Bio modified carbon paste electrode for the detection of Pb(II) ions from wastewater

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ABSTRACT

In recent days, heavy metal pollution in water is one of the serious environmental concerns. Lead is one among the highly toxic heavy metals, and its toxicity arises due to its non-degradation characteristic in living organisms. The monitoring of Pb(II) ions concentration in drinking water is more essential for a healthy human life, and safe environment. In this work, a bio-modified carbon paste electrode (BMCME) was constructed with live cells and thermally dried biomass (extracted protein) from *Pseudomonas aeruginosa* cells and employed for the detection of Pb(II) ions from wastewater. The biomass and biosensor preparation, optimization, the performance of modified biosensor in detection of Pb(II) ions are discussed here. The effect of various parameters, like pH, biomass composition, scan rate, and metal ion concentration, were studied to obtain the best electrochemical response. Further, the active surface of electrode and solution characteristics, Chronocoulometry and Electrochemical impedance spectroscopy were studied. FTIR analysis was done to find the functional groups present in the thermally dried biomass. From the present study, it has been observed that the thermally dried protein biomass electrode (DPBE) has more sensitivity than the bare carbon paste electrode.

Key words | carbon paste electrode, cyclic voltammetry, heavy metals, Pb(II) ions, *Pseudomonas aeruginosa*

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INTRODUCTION

Generally, metallic elements having density 5 g/cm^3 or above are termed as heavy metals (Tchounwou *et al.* 2014). Heavy metal contamination in the environment causes ill effects on any living organisms. In recent years, there has been an increasing environmental and public health issues associated with contamination of water by heavy metals (Ali & Shakoor 2013). Most of the heavy metals are toxic as they accumulate in living organisms and cannot be metabolized or excreted. Due to the above reason, heavy metal contaminated water has to be treated before discharging to the environment. Some of the metals like Hg, Pb, Cr, As, and Cd are very harmful to living organisms even at low concentrations (Nazır & Yuce 2011).

The application of heavy metals in chemical process industries like electroplating, paint, leather processing, mining operation, etc. have been increased exponentially because of the high population and their demand for commodities. In lead-acid battery industries, lead oxide is the major component of the battery paste. The effluent released from the battery industries is the prime source for the Pb(II) ions. The exposure of a high concentration of Pb(II) ions can cause diseases that include problems in hemoglobin synthesis, neurological disorders, kidney diseases, and effects the gastrointestinal tract, etc. (Wang *et al.* 2016). Lead ions in the environment arise from both the anthropogenic and natural sources, and its exposure can occur through food, water, air, and soil. According to Indian standard drinking water specification 1991, the permissible limit of lead in drinking water is 0.01 mg/L (March *et al.* 2015). Over the past decade, many techniques, such as Atomic Absorption Spectroscopy (AAS), Inductive Plasma Coupled Spectroscopy (IPCS), Atomic Fluorescence Spectroscopy (AFS) have been used for determination of lead concentration (Lee *et al.* 2015). These techniques are

doi: 10.2166/wst.2020.045

sensitive and selective, but they require expensive instruments, complex operational procedures, skilled labors, pre-treatment processes, and long detection times. Electrochemical methods could be an alternative to these techniques as they overcome the above drawbacks (Lu *et al.* 2018).

Carbon paste electrodes are the most commonly used electrodes in electrochemical methods because of its simplicity in fabrication and modification, low cost, high efficiency, and eco-friendly (Laghrib *et al.* 2019). Biosensors are promising analytical devices, and several different configurations have been described in the past for heavy metal detection (Bontidean *et al.* 1998). The bio-modified carbon paste electrode (biosensors) was highly selective and sensitive compare to the bare carbon paste electrode. Because microorganisms adsorbs a wide range of chemical substances through their biosorption capacity (Yüce *et al.* 2010). These biosensors offer advantages over the carbon paste electrode like efficient metal recovery, minimization of the volume of chemical, and biological sludge to be disposed of (Slawomir *et al.* 2015). Microorganisms like bacteria, fungi, algae, and yeasts have been used in the preparation of biosensors (Nazır & Yuce 2011). The response of biosensor depends on the properties of Pb(II) ions present in the solution, the cell wall composition of microorganisms, cell physiology, as well as physicochemical factors such as temperature, pH, ionic strength, contact time, and initial metal ion concentration. It involves the active participation of several anionic ligands present in the biomass, such as phosphoryl, carboxyl, carbonyl, sulfhydryl, and hydroxyl groups (Taylor *et al.* 2001). The bio modified carbon paste electrode prepared by dry coated had a detection limit of 6×10^{-7} M for Pb(II) ions by Nazır (Nazır & Yuce 2011).

