



Amino-calixarene-modified graphitic carbon as a novel electrochemical interface for simultaneous measurement of lead and cadmium ions at picomolar level

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Abstract Amino-calixarene-derivatized graphitic carbon electrode has been used in the simultaneous quantification of lead and cadmium ions at picomolar level. The graphitic carbon has been chemically modified using amino-calixarene as an indicator molecule through microwave irradiation, and it has been characterized by NMR, mass, and Fourier transform infrared spectroscopy (FTIR) techniques. The proposed sensor has shown linearity in the concentration range 10–120 pM with detection limits of 3.3 and 3.5 pM for lead and cadmium, respectively. The proposed sensor has been successfully applied to quantify lead and cadmium levels in battery effluents, alloy materials, and sewage water sample matrices. The results obtained by the proposed sensor are in agreement with the results of the standard protocols.

Keywords Amino-calixarene · Graphitic carbon · Anodic stripping voltammetry · Lead · Cadmium · Battery effluents

Introduction

Toxicity due to heavy metal ion presence such as lead and cadmium in groundwater has been a major concern in recent years all over the world [1]. The presence of these metal ions in the environment in larger concentration is mainly due to the

increased human activity in various industrial processes like metallurgical, catalytic, polymer, dye, and fertilizer industries. Because of their high toxicity and prolonged exposure, even at trace-level concentration, these metal ions can cause severe problems in human and aquatic systems [2]. Lead and cadmium have acute and chronic effects on human health. The presence of lead in the environmental samples like water, air, and soil samples may cause neurological, cardiovascular, and reproductive disorders in human kind. The presence of cadmium in water samples may lead to kidney damage; subsequently, it can alter the constitution of the bone, liver, and blood [3]. The prescribed threshold limit values (TLV) of lead and cadmium ions in drinking water are 10 and 3 ppb, respectively, according to the World Health Organization [4]. Hence, it is mandatory to measure these metal ions at ultra trace-level concentration in order to check the quality of drinking water by several governmental and non-governmental agencies [5]. Several protocols have been reported to quantify these metal ions at bulk concentration level. However, the trace-level quantification is a major challenging problem due to the sophisticated instrumentation involved, skilled operators, very tedious sample preparation procedures, etc. Several techniques like flame atomic absorption spectrometry (FAAS), graphite furnace atomic absorption spectrometry (GFAAS), and inductively coupled plasma atomic emission spectrometry (ICPAES) have been routinely used to quantify these elements at ultra trace-level concentration from a variety of sample matrices [6–10]. But, all these techniques are expensive and require skilled personnel to operate and prolonged sample preparation procedures. However, electrochemical methods are possible alternative ones to these techniques due to their high sensitivity, selectivity, and wide variability in their modification strategies. They also provide very wide working linearity, portability, and low cost. Hence, in recent years, a significant emphasis has been laid in the development of

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electrochemical-based sensors in the quantification of several toxic and heavy metal ions [11]. A variety of electrodes have been used in the electrochemical quantification of both inorganic and organic analytes incorporating suitable indicator or modifier molecules on the surfaces of substrate materials. Among these, gold-coated electrodes, silver electrodes, glassy carbon electrodes, carbon paste electrodes, and screen-printed electrodes are significant ones to mention it here [12–22]. Chemically modified electrodes (CMEs) are another class of electrodes extensively used to achieve the target analyte selectivity and specificity based on modifying the carbon substrate surface with an indicator molecule containing electroactive moieties as a part of the molecular structure [23]. The chemical modification of various carbon substrates such as carbon nanotubes (CNTs), carbon nanohorns (CNH), carbon nanofibers (CNF), graphene, graphite, glassy carbon spheres, and boron-doped diamond has been reported [24–30] for measurement of lead and cadmium ions. Poly(4-vinylpyridine-co-aniline)-based solid-state ion sensor was used for cadmium(II) measurement from water and food samples [31]. A microtiter plate-based electrochemical device was developed and used in simultaneous measurement of lead and cadmium ions from standard effluent sample [32]. These electrodes were modified using several methods such as wet impregnation (physisorption), polymer wrapping, covalent attachment, chemisorption, etc. A chemically modified carbon paste electrode containing periodic mesoporous organosilica and cyclodextrins was used in the determination of lead and cadmium from water samples [33, 34]. But, these methods are having limitations such as poor stability, low-adhesive nature, non-uniform distribution of modifier, and uncontrollable thickness of the film resulting in the poor reproducibility of the measurements [35].

