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A Calix[4]arene-tren modified electrode for determination of Lead ions in aqueous solution

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Abstract: In this study, a simple and sensitive electrochemical sensor based on Calix[4]arene-tren (Calix-tren) modified glassy carbon (GC) electrode was developed for the determination of Pb (II) ions. Electrochemical behavior of Calix-tren modified electrodes were investigated by using cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). The results indicate that Calix-tren modified GC electrode provides good electron transmission pathway than bare GC electrode. The amount of Pb (II) was determined by differential pulse anodic stripping voltammetric analysis as a sensitive detection technique. The experimental parameters such as pH, deposition time and deposition potential were optimized. The optimum pH value was selected as 7.0. The effect of deposition potential and deposition time on the peak current was tested and the optimum values were chosen as -1.2 V and 120 s, respectively. Under the optimal conditions, the working range of the developed sensor was determined as 0.48-2.31 µM, limit of detection (LOD) was 0.11 µM and the RSD obtained in the reproducibility study was 2.78 %. It was also found that the developed method could be used in the determination of Pb (II) ions in real samples with satisfactory results.

Keywords: Calix[4]arene; electrochemical sensor; Pb (II).

1. Introduction

The heavy metals are toxic and poisonous at low concentrations. As trace elements, some heavy metals are required to maintain the metabolism of the human body. However, higher concentrations may lead to poisoning. Heavy metal ions pose a harmful risk to the ecological environment and public health due to their high toxicity, accumulation effect in living organisms and non-biodegradable properties [1, 2].

The Pb (II) ion is a representative of heavy metal ions commonly found in the environment. Despite of its lethal and toxicity effects which are known for several centuries, lead is an environmentally important chemical element. The exposure to lead ions through contamination of food, cosmetics and cigarette smoking is not safe for humans. The presence of heavy metal ions, such as Pb (II) in the environment at causes health related problems like anemia, kidney damage, a disorder of the blood, memory loss, muscle paralysis[3]. Hence, it is increasingly important and necessary for the health of human beings to develop analytical methods that enable a fast, selective, sensitive, and convenient determination of Pb (II) in soil, drinking water and biosystem. Some of the approaches included conventional methods such as atomic absorption spectroscopy (AAS) and gas chromatography-mass spectrometry. However, these methods have some disadvantages that limit their effectiveness, such as cost, time-consuming, and the need for early pretreatment procedures.

The role of macrocycles for selectivity of heavy metal ions in electrochemistry has been highlighted in many recent reviews. Over the past several years, calix[n]arenes that are members of

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synthetic macrocycles have attracted major attention from the sensor technology community owing to their preorganized conformational features[4]. Calix[n]arenes are synthesized through base catalyzed electrophilic aromatic substitutions via condensation of p-tertbutyl phenols with formaldehyde a significant group of building blocks. These cyclic supramolecules are easily available on a great scale and have almost unlimited possibilities for different chemical modification[5]. Moreover, the calix[n]arene skeleton can be variously derivatized at both the upper and lower rim to gain a variety of structures with a large range of applications in different areas in electrochemistry. In recent years, calixarenes have gained important attention organized properties for the synthesis of different calixarene derivatives with the suitable complexing gap to recognize various species of heavy metal ions[6, 7].

Herein, by utilizing the unique properties of calixarenes, we have developed an electrochemical biosensor for the determination of Pb (II) in aqueous solutions.

2. Experimental

2.1. Chemicals and apparatus

Potassium chloride (KCl), ethylene diamine (EDA), 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide (EDC), N-hydroxy succinimide (NHS), potassium ferricyanide, dimethyl sulfoxide (DMSO) were purchased from Sigma Aldrich. All electrochemical studies were performed with IVIUM electrochemical analyzer (Ivium Technologies, Netherlands). A conventional three electrode system equipped with a modified glassy carbon electrode (GCE) as the working electrode, a Ag/AgCl electrode (BAS MF 2052) as the reference electrode, and a platinum wire (BAS MW 1034) as the auxiliary electrode, was used for all electrochemical measurements.

