental applications was tested with real water sample obtained from municipal water in Eastern Cape Province, Buffalo City Municipality in South Africa. The real sample was digested in nitric acid (0.2% (v/v)) before carrying out the analysis on ICP-OES and the sensor using SWASV. A concentration of 389 (± 068) ppb Cd(II)was computed for the authentic water sample (n=3) using the proposed sensor (**Fig. 5b**). For collation, ICP-OES analysis presented a concentration of 486 (± 075) ppb Cd(II)when the analysis was implemented in triplicate (n=3).
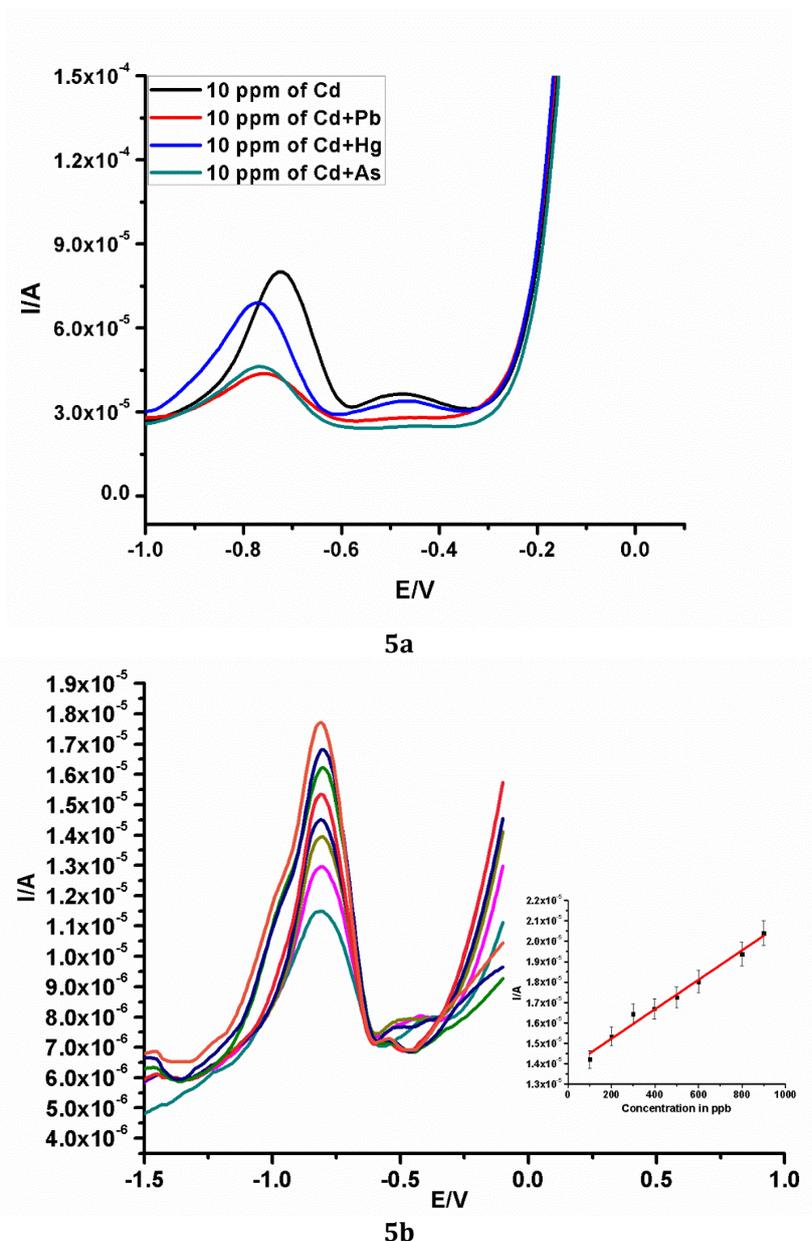

5a

5b

Figure 5: a) SWASV of 10 ppm Cd(II) solution and 10 ppm (Pb, Hg and As) b) SWASV of 100 to 1000 ppb of Cd (II) in a real water sample with calibration plot (inset).

CONCLUSION

The determination of Cd(II) using GCE-AuNPs/PPIwas thoroughly investigated, the optimised conditions aided in obtaining a consistent and reproducible result during the analysis. The GCE-AuNPs/PPI electrode sensed Cd(II) to the lowest value of 0.34 ppb. It was not vulnerable to cations that might obstruct the analysis process except Pb^{2+}, Hg^{2+} and As^{3+}. The GCE-AuNPs/PPI electrochemical sensor enhanced the quantitative signal of Cd(II) in environmental samples and the results were in accord with ICP-OES. Therefore, the developed sensor has a scientific significance and hold good promises for analytical applications.

ACKNOWLEDGEMENTS

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