# Fabrication of novel polymer-modified graphene-based electrochemical sensor for the determination of mercury and lead ions in water and biological samples

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## Abstract

**Background:** This paper presents the application of polyglycine-modified graphene paste electrode (PGMGPE) for the electrochemical detection of Hg (II) and Pb (II) ions in the water and biological samples.

**Method:** The developed electrode was characterized by field emission scanning electron microscopy. Electrochemical techniques such as cyclic voltammetry and differential pulse voltammetry were used to study the behavior of metal ions.

**Results:** The modification process improves the electrochemical behavior of heavy metal ions. The peak current varied linearly with the increase of the concentration leading to a detection limit of 6.6 μM (Hg (II)) and 0.8 μM (Pb (II)), respectively.

**Conclusion:** The developed electrode exhibits good sensitivity, selectivity, stability, and lower detection limit, and was successfully applied to the determination of heavy metal ions in water and biological samples with a good recovery range.

**Keywords:** $HgCl_2$, $PbCl_2$, Graphene, Glycine, Cyclic voltammetry, Blood serum, Water sample

## Introduction

Heavy metal ions are one of the most hazardous pollutants in the environment and are highly toxic. Mainly, environmental pollution by heavy metals is attributed to lead, cadmium, mercury, and copper. Trace heavy metal elements are fundamental to living organisms for a normal and healthy life. Excessive level of heavy metal pollution in the environment could cause harm (Li et al. 2013; Guascito et al. 2008). The accumulation of heavy metal ions in the human body can cause diseases in the central nervous system, liver, kidney, and skin (Bodo et al. 2010). So, it has become an important task to develop a cost-effective and sensitive method for the detection of heavy metal ions. Currently, various techniques have been reported for the detection of heavy metals such as atomic absorption spectroscopy (Liu et al. 2005) and fluorescence spectrometry (Liu

et al. 2005). However, these methods are expensive and time-consuming. In contrast, electrochemical methods (Huang and He 2013; Gherasim et al. 2014; Huakun et al. 2016; Sathish Reddy et al. 2012a, b, 2018; Gururaj et al., 2018; Ongera Gilbert et al. 2009; Mahanthesha et al. 2010; Liu et al, 2012) have advantages over the above techniques such as being inexpensive, highly sensitive, and easy to use. Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) are sensitive techniques for the detection of heavy metals in water.

Many approaches are used for the modification of the working electrode surface by chemicals such as thiolamine (Fu et al. 2013), polymers (Ahuja et al. 2007; McQuade et al., 2000; Mohadesi and Taher, 2007), and monomolecular ligands (Canpolat et al. 2007; Zheng et al. 2006; Zhang et al., 2002; Anandhakumar and Mathiyarasu 2013). Graphene shows a wide application as an electrode material, because it shows very high electrical conductivity, good mechanical properties, fast

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electron transfer rate, and a high specific surface area (Zhao et al. 2012). Graphene has a thin layer of $sp^2$-bonded carbon atoms, stacked in a two-dimensional (2D) honeycomb lattice and belongs to the class of carbon nanomaterials (Konios et al. 2014). It is widely used in various fields including electronics, biological, medicine, energy storage, and catalysis (Gupta et al. 2016, Gupta et al. 2012; Khani et al. 2010; Jain et al. 2006, Jain et al. 1997; Wei et al. 2019; Beitollahi et al. 2014, 2017; Tajik et al. 2014; Movlaee et al. 2017).

In this paper we report the development of an electrochemical sensor based on polyglycine-modified graphene for the determination of $Hg^{2+}$ and $Pb^{2+}$ ions using the cyclic voltammetry (CV) technique. The electrochemical behavior of the heavy metal ions was studied at the bare and modified electrode and it was shown that the redox signal of these two heavy metal ions was promoted by the modified electrode. The developed sensor is **less expensive and shows a** wide linear response range with low detection limit, good stability, and reproducibility. **Short or limited shelf life is the main disadvantage of the developed sensor.** To our best knowledge, no research has been conducted to study the heavy metal ion detection at polyglycine-modified graphene paste electrode.

## Experimental
### Chemicals and reagents
Graphene was obtained from Tokyo Chemical Industries. Glycine and silicone oil were obtained from Nice Chemical Pvt Ltd., Kerala. Disodium hydrogen phosphate and sodium dihydrogen phosphate were obtained from Himedia. Phosphate buffer solution (PBS) 0.1 M was prepared by mixing 0.1 M disodium and sodium dihydrogen phosphate, and diluted with water and used as a supporting electrolyte. The pH was adjusted by adding an acid solution. Other chemicals such as $HgCl_2$ and $PbCl_2$ were of analytical grade and used as received from the manufacturers. Distilled water was used for the preparation of all the solutions.

### Instrumentation
CV and DPV were performed using the CHI6038E (CH Instrument, USA). The electrochemical cell comprises three electrodes; platinum wire and calomel electrode were used as a counter electrode and a reference electrode, respectively. The working electrode used in this study was a 3 mm-diameter unmodified and modified graphene paste electrode. All the experiments were performed at room temperature. pH measurements were carried out using EQ-610 pH meter, which was calibrated before use. Field emission scanning electron microscopy (FESEM) was obtained using the instrument operating at 5.00 kV (DST-PURSE

Laboratory, Mangalore University). All the peak currents were taken with background current.

### Preparation of bare paste electrode
Bare graphene paste electrode was prepared by thoroughly mixing (15 min) 60:40 w/w% of graphene and silicone oil in a small agate mortar. A portion of the paste was then packed into the tip of the electrode of 3 mm diameter. Before each experiment, the surface was smoothed with a tissue paper until a shiny and clean electrode surface was obtained.