The main objective of the present study is to fabricate a biosensor by modifying the carbon paste electrode (CPE) with *P. aeruginosa* cells for the detection of trace amounts of Pb(II) ions from aqueous solutions. *P. aeruginosa* is a gram-negative bacterium, the aerobic rod is belonging to the *Pseudomonadace* bacterial family, and it has been used for heavy metal biosorption study. The negatively charged carboxylate groups in the extracted cell proteins are believed to be responsible for the binding of Pb(II) ions. In this work, *P. aeruginosa* cells were used in two forms, first one, live cells are used for drop coating for electrode surface modification and second, thermally dried protein extract biomass (from *P. aeruginosa* cells) used as a mixed biomass electrode. The experimental results from the bare carbon paste electrode (BCPE) and BMCPE were compared for the detection of Pb(II) ions.

MATERIALS AND METHODS

Reagents

Fine graphite powder of −60 mesh particle size with 98% extra purity was purchased from Loba Chemie Pvt.Ltd. All other chemicals such as heavy paraffin oil, lead nitrate, and sulphuric acid used were of analytical grade. Working standards of Pb(II) solution was prepared from 1,000 mg/L stock solutions. The stock solutions was prepared by dissolving 1.5984 g of lead nitrate in one litter of deionized water.

Preparation of carbon paste electrode

The CPE was prepared by mixing 1 g of carbon powder thoroughly with a known quantity of paraffin oil (0.2 g). The electrode did not bind with carbon properly below 0.2 g of the heavy oil, and the carbon mix seemed to lose its consistency and also the increase resistance above 0.2 g of the heavy oil. The homogeneous mixture was filled to a depth of 5 mm into the glass tube, having 4 mm inner diameter and 40 mm height. A copper wire of 0.01 mm diameter was inserted into the glass electrode to connect with the electrochemical workstation. The completed electrodes were polished with a smooth paper surface and dried for a minimum of 24 hours.

Preparation of bio-modified CPE

P. aeruginosa was obtained from MTCC, Chandigarh (India). A loop of bacteria was taken in a sterilized nutrient broth medium 3 and cultivated in a rotary incubator at a shaking speed of 120 rpm for 24 hours at a temperature of 35 °C (Nazır & Yuce 2011). Population of bacteria was cultivated by adding subculture of bacteria to the nutrient medium. The fully grown culture from the nutrient medium (end of log phase, cell count is 7.2×10^5 cells/ml) was harvested by centrifuged at 6,000 rpm for 15 minutes at 4 °C and washed twice with deionised water to remove impurities. The extracellular protein was precipitated from the supernatant solution by adding ammonium sulphate for 85% saturation at 4 °C. The extracellular protein was pelletized by centrifugation at 12,000 rpm for 20 min. Finally, the crude extracellular protein was separated from the pellet by dissolving in 2 ml of Tris-HCl buffer and dialyzed for 12 hrs with 1 L of the same buffer solution. The protein was then thermally dried at 70 °C for 24 hours, and the dried protein

biomass was powdered using piston mortar and stored in an airtight container for further use. The thermally Dried Protein Biomass Electrode (DPBE) was used in three different concentration ranging from 5–15 wt % to prepare working electrodes.

Another method of bio modification was done by drop coating of the bacterial cell directly on the electrode surface. Harvested bacterial cells were centrifuged and washed with distilled water to remove the nutrient medium and impurities. The medium and impurities free cells are diluted with deionized water and made into known cell concentrations. Around 10 μL of diluted bacterial cells were drop coated onto the CPE surface and then allowed to dry at room temperature for 24 h. All the experiments were repeated thrice and average values were used to plot the graph.

Electrochemical workstation

The batch modes of electrochemical studies were carried out in electrochemical workstation CHI 7201E. A three-electrode system was employed, in which a saturated calomel electrode is used as the reference electrode, platinum electrode as the auxiliary electrode, and the CPE as a working electrode.

Working procedure

Working standards of various concentrations ranging from 1–5 ppm of Pb(II) ions were prepared from a stock solution of 1,000 ppm by dilution method. Cyclic voltammetry (CV) is an electroanalytical technique through which information about the reduction and oxidation potential obtained. The CV was done in the standard potential range between −1 V to 1 V for the evaluation of electrode performances. In chronocoulometry technique, a step potential is applied to the CPE and response received as an integrated form of the current–time. It is a useful technique to measure the charge that flows across the electrode-electrolyte interface, electrode surface area, mechanisms, and kinetics for chemical reactions combined with electron transfer reactions. Electrochemical Impedance Spectrum (EIS) was used to determine resistance and capacitance of electrode, charge transfer resistance, and solution resistance based on the mobility of ions towards the electrode surface. The experiment was conducted with frequency swept ranging from 10^5 Hz to 0.1 Hz for 5 ppm of Pb(II) solution.