The pH values of solutions were measured with Orion 410A+ pH meter and ORION combined pH electrode. All aqueous solutions were prepared with distillated water obtained from Millipore Milli-Q Plus water purification system. ^{1}H NMR spectra were referenced totetramethylsilane (TMS) at 0.00 ppm as the internal standard solutionand recorded on a Varian 400 MHz spectrometer at room temperature (25 ± 1 °C).

2.2. Synthesis of Calix[4]arene-tren derivative

The calix[4]arene derivatives (**1-3**) were synthesized according to reported methods[8, 9]. Calix-tren (**3**): Yield 91 %; ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) 8.39 (t, 2H, NH), 7.25 (d, 4H, ArH), 6.87 (d, 4H, ArH), 4.59 (s, 4H, OCH_2), 4.29 (d, *J*=13.3 Hz, 4H, $ArCH_2Ar$), 3.67 (m, 4H, $HNCH_2$), 3.50 (d, *J*=13.3 Hz, 4H, $ArCH_2Ar$), 2.81 (m, 6H, NCH_2 and $HNCH_2$), 2.51 (t, 2H, NCH_2), 1.38 (s, 18H $C(CH_3)_3$), 1.07 (s, 18H, $C(CH_3)_3$).

2.3. Preparation and characterization of modified electrodes

Before modification, the bare glassy carbon electrode (GCE) surface was polished with alumina slurry, then rinsed throughly with distillated water, followed by ultrasonication in acetonitrile and distilled water for 5 min respectively. After the cleaning process, the GCE was dried in air. Modified electrodes were prepared according to previous study[1]. For this purpose, the modifier solution was prepared by mixing 0.2 mg/mL Calix-tren in chloroform, 10.0 mM EDA, 2.0 mM EDC and 5.0 mM NHS in DMSO, respectively. Then, the bare GCE was immersed in this solution for 1 h. After the modification, the modified electrode was allowed to dry in air. The modification scheme is shown in Figure 2.