Modification of carbon substrate with calixarene moiety has gained much attention in recent years due to their selective recognition and complexation with metal ions. Calixarenes and its derivatives with suitable functional moieties have been used as a sensing material in the electroanalysis of toxic metal ions recently [36, 37]. Mahajan et al. have used poly(vinylchloride) (PVC) matrix membrane based on Schiff base *p*-tert-butyl calix[4]arene derivative as an ion-selective electrode in silver(I) quantification [38]. Mandlier et al. have successfully extracted and quantified uranyl ions from aqueous solution using a self-assembled monolayer composed of cysteamine to which 4-sulfonic calixarene was electrostatically anchored on the surface of gold electrode [39]. Similarly, Hanna et al. have used ferrocene-substituted calixpyrrole as a neutral redox-active receptor incorporating into carbon paste electrode to recognize anions such as F^- , Cl^- , Br^- , and $H_2PO_4^-$ in aqueous medium [40]. Hart et al. have used calixarene derivatives as an indicator molecule in the determination of Pb^{2+} and Cd^{2+} ions using screen-

printed carbon electrodes [21, 22]. Zazoua et al. have used cadmium-sensitive electrode based on tetraacetone derivative of calixarene moiety using electrochemical impedance spectroscopy [41]. In the present report, amino-calixarene-modified graphitic carbon has been used as a novel electrochemical interface to quantify lead and cadmium ions simultaneously at trace level from various sample matrices using cyclic voltammetry and differential pulse anodic stripping voltammetry (DPASV) techniques.

Experimental

Chemicals and reagents

All reagents used were of Analar grade and used without any further purification. Graphite (dia. $<20\ \mu\text{m}$), lead nitrate, cadmium nitrate, and potassium bromide (Fourier transform infrared spectroscopy (FTIR) grade, purity, 99.99 %) were obtained from Sigma-Aldrich. Acetic acid, sodium acetate, and sodium hydroxide were purchased from SD Fine Chemicals, Mumbai. All pH solutions in the range 2–8 were prepared using ultra pure double-distilled water from Millipore water purifier with a resistivity of not less than $18.2\ \text{M}\Omega\ \text{cm}^{-1}$ at $25\ ^\circ\text{C}$. Stock solutions of lead and cadmium ionic solutions were prepared using corresponding salts. Working standards were prepared by diluting the stock solutions on the day of use.

Apparatus

All electrochemical measurements were carried out using an electrochemical workstation [CH Instruments, TX, USA, model: CHI 619B] at room temperature ($25 \pm 2\ ^\circ\text{C}$) in an electrochemical cell of volume 10 mL with a standard three-electrode configuration. Chemically modified glassy carbon electrode (dia. = 5 mm) acted as the working electrode and Ag/AgCl (3 M KCl) as a reference electrode (CH Instruments, TX, USA). Platinum wire acted as the counter electrode. All the solutions were degassed using high-purity nitrogen gas for 10 min before all electrochemical measurements. All pH measurements were carried out using a pH meter (Control Dynamics, Mumbai, India model: APX 175). Infrared measurements were recorded using FTIR spectrometer (Bruker, model: 8400S) in the range $400\text{--}4000\ \text{cm}^{-1}$ with a resolution of $4\ \text{cm}^{-1}$. Microwave experiments were conducted using a domestic microwave oven. ^1H NMR spectra were recorded using 400-MHz NMR spectrometer (Bruker) using dimethylsulfoxide (DMSO- d_6) as solvent and tetramethylsilane (TMS) as an internal standard. The mass spectral data was recorded using GCMS (Shimadzu, Japan, model: QP 2010S).