RESULTS AND DISCUSSION

Effect of pH on Pb(II) ions detection

The effect of pH was studied using CV for BCPE in the range of 3–7 for an initial Pb(II) concentration of 5 ppm. The reduction and oxidation peaks were observed in the range of pH 3–3.5. Further increase in pH, the redox reaction does not exist, as shown in Figure 1. The reduction peak current values are obtained at 2.5×10^{-6} A and 3.75×10^{-6} A at 0.3 V for 3 and 3.5 pH, respectively. From the experimental results, the activity of the functional group on the electrode surface for binding heavy metals and active participation of the metal ions towards bio-sorption were strongly influenced by pH. Biosorption of metal ions is decreased due to metal ions involvement in hydrolysis and forms hydroxylated complexes (Pb $(OH)^+$) at high pH value. Graphite particle interacts with the hydronium ions (H_3O^+) at pH below three due to which the surface of the electrode gets positively charged and results in repulsion with Pb(II) ions. In the pH range from 3 to 3.5, the electrode surface gets exposed to amino, carboxyl, and phosphate groups and carries a negative charge on the electrode surface, so the electro reduction of positively charged Pb(II) ions was high (Ho 2005).

Cyclic voltammetry of Pb(II) ion

Cyclic voltammetry was performed in the range of −1 V to 1 V by maintaining a constant scan rate and initial Pb(II) concentration as 0.1 V/s and 5 ppm, respectively (Figure 2). The experiment was conducted for the BCPE, thermally dried protein biomass electrode (DPBE) (5%, 10% & 15%

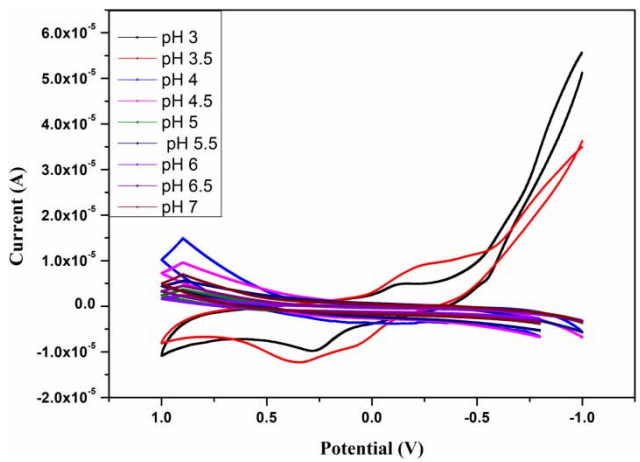

Figure 1 | Effect of pH on detection of Pb(II) ions using CV.

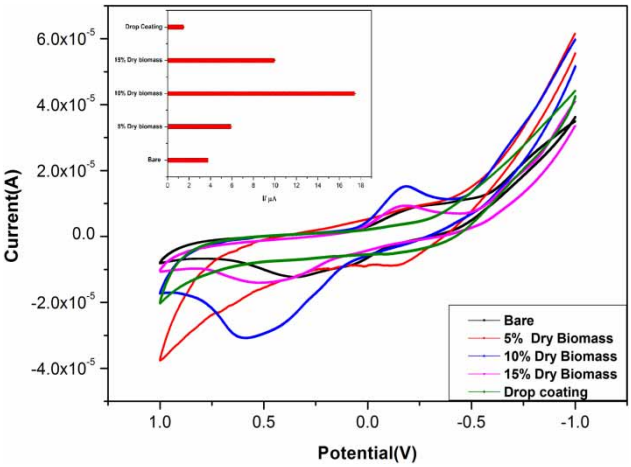

Figure 2 | Cyclic Voltammetry for bare and bio- modified electrodes.

of weight) and bacterial cell drop coated electrode (BCDE) at a pH of 3.5.

The experimental results are showing the presence of both cathodic and anodic peaks (at +0.6 V & −0.2 V), which indicate the Pb(II) redox reaction is reversible. And also, the thermally dried biomass electrodes were having high cathodic and anodic current values when compared to the other electrodes (BCPE and BCDE) for Pb(II) ion redox reactions. The maximum redox peak current has been observed for a 10% DPB electrode, such as 1.7 $*10^{-5}$ A and 7.8$*10^{-6}$ A for the reduction and oxidation at 0.6 V and −0.2 V, respectively. The dried protein biomass electrode (10%) has more than fourfold peak current value of BCPE at the optimum working condition.