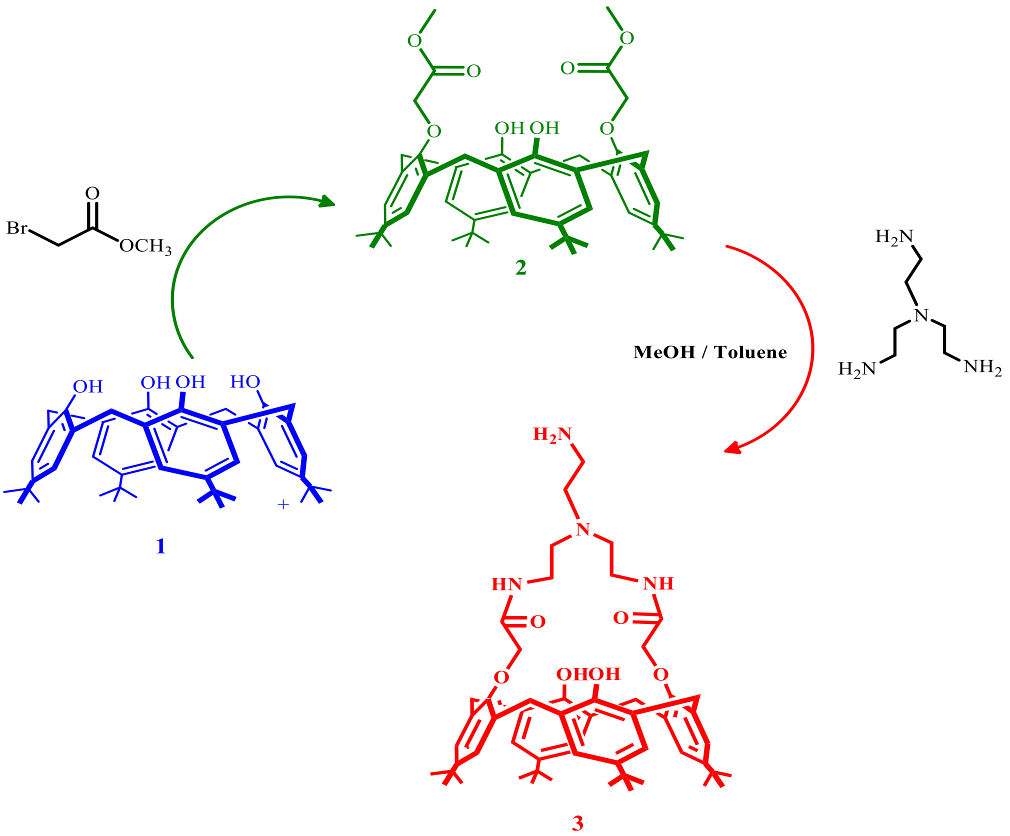

Figure 1. Synthesis of calix[4]arene-tren derivative **(3)**

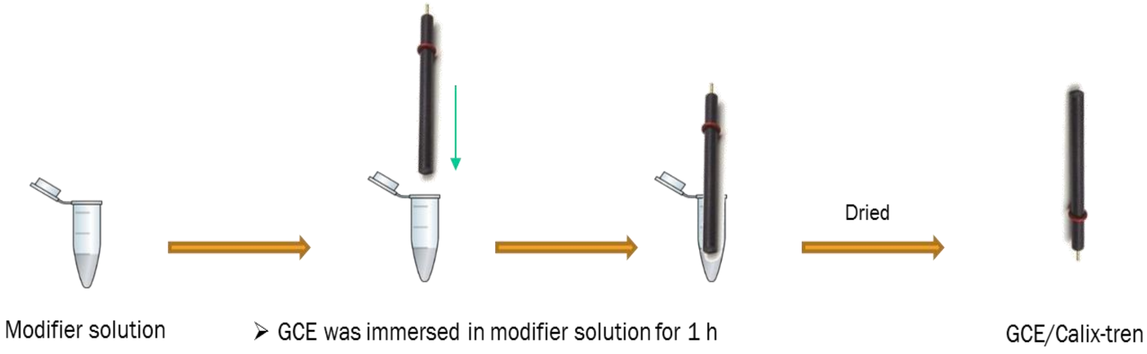

Figure 2. Scheme of the modification process

The proposed binding interaction of GC/Calix-tren electrode with Pb (II) ion is shown in Figure 3.

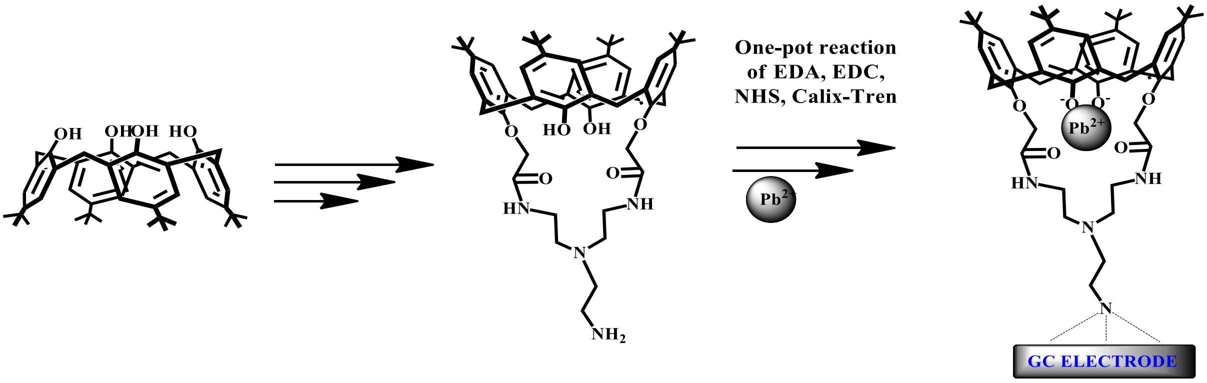

Figure 3. Proposed binding interaction of GC/Calix-tren electrode with Pb (II) ion

2.4. Electrochemical procedure

Electrochemical properties of GC/Calix-tren and GC electrode surface were characterized by CV and EIS measurements in 5.0 mM $Fe(CN)_6^{3-/4-}$ solution containing 0.1 M KCl. Surface characterizations of the prepared electrodes were examined using Scanning Electron Microscopy (SEM) technique. Under the optimum conditions, current response of the GCE/Calix-tren electrode was measured by differential pulse anodic stripping voltammetry (DPASV) [10]. All measurements were carried out in pH 7.0 0.1 M potassium chloride and at room temperature.