## Results and discussion
### Preparation of modified paste electrode
The electropolymerization technique was used for the preparation of PGMGPE. The prepared BGPE was kept in the electrochemical cell containing glycine ($1\times10^{-3}$ M) and 0.1 M PBS of pH 5.7. The electropolymerization was carried out at the potential window from 0.5 V to 1.5 V at a scan rate of 0.1 V/s (Fig. 1). The electropolymerization cycles were optimized as ten cycles, because after ten cycles the peak current started decreasing (data not shown). Therefore, ten cycles were chosen as the optimum scan number.

### Structural features of BGPE and PGMGPE
The morphological characterization of BGPE and PGMGPE was examined by FESEM. Figure 2a shows the morphology of BGPE, and Fig. 2b shows the morphology of PGMGPE. It was seen that BGPE contained flakes of graphene with an irregular surface and it was covered with a polymer film after electropolymerization with glycine, confirming that the BGPE was modified with a polymer film.
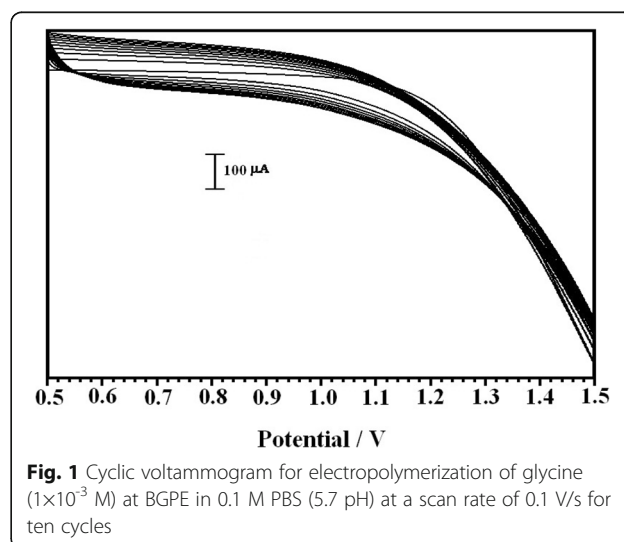


**Fig. 1** Cyclic voltammogram for electropolymerization of glycine ($1\times10^{-3}$ M) at BGPE in 0.1 M PBS (5.7 pH) at a scan rate of 0.1 V/s for ten cycles
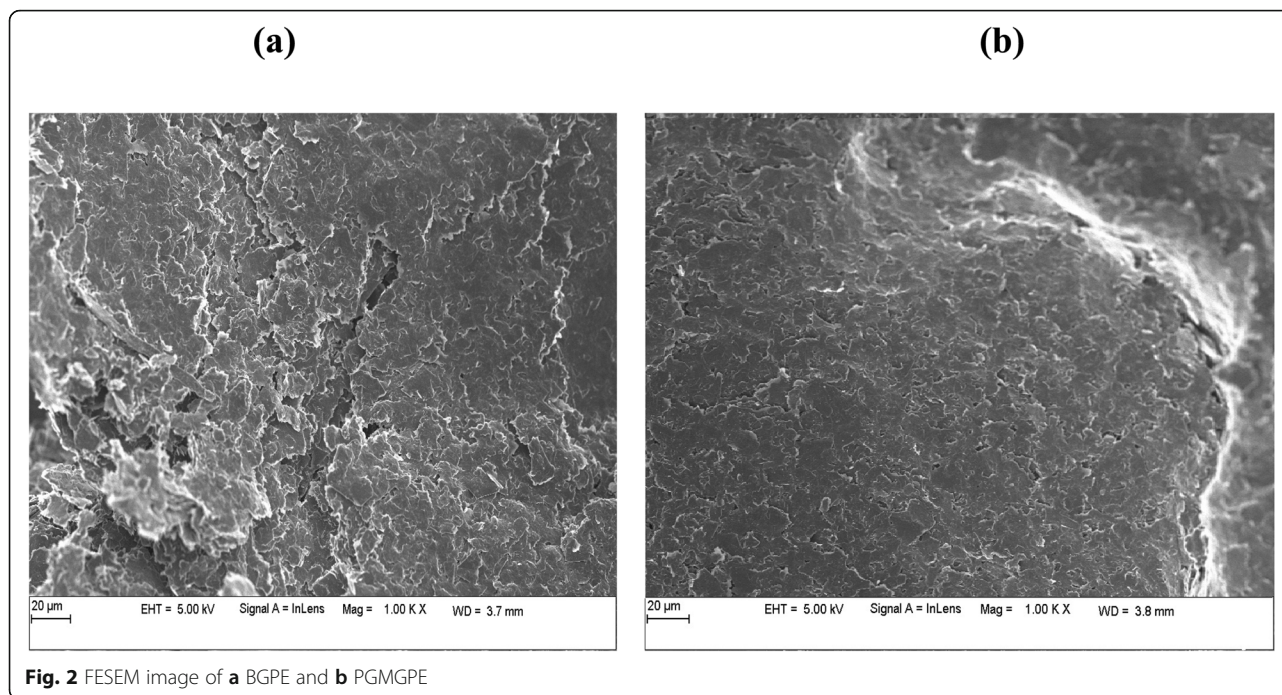
**Fig. 2** FESEM image of **a** BGPE and **b** PGMGPE
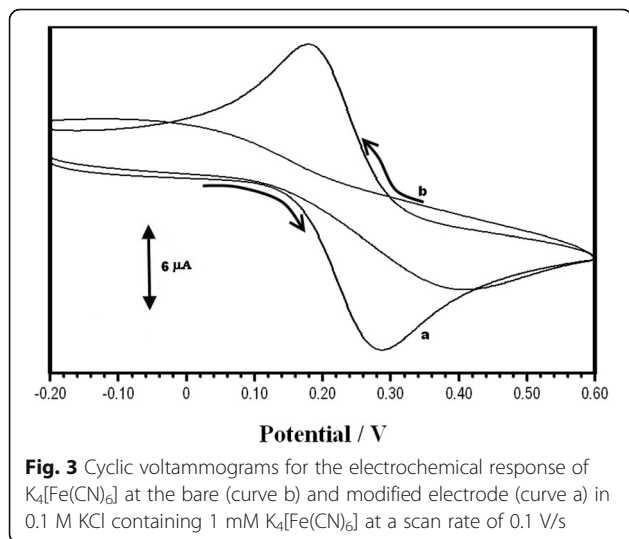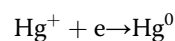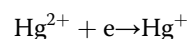
## Electrochemical behavior of K$_4$[Fe(CN)$_6$]