Effect of scan rate

The effect of the scan rate was investigated in the range of 0.01 V/s to 0.1 V/s for BCPE and bio-modified electrodes (DPBE and BCDE) by maintaining constant pH and initial Pb(II) concentration as 3.5 and 5 ppm respectively. As the scan rate increased, both the cathodic and anodic peak current values increased linearly, as shown in Figure 3; which might be due to the redox reactions controlled by initial metal ion concentration and diffusion of metal ions. The cathodic peak current (Ipc) values of 10% DPBE were plotted with the square root of the scan rate ($v^{1/2}$) (the figure is not shown) follows a linear regression equation with $R^2 = 0.9639$ as given below Equation (1)

$$Ipc = 0.00147\, v^{1/2} + 0.00005 \quad (1)$$

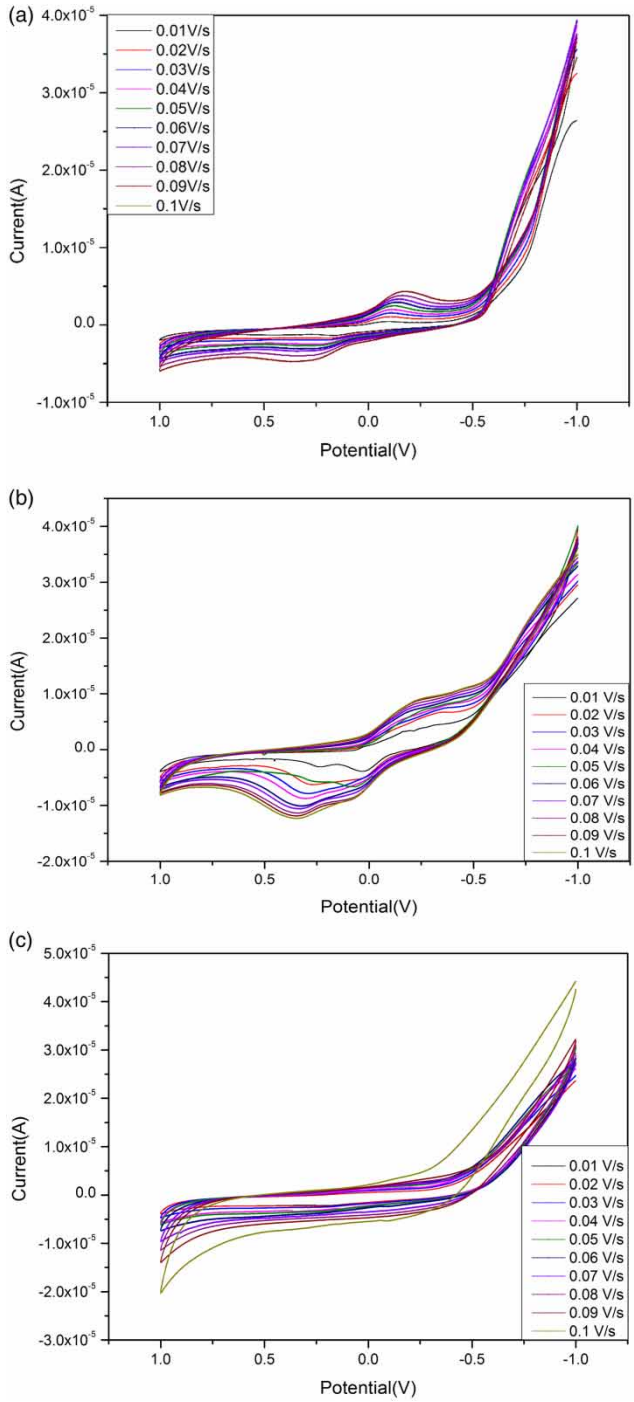

Figure 3 | Effect of scan rate on the reduction of Pb(II) ion. (a) BCPE (b) 10% DPBE and (c) BCDE.

The optimum scan rate was to be found 0.1 V/s for both the bare and bio-modified electrodes, in which the cathodic and anodic peak current values were high. Hence all the experimental studies were carried out with the scan rate of 0.1 V/s. The electrochemical redox reactions

take place at the DPBE – Pb(II) solution interface, as shown in Equations (2) and (3).

$$Pb^{2+} + 2e^- \rightarrow Pb \quad E^0 = 0.6V \tag{2}$$

$$Pb \rightarrow Pb^{2+} + 2e^- \quad E^0 = -0.2V \tag{3}$$

Effect of initial metal ion concentration

The effect of Pb(II) ion concentration in water was studied in the range of 1 ppm to 5 ppm to find the electrochemical behaviour of electrode and electrolyte solution. The peak current values increase linearly with an increase in Pb(II) ion concentration from 1 ppm to 5 ppm. An increase in Pb(II) ion concentration increased the number of Pb(II) ions diffusion towards electrode surface, and also, the number of ions involved in redox reaction increased, thereby peak current increased linearly as illustrated in Figure 4. The ANOVA test results of the dependent variables (Concentration) and their response (Current) showed that the p value is less than 0.05 for all three electrodes, and Regression Coefficient, $R^2 \geq 0.9752$ which shows the experimental data is statistically significant.