The performance of the newly modified glassy carbon electrode (GCE/Calix-tren) is based on the deposition of Pb (II) from aqueous solution onto the surface of the modified electrode by forming complexes with the modifier. The electrochemical performance of the metal ion on the glassy carbon electrode modified with Calix-tren was explored with respect to the effect on the stripping parameter. Lastly, a calibration curve was plotted under optimized parameters.

The possible steps are explicated below with the optimized experimental values, the likely phases are clarified under ("aqueous" or "surface" subscript means the compound is in aqueous solution or on the electrode surface, respectively):

Deposition of Pb (II) [11]

$$\text{Pb (II)}_{\text{(aqueous)}} + \text{(Calix-tren)}_{\text{(surface)}} \rightarrow \text{[Pb (II) - (Calix-tren)]}_{\text{(surface)}}$$

Reduction of accumulated Pb (II)

$$\text{[M}^{2+}\text{ - (Calix-tren)]}_{\text{(surface)}} + 2e^- \rightarrow \text{[M}^{0}\text{ - (Calix-tren)]}_{\text{(surface)}}\text{(at -1.2 V)}$$

Stripping of reduced Pb (II)

$$\text{[M}^{0}\text{ - (Calix-tren)]}_{\text{(surface)}} \rightarrow \text{M}^{2+}_{\text{(aqueous)}} + \text{(Calix-tren)}_{\text{(surface)}} + 2e^- \text{ (scan from -1.5 to - 1.0 V)}$$

3. Results and Discussion

3.1. Characterization of Calix[4]arene-tren

The structure of the synthesized calix-tren derivative[8] was confirmed by ^{1}H NMR analysis (Figure S1).

3.2 Morphologies and electrochemical characterization of electrodes

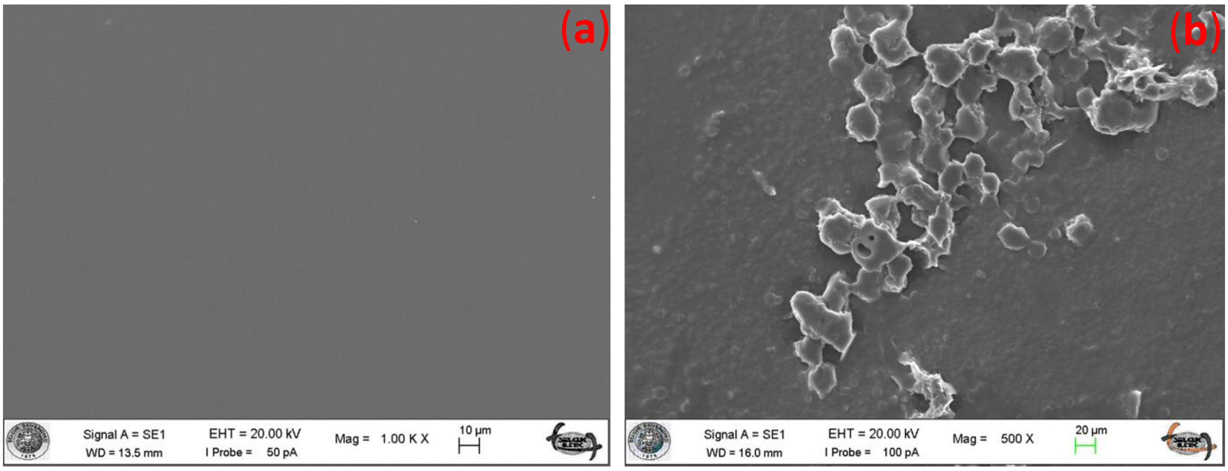

Figure 4. SEM micrographs of the BGCE (a), GCE/Calix-tren (b)

The surface morphologies of the bare GCE and GCE/Calix-tren were investigated using SEM. SEM micrographs of bare GCE and GCE/Calix-tren are shown in Figure 4. The surface morphology of bare GCE (Figure 4.(a)) is different from than that of GCE/Calix-tren (Figure 4.(b)). As seen in Figure 4 (a), bare GCE exhibits a more uniform and smooth structure. After the modification, well dispersed Calix-tren were observed onto BGCE (Figure 4.(b)).