The electrochemical behavior of K$_4$[Fe(CN)$_6$] was studied at the bare and modified electrode in 0.1 M KCl as a supporting electrolyte with 1 mM K$_4$[Fe(CN)$_6$]. Figure 3 shows the cyclic voltammogram of K$_4$[Fe(CN)$_6$] at the bare (curve b) and the modified electrode (curve a). The modified electrode shows well-defined oxidation and reduction peaks at 0.248 V and 0.183 V. The modified electrode showed an enhancement in the peak current with increase in electron transfer kinetics. This confirmed that the electrode surface property was significantly changed and showed the good electrocatalytic activity of modified electrode toward K$_4$[Fe(CN)$_6$]. The surface area can be estimated by the Randles–Sevcik equation:



**Fig. 3** Cyclic voltammograms for the electrochemical response of K$_4$[Fe(CN)$_6$] at the bare (curve b) and modified electrode (curve a) in 0.1 M KCl containing 1 mM K$_4$[Fe(CN)$_6$] at a scan rate of 0.1 V/s

$$I_{\mathrm{p}} = 2.69 \times 10^5 n^{3/2} A D_0^{1/2} C_0 v^{1/2}$$

where $I_{\mathrm{p}}$ is the peak current in $A$, $C_0$ is the concentration of the electroactive species (mol/cm$^3$), $n$ is the number of electrons involved in the reaction, $D_0$ is the diffusion coefficient in cm$^2$/s, $v$ is the scan rate (V/s), and $A$ is the electroactive surface area (cm$^2$). For the modified electrode, the surface area is maximum (0.03 cm$^2$) as compared to the bare electrode (0.02 cm$^2$).

## Electrochemical investigation

CV was investigated to check the electrode behavior before and after the modification. A small anodic and cathodic peak was observed on the BGPE (Fig. 4 (curve b)) in 0.1 M PBS at pH 4.5 in the potential window from -0.10 V to 0.50 V for HgCl$_2$. It showed that the electron transfer between the electrode and analyte (HgCl$_2$) in the solution occurred very slowly. Two reduction peaks were observed for HgCl$_2$ at 0.119 V and 0.0407 V, which were shifted to 0.133 V and 0.015 V at PGMGPE (Fig. 4 (curve a)) with an increase in both peak currents. This result shows that the electron transfer rate increased at PGMGPE. The mechanism for the reduction process is explained as follows:

$$\mathrm{Hg}^{2+} + e \rightarrow \mathrm{Hg}^{+}$$

$$\mathrm{Hg}^{+} + e \rightarrow \mathrm{Hg}^{0}$$

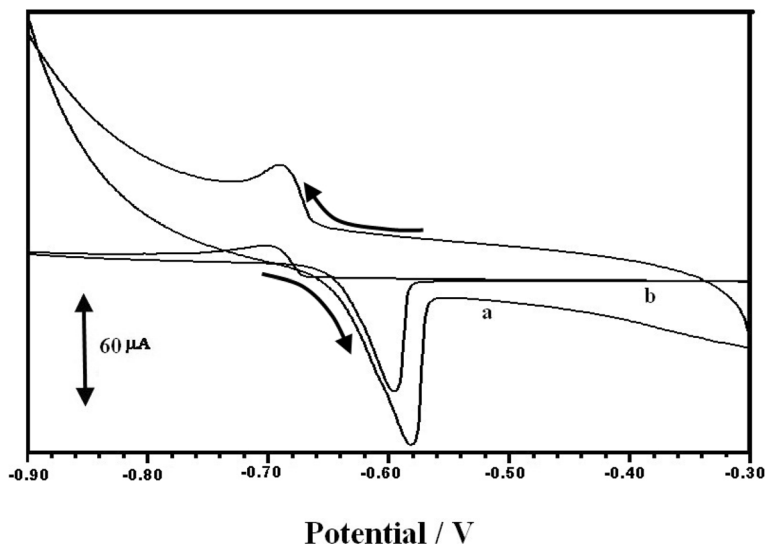Figure 5 shows the CV response of PbCl$_2$ at the BGPE (curve b) and PGMGPE (curve a). A small
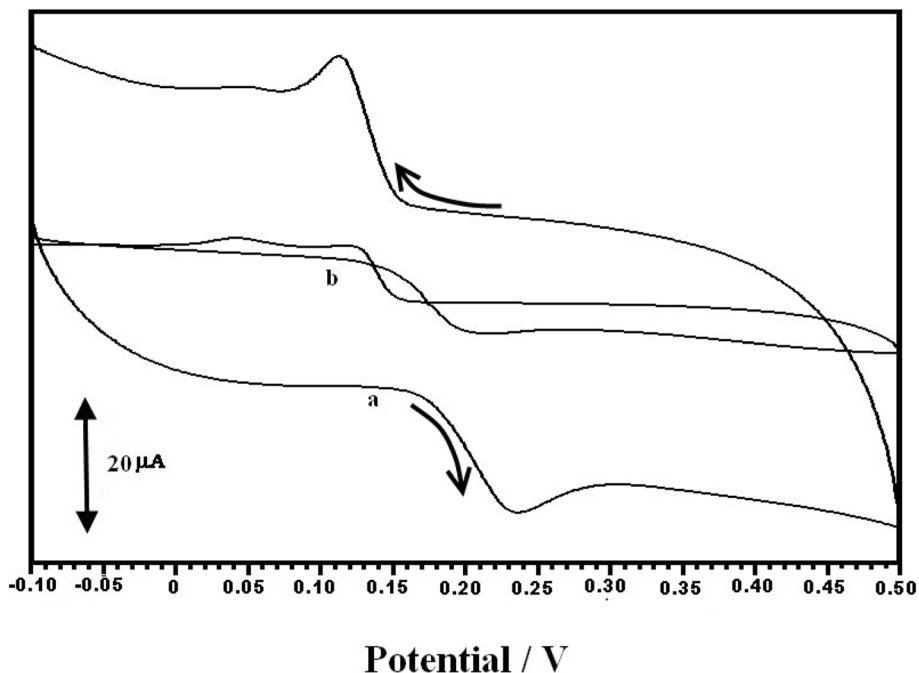
**Fig. 4** Cyclic voltammograms of 1 mM HgCl$_2$ at BGPE (curve b) and PGMGPE (curve a) in 0.1 M PBS (pH 4.5) at a scan rate of 0.1 V/s