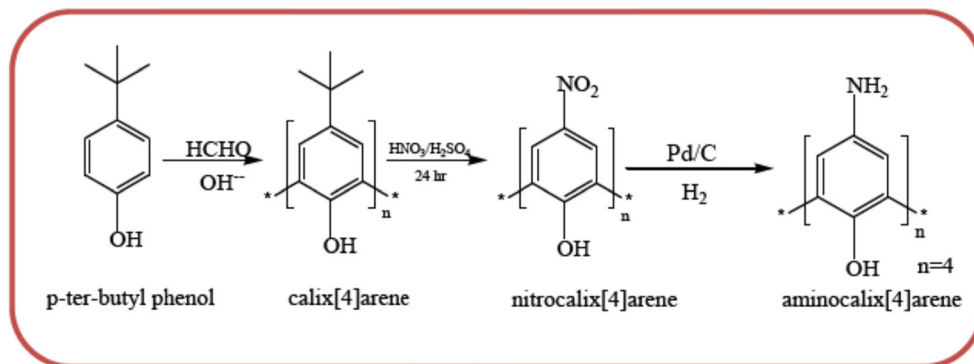
Analytical procedure

The simultaneous determination of Pb^{2+} and Cd^{2+} ions was carried out using DPASV in the potential range from -1.0 to 0.0 V with an amplitude of 0.01 V and a pulse width of 0.05 s. Known amounts of both lead and cadmium ions were taken in an electrochemical cell of 10-mL -volume capacity containing 4 mL of sodium acetate–acetic acid buffer solution (pH 6) and 4 mL of 1 M potassium nitrate, which is fitted with a tab-controlled magnetic stirrer. The CME was immersed into the above-stirred solution for 2 min to preconcentrate the metal ions at open circuit potential. Then, the preconcentrated metal ions were reduced at a reduction potential of -1.2 V and subsequently stripped off from the electrode surface into the bulk of the electrolytic solution by sweeping the potential in the positive direction after 20 s of equilibration time. Then, the modified electrode is gently washed with a small quantity of distilled water for further use.

Synthesis of modifier

Calixarene was prepared using *p*-tert-butylphenol and formaldehyde as per the reported literature method [42]; subsequently, 1 g of calixarene (1.54 mM) was taken in 100-mL round-bottom flask to which 20 mL of conc. nitric + sulfuric acid mixture (1:1) was added and stirred at 10 °C for 24 h. Yellow-colored solid obtained was filtered after the addition of 80 mL of distilled water. Then, it was washed with methanol and dried at room temperature. The obtained solid was recrystallized using acetone [43]. Then, in order to reduce the nitro to amino calixarene, 5 mg of nanopalladium/carbon composite was added under hydrogen atmosphere into 50-mL flask containing 1 g of *p*-nitrocalixarene and the reaction mixture was stirred for $15\text{--}30$ min. Then, the reaction mixture was cooled at room temperature to obtain the desired product (Scheme 1).

Scheme 1 Synthesis of amino-calixarene



Characterization

The prepared compounds of calixarene and amino-calixarene were characterized by spectroscopic tools to ascertain the functional groups as well as its molecular mass.

FTIR study

The infrared spectra of calixarene and amino-calixarene were recorded in the wave number range $4000\text{--}400$ cm^{-1} to confirm the presence of functional groups in the synthesized molecule. A weak stretching frequency was observed at 3166 cm^{-1} due to the vibration of OH groups of cyclic tetramer. The bands at 1449 and 1391 cm^{-1} might be due to the --COH bending vibrations (Fig. 1). The spectrum of amino-calixarene (Fig. 2) showed a band at 1342 cm^{-1} corresponding to the --C=N-- stretching and the band at 1530 cm^{-1} due to --N--H bending and 3285 cm^{-1} --N--H stretching, which were not found in the spectrum of calixarene. These results confirmed the presence of amino groups on the calixarene moiety.

GC-MS study

The synthesized calixarene molecule and its molecular mass were determined by the GC-MS study. A molecular ion peak at m/z 648 (Fig. 3) was observed, which corresponds to the molecular weight of the synthesized compound. The peak observed at m/z 592 is due to the loss of one *tert*-butyl group from one of the upper rims of the compound.