Ferro-ferricyanide ion ($Fe(CN)_6^{3-/4-}$) was used as redox probe to investigate the electron transfer properties of bare GCE and modified GCE. Cyclic voltammetry of the redox probes such as ferrocyanide system is a convenient and useful tool to investigate the characterization of modified electrode surfaces [12]. Figure 5 shows the cyclic voltammograms of the bare GCE and GCE/Calix-tren electrodes at a scan rate of 100 mV s^{-1} in redox probe solution including 0.1 M KCl. When Calix-tren was modified on the electrode, the redox current decreased. This suggested that Calix-tren acted as the blocking layer for electron and mass transfer that hinders the diffusion of ferricyanide toward the electron surface, which obviously also prove that Calix-tren successfully immobilized on the GCE surface.

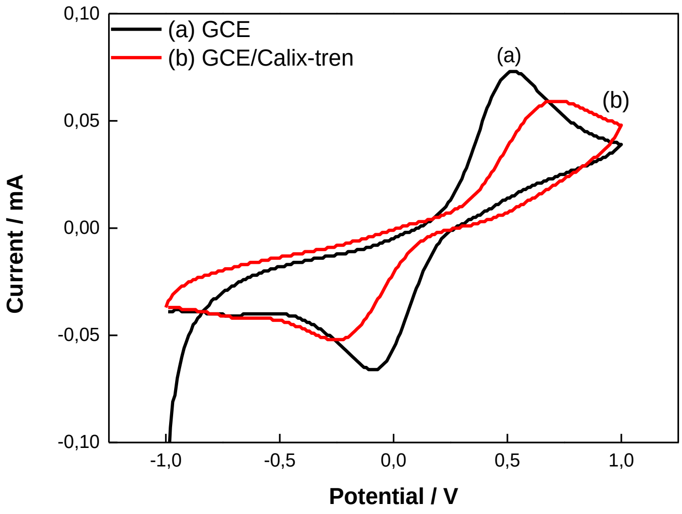

Figure 5. CVs of GCE (a), GCE/Calix-tren (b) electrode at scan rate of 100 mV s^{-1} in 0.1 M KCl containing 5.0 mM $Fe(CN)_6^{3-/4-}$.

The capability of electron transfer on these electrodes was also investigated by EIS. EIS is an effective method to monitor the impedance changes of the electrode surface during the fabrication process. Figure 6 shows the Nyquist plot of EIS at GCE and GCE/Calix-tren. It can be seen that a small well-defined semi-circle was obtained at the bare GCE, indicating small interface electron resistance (R_{ct}). And, the R_{ct} increased further remarkably after Calix-tren was immobilized on the GCE. This result showed that Calix-tren was successfully immobilized on the GCE surface.

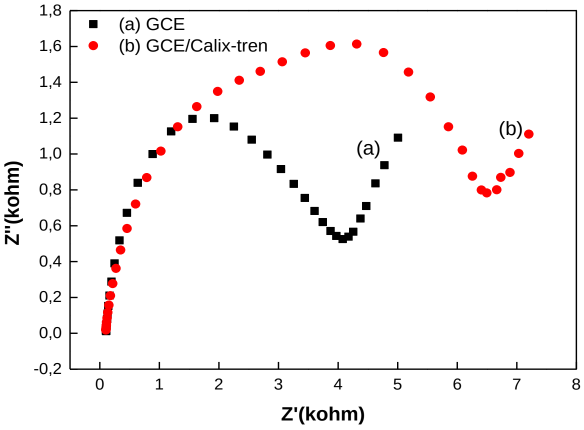

Figure 6. The Nyquist plots of (a) GCE, (b) GCE/Calix-tren in 0.1 M KCl containing 5.0 mM $Fe(CN)_6^{3-/4-}$

3.3. Optimization of experimental conditions

In order to determine optimum experimental conditions, the effect of pH, working potential and deposition time were investigated.