current response observed at the bare electrode showed the difficulty of the metal ions to be adsorbed on to the bare electrode. On the other hand, for the modified electrode, the peak current value was larger than that obtained for the bare electrode, showing that the glycine film could be as an excellent supporting material for the heavy metal sensor. The polyglycine film exhibited a strong adsorption power of the heavy metal ions, and hence improved the surface sensitivity of the electrode.

## Effect of varying pH

The pH for the determination of heavy metal ion has a significant effect on the voltammetric behavior. The effect of different pH values on the electrochemical response was studied in the pH range from 3.5 to 5.5. Figure 6a shows the cyclic voltammograms for HgCl$_2$ at different pH values at a scan rate of 0.1 V/s in the potential window from -0.10 to 0.50 V. It was observed that the peak current for HgCl$_2$ is maximum at pH 4.5. The decrease in the



**Fig. 5** Cyclic voltammograms of 1 mM PbCl$_2$ at BGPE (curve b) and PGMGPE (curve a) in 0.1 M PBS (pH 4.5) at a scan rate of 0.1 V/s
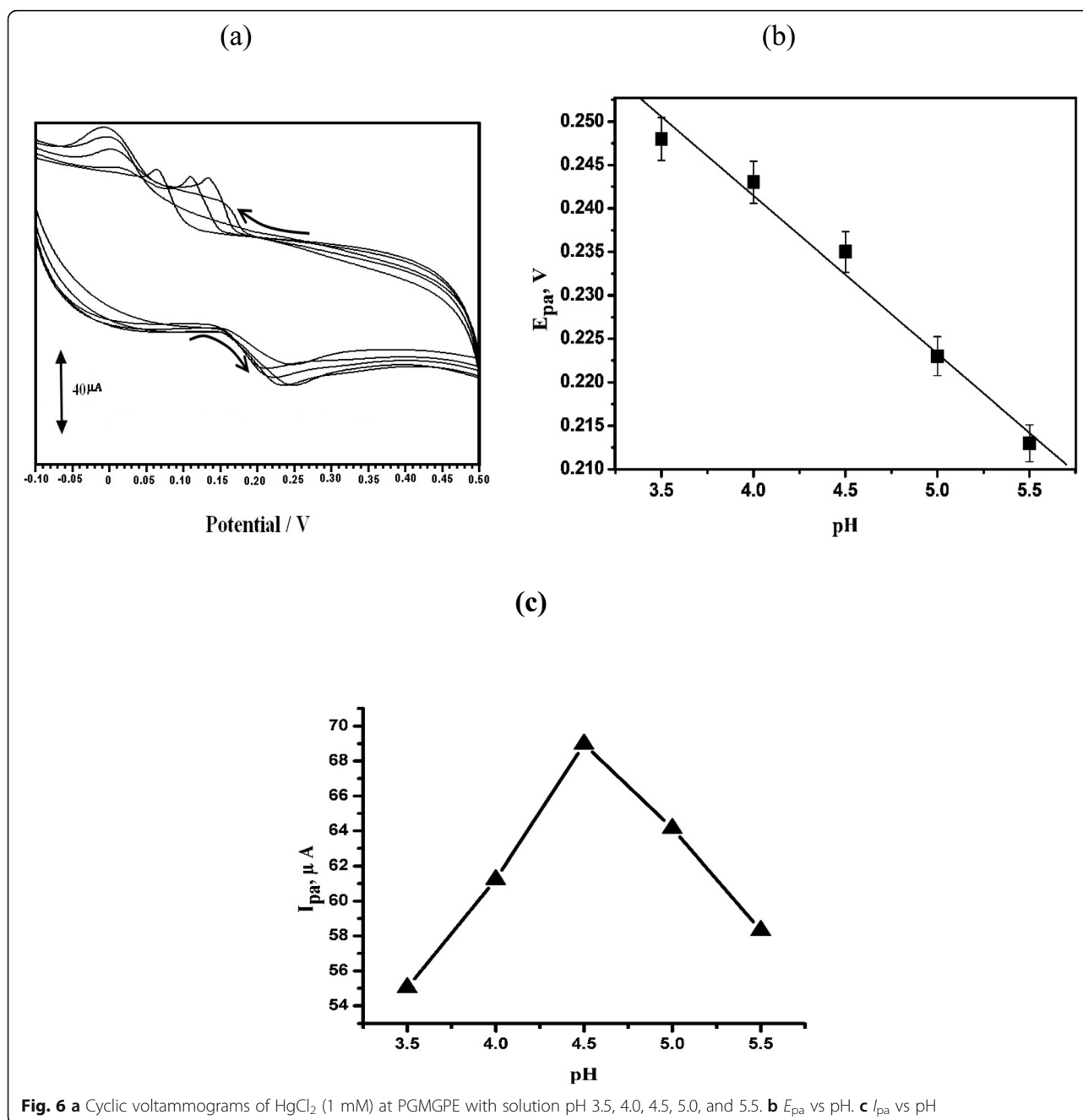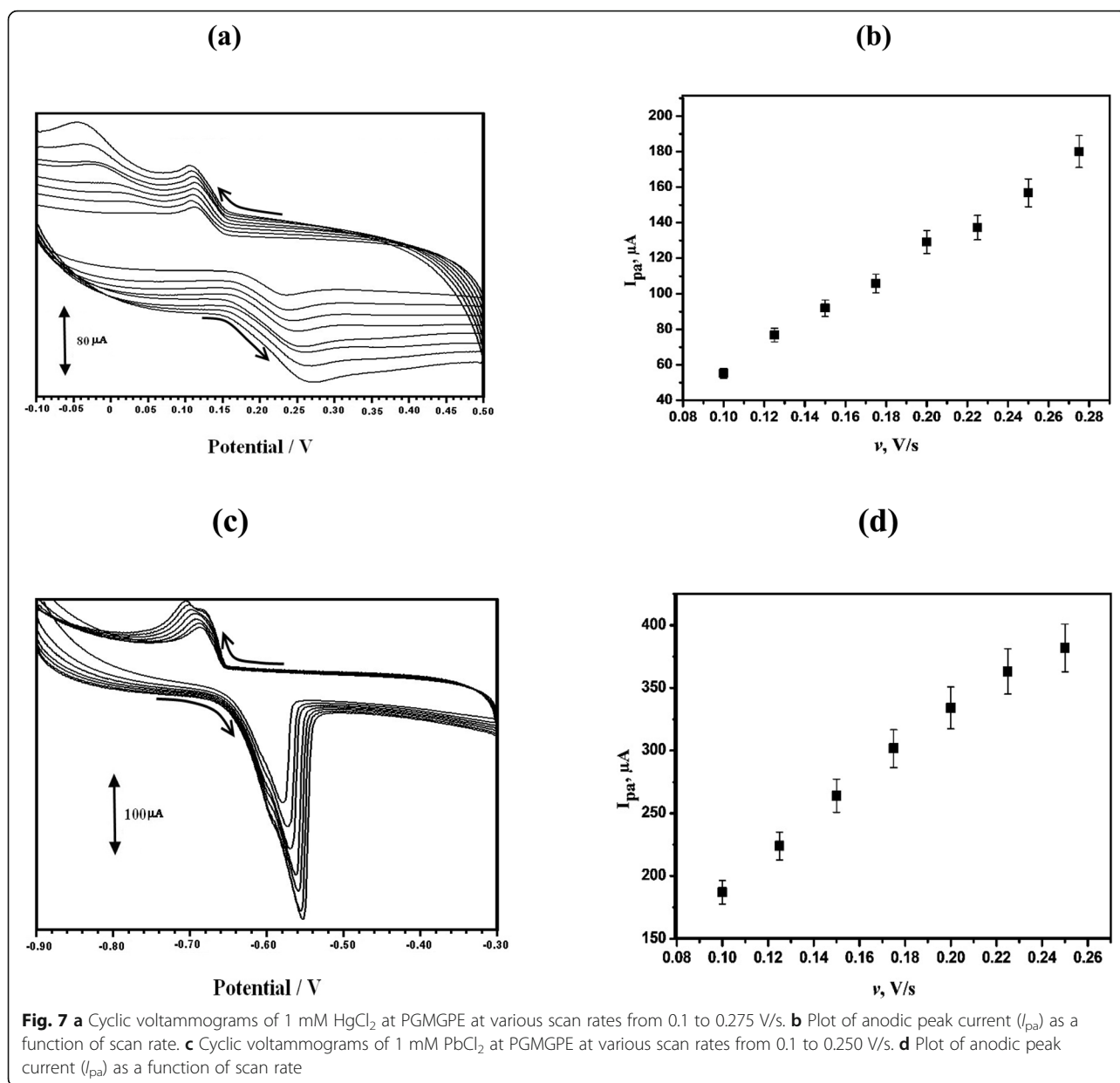
**Fig. 6 a** Cyclic voltammograms of HgCl$_2$ (1 mM) at PGMGPE with solution pH 3.5, 4.0, 4.5, 5.0, and 5.5. **b** $E_{pa}$ vs pH. **c** $I_{pa}$ vs pH

current at pH lower than 4.5 is explained by the protonation process, which affects the hydrophilic character of the electrode. The decrease in the current at pH higher than 4.5 is attributed to the hydrolysis of Hg$^{2+}$ ions. Therefore, all electrochemical measurements were carried out in 0.1 M PBS at an optimal pH 4.5. The linear shift in the oxidation potential is describes by the equation: $E_{pa}$ (V) = 313.4-18 pH, with the correlation coefficient of 0.99 (Fig. 6b). The relation between the peak current and pH is shown in Fig. 6c.