Lower limit of detection of Pb(II) ion

The LLOD of Pb(II) ions for bare and bio-modified electrode was studied using CV. The LLOD value was found to be 10^{-2} ppm, 10^{-3}, and 10^{-5} ppm for BCPE, BCDE, and DPBE electrodes, respectively, as illustrated in Figure 5. Due to the high conductivity, and the existence of more functional groups in the extracted dried protein biomass, the DPBE has more detecting ability. This bio-modified electrode had high sensing ability, and better LLOD compared to previous research findings like Salih, reported 0.3 μg/L as LLOD for detection of lead ion using square wave

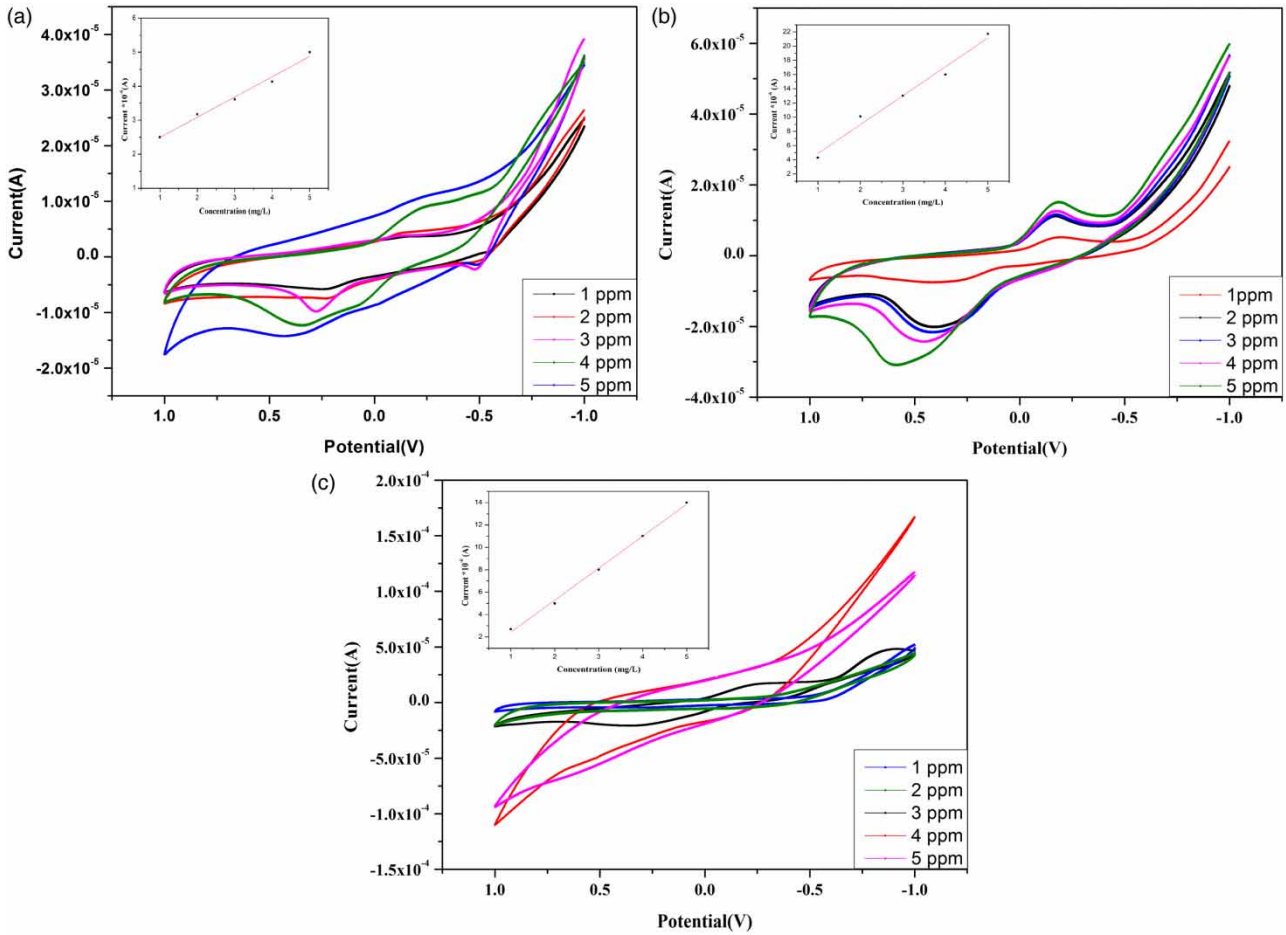

Figure 4 | Effect of initial Pb(II) ion concentration (a) BCPE: (b) 10% DPBE and (c) BCDE.