^1H NMR study

^1H -NMR spectra were recorded using Bruker 400-MHz instrument with TMS as the internal standard and $\text{DMSO-}d_6$ as the solvent. A broad singlet observed at 8.69 ppm corresponds to the four phenolic --OH groups of the calix[4]arene moiety. Methylene protons resonated at 3.80 ppm as a singlet, whereas

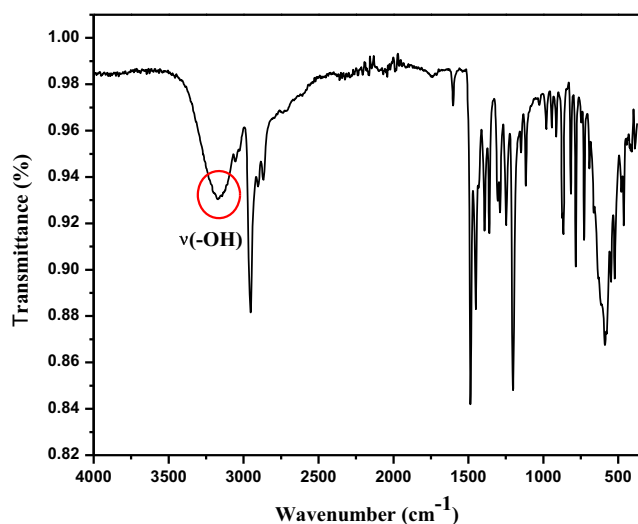


Fig. 1 FTIR spectrum of calixarene

the singlet observed at 1.09 ppm corresponds to the methyl group of the tert-butyl moieties (Fig. 4).

Covalent modification of graphitic carbon with amino-calixarene

One gram of graphitic carbon powder in 100-mL beaker containing 10 mL of conc. HNO_3 was irradiated with microwave energy (15 % of total 600 W) for about 2 min to induce carboxylic groups on the surface of graphitic carbon particles. Then, 500 mg of amino-calixarene was added and irradiation was continued for two more minutes. The chemically modified graphitic carbon powder was washed thoroughly with acetonitrile several times to remove the unreacted and physisorbed modifier molecules. Then, the reaction mixture was washed with ample quantities of water to remove the excess of acid present in it. Finally, the carbon powder

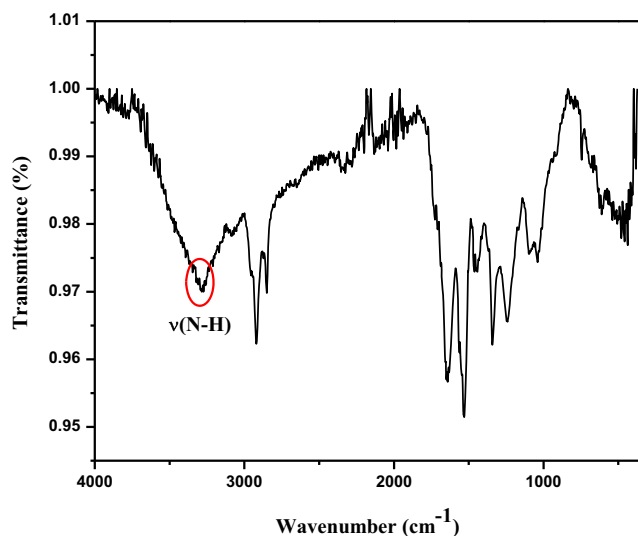


Fig. 2 FTIR spectrum of amino-calixarene

particles were washed with acetone to remove the moisture. The functionalized carbon powder was dried by placing in a fume hood for a period of 10 h and stored in an airtight container prior to its use [44] (Scheme 2).

Chemical modification of glassy carbon electrode

Chemically modified graphitic carbon particles (5 mg) were added into 5 mL of water in glass vial and sonicated for 30 min to achieve uniform dispersion. Then, 25 μL of dispersed solution was drop casted onto the glassy carbon electrode (Scheme 3). The electrode was allowed to dry for a period of several hours to remove the solvent from the surface of electrode at ambient conditions. This procedure was repeated several times to get uniform distribution of modified graphite particles on glassy carbon electrode surface.