**Effect of scan rate**

To study the nature of the electron process, the effect of various scan rates was evaluated in 0.1 M PBS of pH 4.5 from 0.1 to 0.275 V/s. Figure 7a shows the effect of scan rate on the peak current for HgCl$_2$. It was observed that as the scan rate increased, the peak current also increased, and the potential was shifted to the more positive side. It was observed that the peak potential was shifted from 0.235 V to 0.270 V. The linear relationship between the peak current and scan rate is described by the
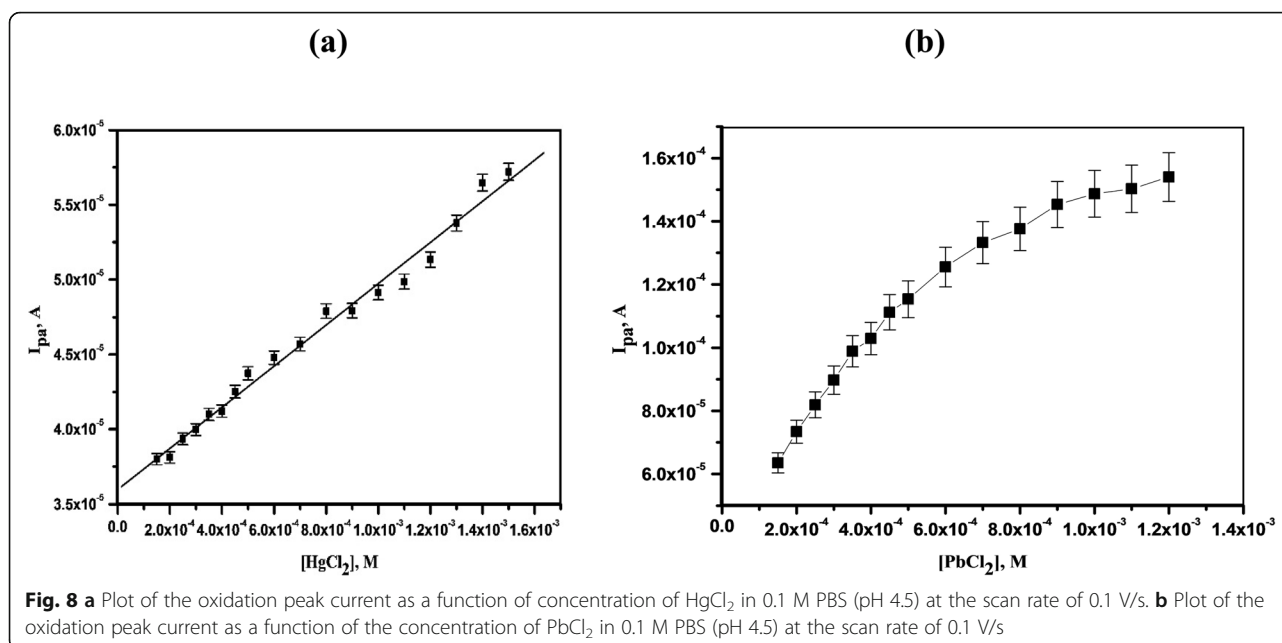
**Fig. 7 a** Cyclic voltammograms of 1 mM $HgCl_2$ at PGMGPE at various scan rates from 0.1 to 0.275 V/s. **b** Plot of anodic peak current ($I_{pa}$) as a function of scan rate. **c** Cyclic voltammograms of 1 mM $PbCl_2$ at PGMGPE at various scan rates from 0.1 to 0.250 V/s. **d** Plot of anodic peak current ($I_{pa}$) as a function of scan rate

following equation: $I_{pa}$ (μA) = -11.34 + 682.57 $v$ (V/ s), with the correlation coefficient of 0.99 (Fig. 7b). It indicates that the electrode process is adsorption controlled.

Figure 7c shows the cyclic voltammograms for $PbCl_2$ for different scan rates. It was seen that as the scan rate increased, the peak current also increased and peak potential was shifted toward less negative from 0.1 to 0.250 V/s in 0.1 M PBS having pH 4.5. There is a linear relationship between the peak current and scan rate as observed in the linear regression equation of $I_{pa}$ (μA) = 60.17 + 1334.4 $v$ (V/s), with the correlation coefficient of 0.994 (Fig. 7d), indicating that the electrode process is adsorption controlled.

## Effect of concentration

The effect of concentrations on the peak current of $HgCl_2$ and $PbCl_2$ at PGMGPE was studied using CV in 0.1 M PBS, 4.5 pH, at the scan rate of 0.1 V/s. It was seen that as the concentration increased, the peak current also increased in the range of $1.5 \times 10^{-4}$ to $1.5 \times 10^{-3}$ M for $HgCl_2$. Two linear ranges were observed for $PbCl_2$ as follows: $2 \times 10^{-4}$ to $4.5 \times 10^{-4}$ M and $5 \times 10^{-4}$ to $1.2 \times 10^{-3}$ M. A linear relationship was observed between the concentration and peak current in the linear equation: $I_{pa}$ (A) = $3.59 \times 10^{-4}$ +0.013 [$HgCl_2$] (M) with the correlation coefficient of 0.993 (Fig. 8a), and $I_{pa}$ (A) = $4.44 \times 10^{-5}$ +0.149 [$PbCl_2$] (M) with the correlation coefficient of 0.996 (Fig. 8b). The detection limit was calculated by the following equation: DL= 3S/N (Manjunatha, 2018a, b;

**Fig. 8 a** Plot of the oxidation peak current as a function of concentration of HgCl$_2$ in 0.1 M PBS (pH 4.5) at the scan rate of 0.1 V/s. **b** Plot of the oxidation peak current as a function of the concentration of PbCl$_2$ in 0.1 M PBS (pH 4.5) at the scan rate of 0.1 V/s

Manjunatha et al., 2018), where $S$ is the standard deviation for the blank (5 runs) and $N$ is the slope obtained from the calibration curve, and was obtained as 6.6 μM (HgCl$_2$) and 0.8 μM (PbCl$_2$). The limit of detection is used to describe the smallest concentration of an analyte that can be reliably measured by an analytical procedure. The comparison of the detection limit of the present work with other works is shown in Table 1 (Lu et al. 2015; Cesarino et al. 2008; Martinez-Huitle et al. 2010; Wang et al. 2011; Othman et al. 2016).