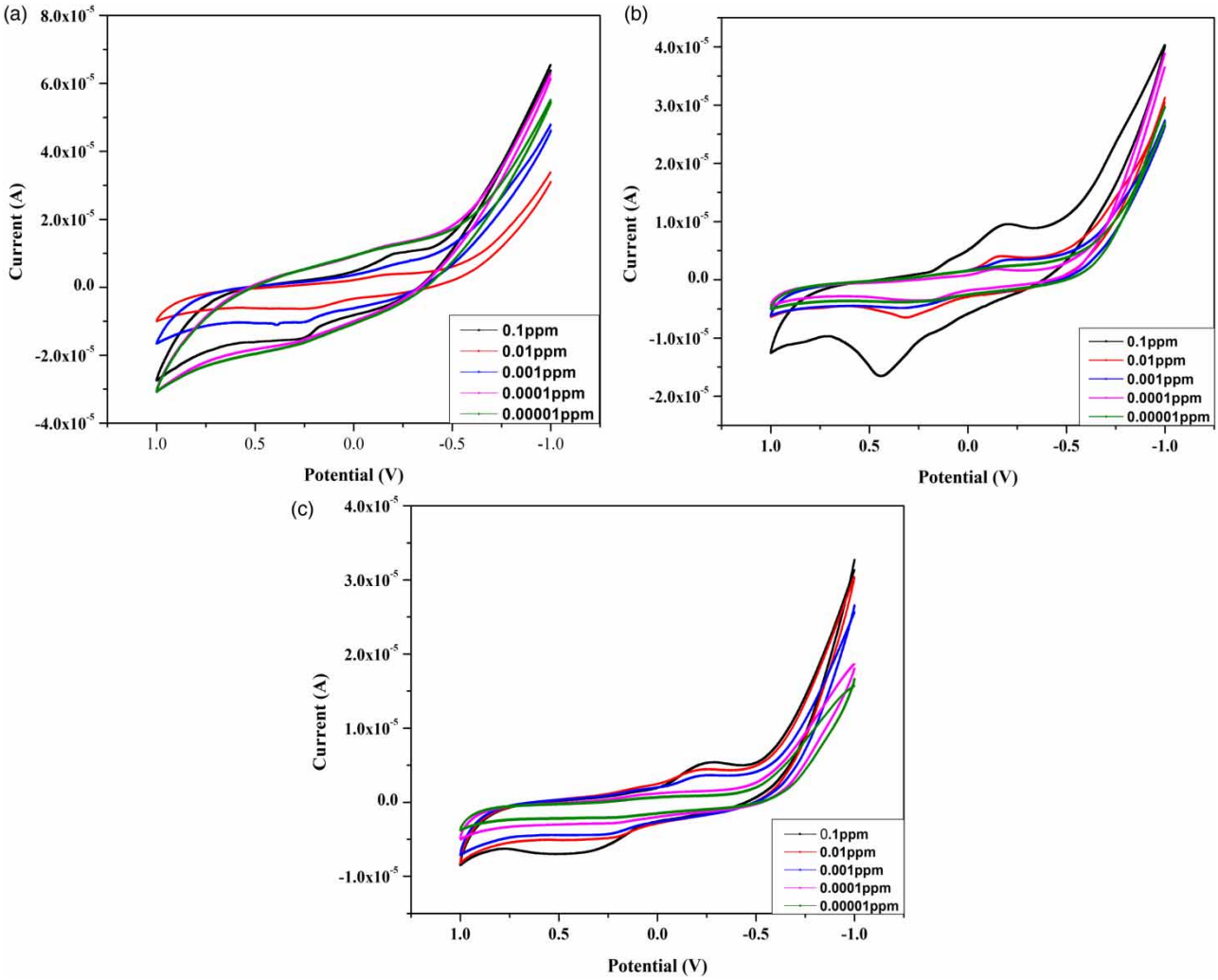

Figure 5 | LLOD of Pb(II) ion. (a) BCPE: (b) 10% DPBE and (c) BCDE.

voltammetry method for bismuth/Poly(1,8-diaminonaphthalene) modified carbon paste electrode (Salih *et al.* 2015). Dali H *et al.* reported LLOD for Pb(II) ions as 10^{-8} M by using differential pulse anodic stripping voltammetry (Dai *et al.* 2016). There are different methods available to measure the trace amount of lead ion concentration in wastewater like Inductively coupled plasma mass spectrometry (ICP-MS), Inductively coupled plasma atomic emission spectrometry (ICP-AES) and Graphite furnace atomic absorption spectroscopy (GFAAS) but their sensitivity in terms of lower level of detection (LLOD) are 0.0006 mg/L, 0.0042 mg/L and 0.0007 mg/L, respectively (Deibler & Basu 2013). Whereas, the LLOD of bio modified electrode is 0.00001 mg/L which means the electrode is highly sensitive to Pb(II) ions in wastewater compared to above mentioned conventional methods.