Results and discussion

Electrochemical behavior of amino-calixarene-modified electrode

The electrochemical response of amino-calixarene-modified electrode in presence of lead and cadmium ions was first examined using cyclic voltammetry technique in order to understand the potential affinity of the modifier molecule toward Pb^{2+} and Cd^{2+} in aqueous medium. The typical cyclic voltammetric response in presence and absence of metal ions at calixarene and amino-calixarene-modified interfaces in the potential window from -1.0 to 0.0 V is shown in Fig. 5 (a–d). The resulting voltammograms have showed well-defined oxidative and reductive peaks for the CME in presence of metal ions, indicating that the modifier molecule could be used in the quantitative study. The glassy carbon electrode modified with calixarene in absence of metal ions (Fig. 5 (a)) has not shown any anodic signals but showed a small cathodic split signal, which might be attributed to the fact that the electrode surface unevenness is caused by that during drop-casting method. However, the same electrode (Fig. 5 (c)) in presence of metal ions has shown well-defined oxidative and reductive peaks with small peak current intensities. But, the amino-calixarene-modified electrode exhibited strong oxidative peaks with increased peak currents in comparison with calixarene-modified interface. However, amino-calixarene-modified electrode in presence of metal ions showed significant anodic peaks and weak split cathodic peaks Fig. 5 (b). The splitting of cathodic signals of amino-calixarene-modified electrode in presence of electrolyte solution containing target analytes, i.e., Pb(II) and Cd(II) ions, was observed at a potential of -0.55 and -0.80 V, respectively. The splitting of cathodic peaks might be due to the uneven electrode surface formed during the drop-casting method. or it could also be due

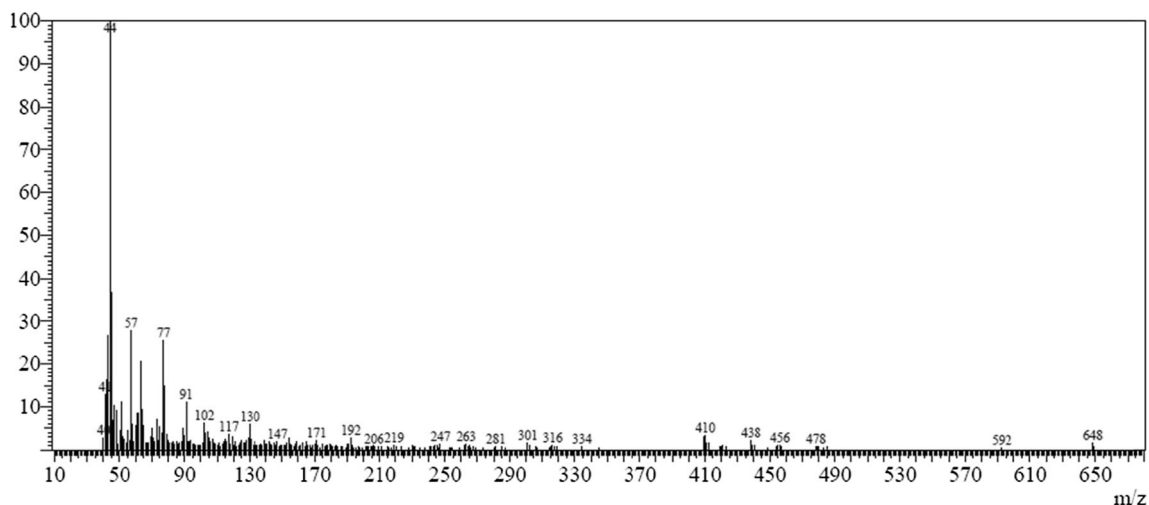


Fig. 3 GC-MS spectrum of calixarene

to any extraneous redox processes occurring during electrochemical study. The voltammogram of the unmodified electrode has been shown in Fig. 5 (d), and no splitting of the cathodic peaks was observed. These studies revealed that the chemically modified electrode (CME) surface could be efficiently used in the measurement of lead and cadmium ions simultaneously at trace level.