### Simultaneous study

The possible interference of the two metal ions was evaluated by simultaneous analysis of HgCl$_2$ and PbCl$_2$. Figure 9a shows the CV response of HgCl$_2$ (1 mM) (b) and PbCl$_2$ (1 mM) (a) recorded from -0.7 to 0.3 V at 0.1 V/s in 0.1 M PBS (pH 4.5). Figure 9b shows the DPV response of HgCl$_2$ (1 mM) (b) and PbCl$_2$ (1 mM) (a) recorded from -0.7 to 0.3 V at 0.1 V/s in 0.1 M PBS (pH 4.5). The clean separation of the two potential peaks shows the possibility of the simultaneous determination of HgCl$_2$ and PbCl$_2$. At an identical time, the interference study was also carried in the sample
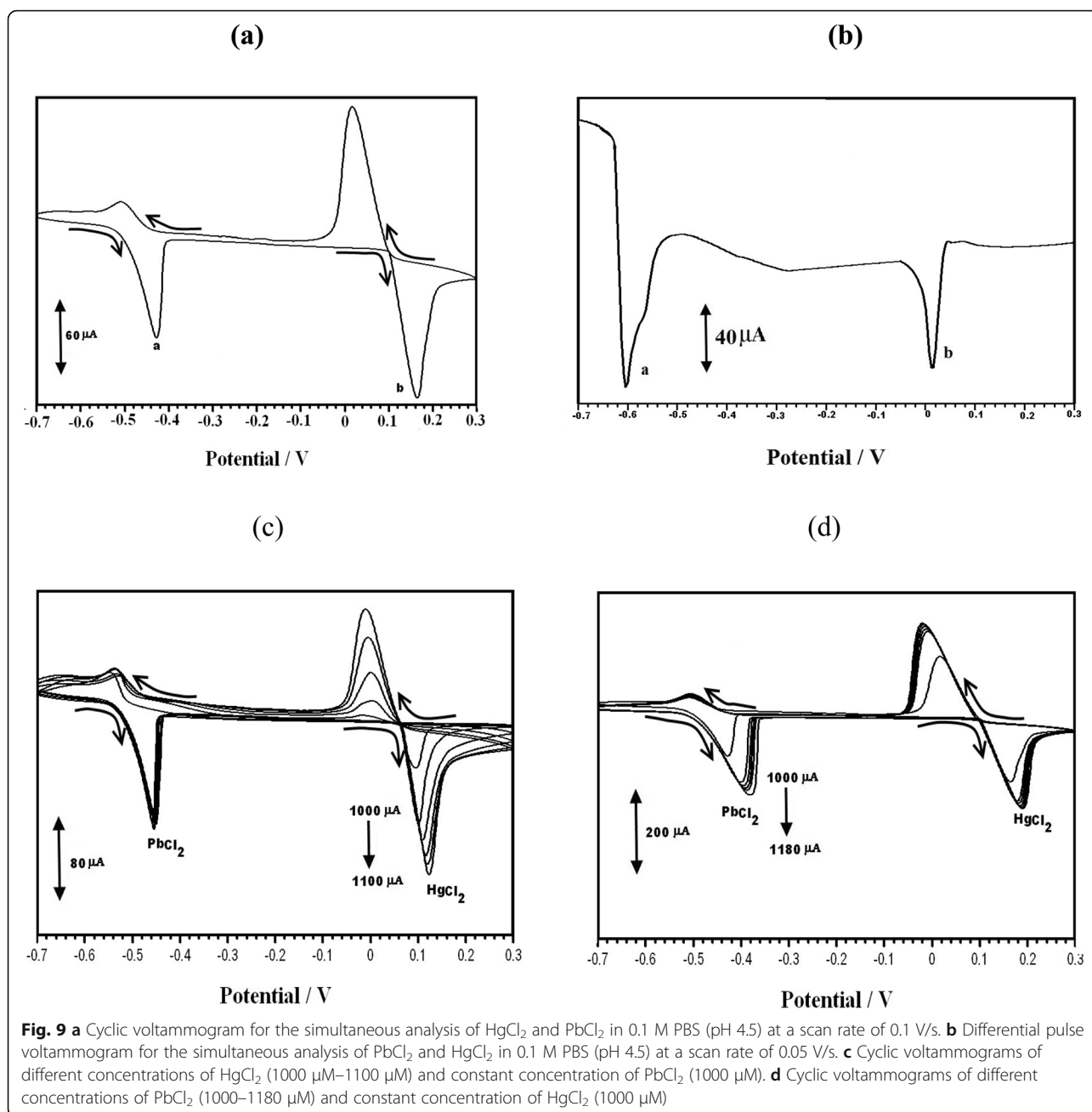
of the mixture containing HgCl$_2$ and PbCl$_2$. This was achieved by changing the concentration of one species and keeping the other constant and recording CVs. Figure 9c shows the CVs of HgCl$_2$ with different concentrations (1000 μM-1100 μM), while keeping the concentration of PbCl$_2$ as 1000 μM. There was no change in the peak current for PbCl$_2$, while the peak current for HgCl$_2$ increased linearly. In the next step, the concentration of HgCl$_2$ was varied from 1000 μM–1180 μM by keeping the concentration of PbCl$_2$ (1000 μM) constant, and only the peak current of HgCl$_2$ was increased linearly with the concentration (Fig. 9d). This result shows that HgCl$_2$ and PbCl$_2$ exist independently in their mixture of samples.