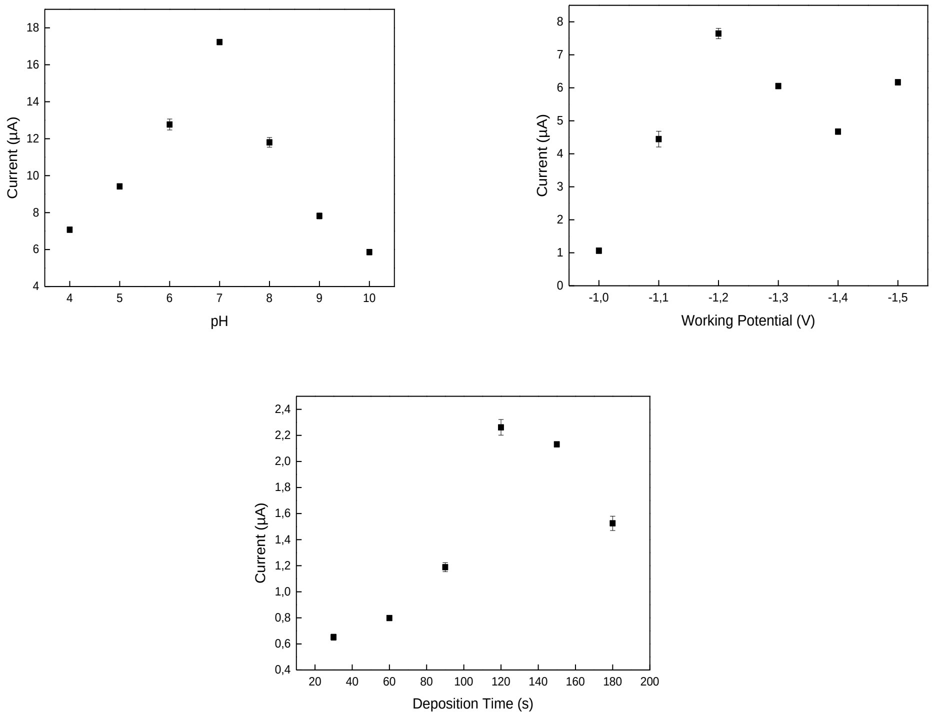

Figure 7. The effect of pH, working potential and deposition time on the response on the response of GCE/Calix-tren

The effect of pH on the currrent response was investigated at a range of 4.0-10.0. The peak current was increased from pH 4.0 to 7.0 and decreased after pH 7.0 and maximum peak current was obtained at pH 7.0.

Deposition potential is another importance factor to effect the performance of sensor. The effect of deposition potential on the peak current was tested at a range of (-1.0) - (-1.5) V. As the highest current was obtained with -1.2 V, this potential was used for further experiments.

The effect of deposition time on the peak current was also examined in the range between 30 - 180 s and 120 s was chosen as an optimum value.

3.4. Analytical performance of the developed sensor

Differential pulse anodic stripping voltammetry technique was chosen to estimate the linear range, limit of detection and limit of quantification, because of its excellent current sensitivity and selectivity in a low background. Under the optimum conditions, DPASV response for different concentration of Pb (II) are shown in Figure 8.

The peak currents linearly proportional to Pb (II) concentration over the range of 0.48-2.31 µM. The correlation equation for determination of Pb (II) :

$$I_p(\mu A)=231.67C_{Pb(II)}+105.48 \ (R^2=0,9943)$$

The limit of detection (LOD) and the limit of quantification (LOQ) from the calibration curve were found to be 0.11 µM and 0.36 µM, respectively. LOD and LOQ were calculated using the following equations[13]:

$$LOD=3s/m$$
$$LOQ=10s/m$$

Where s is the standard deviation of the current of the lowest concentration of the linearity range, m is the slope of the related calibration curve.