The oxidative peaks were significant in comparison with reductive peaks in the CV study; hence, to improve the

measurement efficiency in the present protocol, the anodic stripping voltammetric technique was adapted in the current electrochemical study. The peak potentials in the stripping analysis have shifted toward more negative potential than in cyclic voltammetry due to the complexation phenomenon between the ligand molecules (CO–NH groups in the modifier molecule) and metal ions [45]. All these observations reveal that the working electrode modified with amino-calixarene as an indicator molecule could be used as a thin film in the

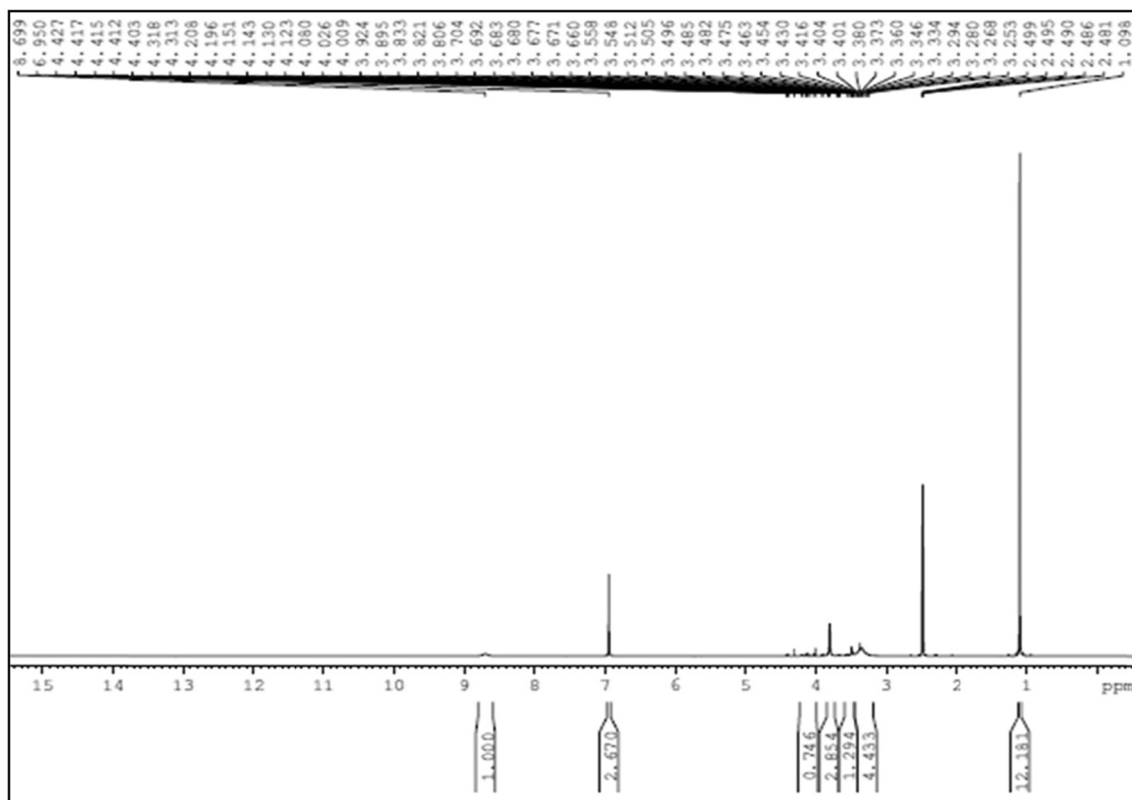
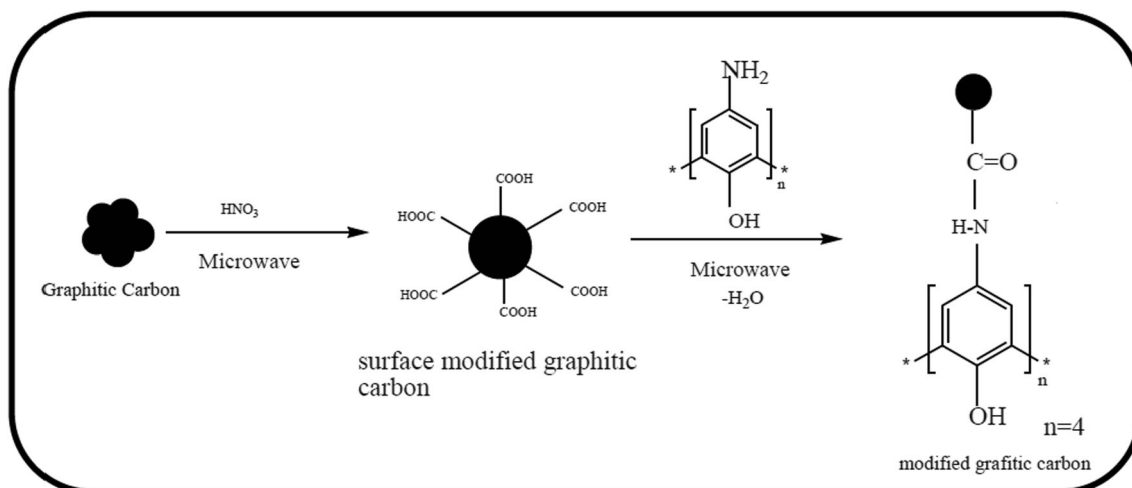