### Application of the modified electrode to the real sample
#### Water sample

The analytical performance of the prepared electrode in practical application was evaluated by measuring the activity of heavy metal ions in the real water sample. The sensor was tested and validated using the water sample in the potential -0.1 to 0.50 V with a scan rate of 0.1 V/

**Table 1** Comparison between the detection limit of the proposed method with other previously reported methods

| Electrode | Technique | Metal ion | Detection limit (μM) | Reference |
|---|---|---|---|---|
| Graphene–MnO$_2$ | LSV | Hg$^{2+}$ | 2 | Lu et al. 2015 |
| CPE–SBA-15 | DPASV | Hg$^{2+}$ | 0.4 | Cesarino et al. 2008 |
| GCE/CT | DPV | Pb$^{2+}$ | 0.8 | Martinez-Huitle et al. 2010 |
| GCE/PANI | SWV | Pb$^{2+}$ | 0.1 | Wang et al. 2011 |
| Ag/DHE | CV | Pb$^{2+}$ | 0.76 | Othman et al. 2016 |
| PGMGPE | CV | Hg$^{2+}$ | 6.6 | Present work |
| | | Pb$^{2+}$ | 0.8 | |

**Fig. 9 a** Cyclic voltammogram for the simultaneous analysis of $HgCl_2$ and $PbCl_2$ in 0.1 M PBS (pH 4.5) at a scan rate of 0.1 V/s. **b** Differential pulse voltammogram for the simultaneous analysis of $PbCl_2$ and $HgCl_2$ in 0.1 M PBS (pH 4.5) at a scan rate of 0.05 V/s. **c** Cyclic voltammograms of different concentrations of $HgCl_2$ (1000 μM–1100 μM) and constant concentration of $PbCl_2$ (1000 μM). **d** Cyclic voltammograms of different concentrations of $PbCl_2$ (1000–1180 μM) and constant concentration of $HgCl_2$ (1000 μM)

s. In the groundwater sample, no signal was observed for the metal ions ($Hg^{2+}$ and $Pb^{2+}$); however when different concentrations of $HgCl_2$ and $PbCl_2$ were added to the sample, current peaks were observed. Table 2. shows the recovery ranges of Hg (II) and Pb (II). The obtained result shows that the developed electrode can have a suitable potential applicability in environmental monitoring.

### Biological sample

Blood sample (2 ml) was collected from the nearest district hospital. The serum was prepared by centrifuging the blood sample at 5000 rpm for 5 min. 1 ml of the

**Table 2** Result for the determination of Hg (II) and Pb (II) ions in groundwater

| Sample | Added (μM) | Found (μM) | Recovery (%) |
|---|---|---|---|
| HgCl2 | 150 | 147.75 | 98.5 |
|  | 200 | 202 | 101 |
| PbCl2 | 40 | 39.1 | 97.84 |
|  | 60 | 60.7 | 101.2 |

**Table 3** Determination of metal ions in the blood sample

| Metal ion | Added (μM) | Found (μM) | Recovery (%) |
|-----------|-----------|-----------|-------------|
| $Hg^{2+}$ | 100 | 79.92 | 79.92 |
|           | 1300 | 1280.63 | 98.51 |
| $Pb^{2+}$ | 80 | 69.31 | 86.63 |
|           | 100 | 91.30 | 91.30 |

sample was dissolved in 25 ml of PBS and made up to the mark, and the experiment was carried out with the standard addition method. Table 3 shows the recovery ranges of metal ions in the blood sample.

### Sensor stability and reproducibility

To investigate the stability of the sensor, the current behavior was studied before and after 25 cycles in 0.1 M PBS, at 4.5 pH and scan rate of 0.1 V/s. It was observed that even after 25 cycles, 85% of the initial current was retained, showing that the developed sensor had good stability. Reproducibility was studied with three successive removals of the electrode, keeping the solution same. It was observed that the relative standard deviation of 2.85% for the analyte indicated that the electrode had acceptable reproducibility.

### Novelty statement

In this work, a novel electroanalytical method which showed good sensitivity and comparable with previous reports was presented. The method is based on the subduing of the peak current of the modifier due to the analyte in a modified carbon paste electrode.

## Conclusions

In this study, an electrochemical sensor based on polyglycine-modified graphene paste electrode (PGMGPE) was developed for the quantification of trace Pb (II) and Hg (II). The developed electrode exhibits good sensitivity, selectivity, good stability, and lower detection limit. It was shown that the developed electrode provides an alternative strategy for the electrochemical determination of heavy metal ions. The modified electrode has been used to determine the Pb (II) and Hg (II) in water and blood samples. The result obtained in the analysis of Hg (II) and Pb (II) in water and blood samples had a good recovery, demonstrating the applicability of the method for real sample analysis.

### Abbreviations

CV: Cyclic voltammetry; DPV: Differential pulse voltammetry; PBS: Phosphate buffer solution; PGMGPE: Polyglycine-modified graphene paste electrode; BGPE: Bare graphene paste electrode; FESEM: Field emission scanning electron microscopy; LSV: Linear sweep voltammetry; DPASV: Differential pulse anodic stripping voltammetry; SWV: Square wave voltammetry; $K_4[Fe(CN)_6]$: Potassium ferrocyanide; CPE: Carbon paste electrode; CT/ GCE: Chitosan/glassy carbon electrode; GCE/PANI: Glassy carbon electrode/ polyaniline; Ag/DHE: Silver electrode/dithizone

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