Chronocoulometry

Chronocoulometry (CC) studies were conducted for bare, DPBE, and BCDE electrodes. CC is a dominant electrochemical technique that provides information about reduced species. The charge that flows across the electrode-electrolyte interface was measured at the change in the electrode's potential from the no flow of current to flow of faradic current (Ansonl 1966). The experimental conditions were adjusted if the electrolytes adsorbed on the surface of the electrode. The step-change in potential was limited by a semi-infinite linear diffusion, the variation in charge with respect to time was studied using Cottrell Equation (4) (Christie *et al.* 1964),

$$ip = 2nFAD^{1/2}Ct^{1/2}\pi^{-1/2} \quad (4)$$

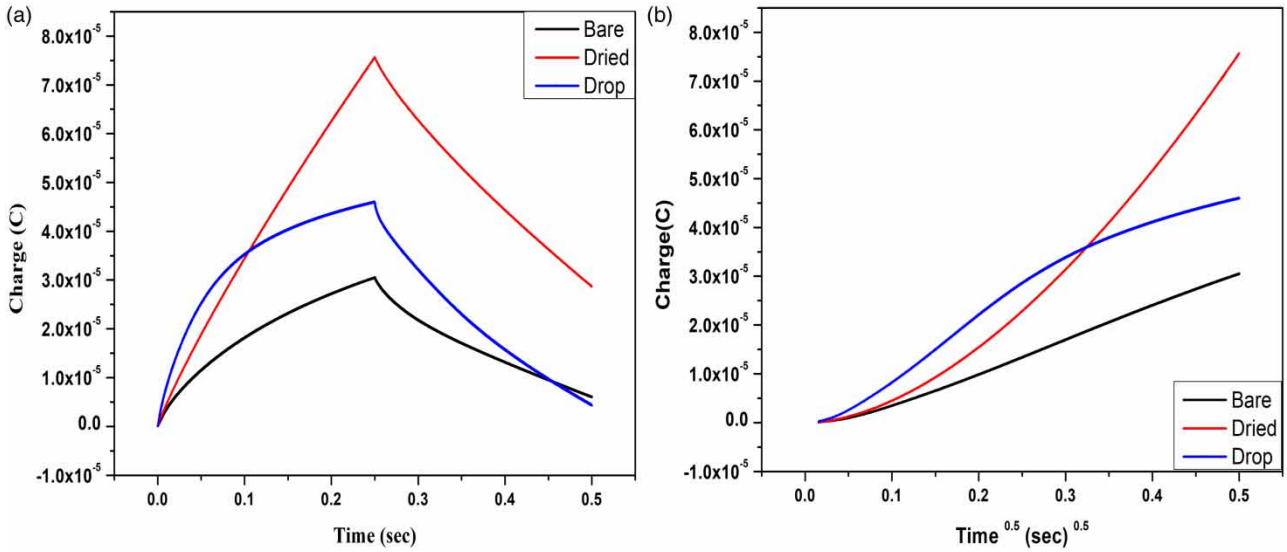

Figure 6 | (a) Chronocoulometry curves for the modified and unmodified electrodes. (b) Anson model chronocoulometry curves for the modified and unmodified electrodes.

From the graph, the slope value denoted $2nFACD^{1/2}\pi^{-1/2}$, where 'n' indicates the number of electrons transferred, 'F' represents the Faraday constant (C/mole), 'C' indicates concentration of Pb(II) ion in the solution (mole/cm^3), 'D' denotes the diffusion constant of the Pb(II) ion (cm^2 s^{-1}) and 'Q' represents the difference between chronocoulometric intercept values for bare and DPB electrode. The active surface area 'A' was calculated from the slope and found to be 0.09425 cm^2 (Li 2015; Peng *et al.* 2014). This process was favorably controlled by diffusion because the charge is linearly dependant on the square root of time (Paramasivam 2013; Radhi 2014), as shown in Figure 6.

Electrochemical impedance spectroscopy

The electrochemical impedance spectrum was studied to determine the resistive and capacitive properties of the electrolyte solution and electron transfer on the electrode surface. Here in this technique, excitation frequency f was varied over an applied potential (E), and the impedance is a ratio of E(t) and I(t). Where E(t) is the change of voltage-time function, and I(t) is the change of current time function. The interface model of the experimental data was simulated to calculate the solution resistance (Rs), charge transfer resistance (Rct); results are shown in Table 1. EIS confirms that at higher frequencies, diffusion limits the electrochemical activity, as shown in Figure 7 (Paramasivam *et al.* 2018).