Fig. 4 ^1H NMR spectrum of calixarene



Scheme 2 Chemical modification of graphitic carbon powder

quantitative application study. In the proposed interface, the modifier molecule containing -CONH groups acts as a chelating agent, and during preconcentration step, metal ions accumulate on the electrode interface through complexation phenomenon. During electrochemical turnover, the accumulated metal ions will reduce to metallic state and subsequently gets oxidized to ionic state producing peak current proportional to the concentration of metal ions accumulated on the electrode interface [27]. The binding behavior and complexation mode between modifier molecule and the target metal ions are schematically shown in Scheme 4.

Optimization study

In order to achieve the maximum efficiency of amino-calixarene-modified electrode in the electrochemical quantification of Pb^{2+} and Cd^{2+} ions under aqueous medium, all the reaction variables like medium pH, preconcentration time, and reduction potential were optimized.

Effect of pH

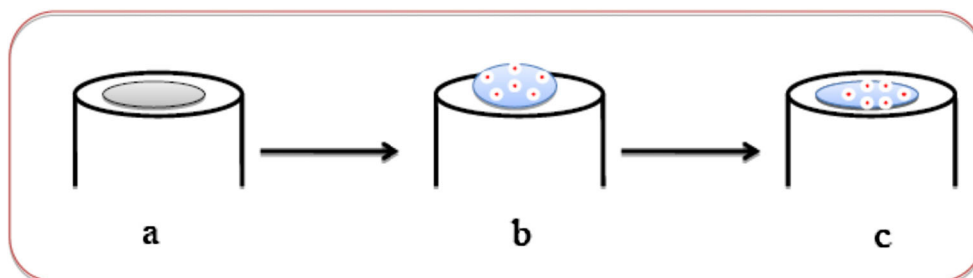
The effect of pH on the anodic stripping voltammetric (ASV) response of the modified electrode in the range pH 2–8 was investigated using 8 mL of 1 M KNO_3 as supporting electrolyte and 1 mL of 1-mM solutions of each of lead and cadmium

ions. The desired pH was adjusted using acetate buffer solution. It was found that the peak current increased sharply with increasing pH up to 6; this is due to the increasing complex formation of lead and cadmium with chemically modified amino-calixarene electrode surface. At higher pH, the decrease of the anodic peak currents might be the cause of hydrolysis, leading to the metal hydroxide formation. Hence, pH 6 was used as an optimum pH for the electrolyte in all further studies (Fig. 6).