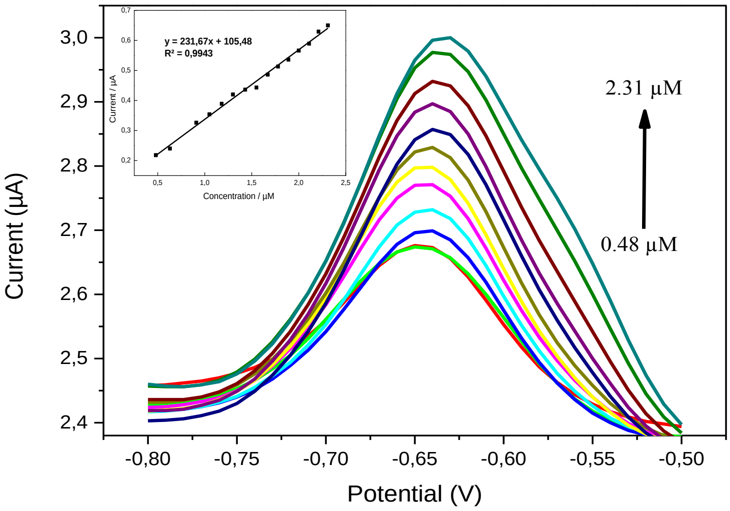

Figure 8. Differential pulse voltammograms of the GCE/Calix-tren electrode in 0.10 M KCl (pH 7.0) containing different Pb (II) concentrations, Inset: Calibration plots of GCE/Calix-tren

The repeatability for the same electrode was calculated from the relative standard deviation (RSD) of lead currents and it was found to be 3.71% (n=7).

The reproducibility was calculated using three different electrodes prepared in the same way. The RSD of sensitivities of three electrodes was 2.78%. The results show that the reproducibility and repeatability of the prepared sensor is acceptable level.

3.5. Interference studies

In order to measure of selectivity of the sensor, the effect of some interfering substances such as Cd (II), Co (II), Cu (II), Fe (II), Ni (II) and Zn (II) was examined. Figure 9 shows the comparison between the current response of the control which is a solution containing 1 mM Pb (II) in KCl solution with the current magnitude of the control in the presence of different metal ions.

Compared with the current response change of sensor to Pb(II), the relative current response changes for Cd (II), Co (II), Cu (II), Fe (II), Ni (II) and Zn (II) were found to be as -1.0%, 4.20%, 4.70%, -3.10% and 8.20%, respectively. When Fig. 9 is examined, it is concluded that the interference effect of each species is quite low and it did not significantly affect the Pb (II) determination.

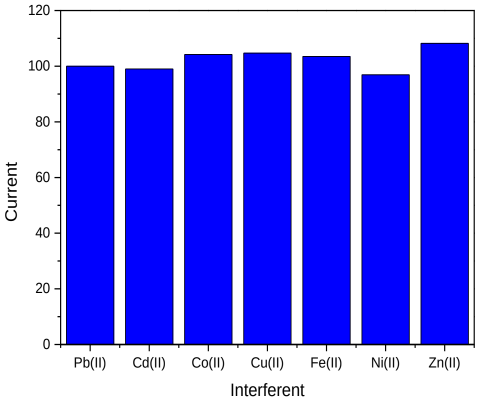

Figure 9. The effect of the interfering substances on electrochemical responces of Pb (II) at GCE/Calix-tren

3.6 Real sample analysis

To demonstrate the applicability of the sensor in practical analysis, it was used to detect Pb (II) in wastewater. The standard addition method was used for the analysis of prepared samples. In this method, additions of standard Pb (II) solution were made to the waste water, and a multiple addition calibration curve was obtained.

Table 1. Determination of Pb (II) in waste water

Sample	Analyte	Found (mg/L) ± SD[a]
Waste water	Pb (II)	0.362+0.004

[a] Average of 5 determinations

As can be seen in Table 1, the amount of Pb (II) in waste water was found to be 0.362+0.004 mg/L. The obtained results show that the proposed sensor provided a new electrochemical sensing approach for the determination of Pb (II) in environment residues.

4. Conclusion

The calixarene modified electrode (calix-tren) for the detection of Pb (II) was sucessfully prepared. The working range of the developed electrochemical sensor was determined as 0.48-2.31 µM, limit of detection (LOD) was 0.11 µM and the RSD obtained in the reproducibility study was 2.78 %. Calix-tren was able to retain its selectivity for Pb (II) response in presence of Cd (II), Co (II), Cu (II), Fe (II), Ni (II) and Zn (II) ions. It was also found that the proposed electrochemical sensor possessed great advantages such as low cost, good selectivity, good reproducibility and could be used in the determination of Pb (II) ions in aqueous solution with satisfying results.

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