Table 1 | Electrochemical parameters evaluated using impedance spectra

Electrode	Charge transfer resistance Rct (Ω)	Solution resistance Rs (Ω)
Dried	2,875	445.4
Drop	3,453	710
Bare	4,876	845.5

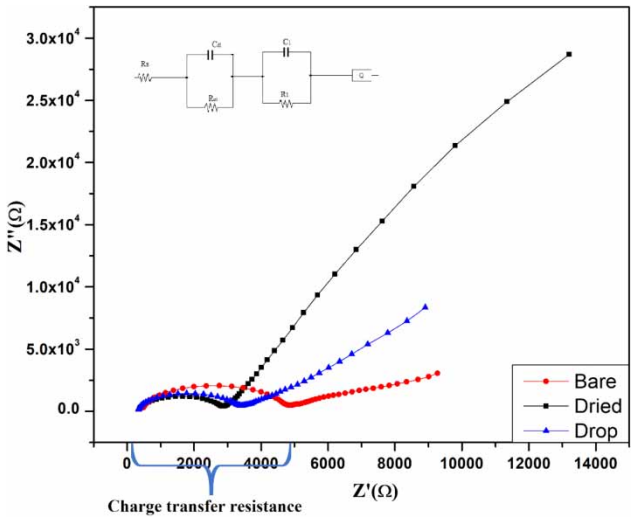

Figure 7 | Impedance spectra coupled with an equivalent circuit for bare CPE and Bio- modified CPE.

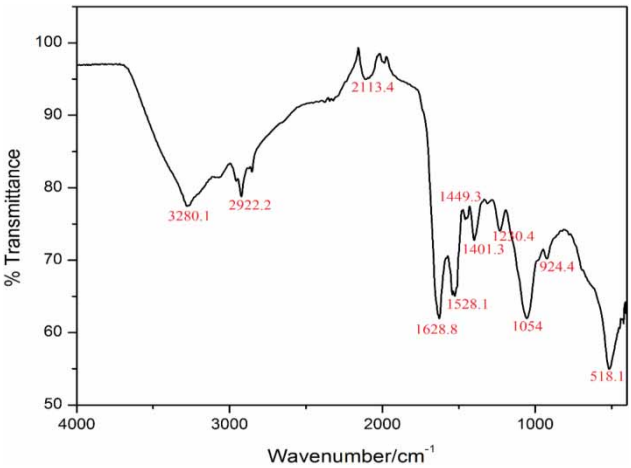

Figure 8 | FTIR for extracted dried biomass of *Pseudomonas aeruginosa*.

Characterization of dried biomass of *Pseudomonas aeruginosa*

FTIR spectra of the extracted protein dried biomass of *Pseudomonas aeruginosa* cells are shown in Figure 8. The FTIR spectra show the presence of different functional groups. Some of these functional groups interacted with the Pb(II) ions, which might be the reason for DPBE have high current values and interaction even in low ion concentration. From the literature, it is known that strong and broadband at 3,280 cm^{-1}, confirms the H-bonded OH groups, NH2 stretching (adenine, quinine, cytosine) present. At 2,922 cm^{-1} could be related to Aliphatic C-H stretching (fatty acids) and 1,628 cm^{-1} NH_2 bending, C = O, C = N stretching (amide I and II). 1,449.1 cm^{-1} C-H deformations of CH_2 or CH_3 groups in aliphatic. 1,401 cm^{-1} C-H bending, -CH_3 stretch (fatty acids), 1,230.4 C-N stretching (amide III), 1,054 cm^{-1} C-O, PO–2 stretching (glycopeptides, ribose), 924 cm^{-1} P-O-C, P-O-P stretching (phospholipids, ribose-phosphate chain pyrophosphate), 518.1 cm^{-1} C-O-C, P-O-C bonding (RNA, aromatics) (Filip & Hermann 2001).

CONCLUSION

The performance of bio-modified carbon paste electrode was evaluated at two different forms (DPBE & BCDE). The Pb(II) ion detection performance of the DPB electrode was improved fourfold compared to the bare electrode. The LLOD of Pb(II) ions by DPBE (10%) was found to be $1*10^{-5}$ mg/L under optimized condition, which shows that the DPBE surface has more electrochemical interactions, even at low concentration of Pb(II) ions. The active surface area of the DPBE was calculated using chronocoulometry as 0.09425 cm^2. From the EIS, the electron transfer resistance values of electrodes found to be 4,876 Ω and 2,875 Ω for bare and 10% DPBE respectively. The *Pseudomonas aeruginosa* cells modified electrode was found to be an effective and selective biosensor for the detection of Pb(II) ions in wastewater.

ACKNOWLEDGEMENTS

It is grateful to acknowledge the financial support of National Institute of Technology Calicut, India (Institute student innovative project), and KSCSTE, Thiruvananthapuram, Kerala Project (Ref No.: TP/16/2015/KSCSTE) and DST, SREB (Ref No.: EEQ/2018/001261).

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First received 22 September 2019; accepted in revised form 24 January 2020. Available online 4 February 2020