Effect of preconcentration potential

The effect of the preconcentration potential on the anodic peak current of lead and cadmium ions was examined by varying the potential range from -0.6 to -1.4 V; well-defined peak currents were obtained. In this method, preconcentration can be achieved by keeping the electrode at particular potential in order to reduce the metal ions to their metallic state, which is reoxidized to their respective ions giving an anodic stripping peak during the anodic potential scan. The peak currents increase with increase of potential from -0.6 to -1.2 V for lead and cadmium ions due to the reduction of more Pb^{2+} and Cd^{2+} ions. Further increase in the reduction potential from -1.2 to -1.4 V leads to a steady-state current due to the hydrogen evolution at higher reduction potentials, which interfere in the determination of Pb^{2+} and Cd^{2+} ions [46–48]. Hence, a

Scheme 3 Chemical modification of glassy carbon electrode (GCE) surface by drop casting: *a* bare electrode, *b* modifier drop, and *c* modified electrode surface



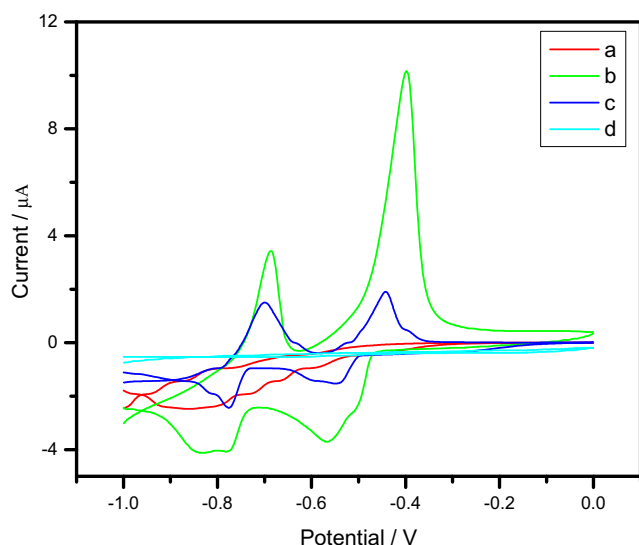


Fig. 5 Overlaid cyclic voltammograms of chemically modified glassy carbon electrode: *a* calixarene-modified electrode in absence of metal ions, *b* amino-calixarene-modified electrode, *c* calixarene-modified electrode, and *d* glassy carbon electrode in presence of 1-mM solution each of Pb^{2+} and Cd^{2+} ions in acetate-acetic acid buffer (pH 6) containing 1 M KNO_3 as supporting electrolyte. Scan rate, 100 mV/s

reduction potential of -1.2 V was used as the optimum condition in all further studies.

Effect of preconcentration time

The effect of time to preconcentrate the analyte species from the bulk of the solution to the electrode interface was studied. During this preconcentration step, the metal ions interact with the surface functional moieties through complexation and accumulate on the electrode surface. The effect of deposition time was studied between 1 and 7 min on the anodic stripping peak currents of Pb^{2+} and Cd^{2+} . The dependence of the differential pulse anodic stripping peak current was carried out in a buffer solution of pH 6 containing 1 M KNO_3 as supporting electrolyte. The peak currents increase from 1 to 5 min and then remain almost constant after 5 min. It might be due to the

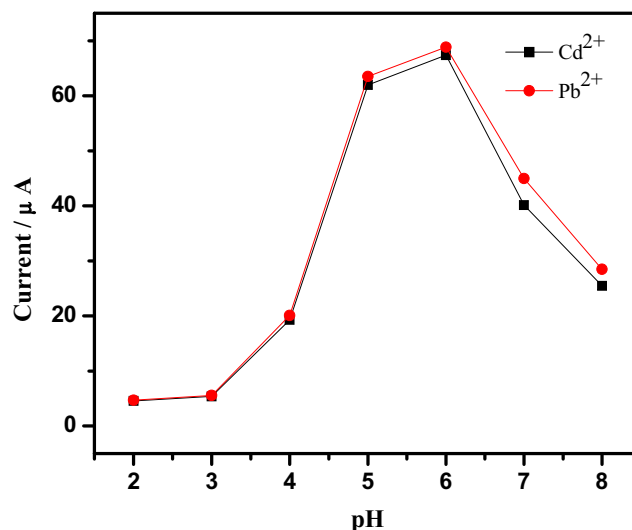
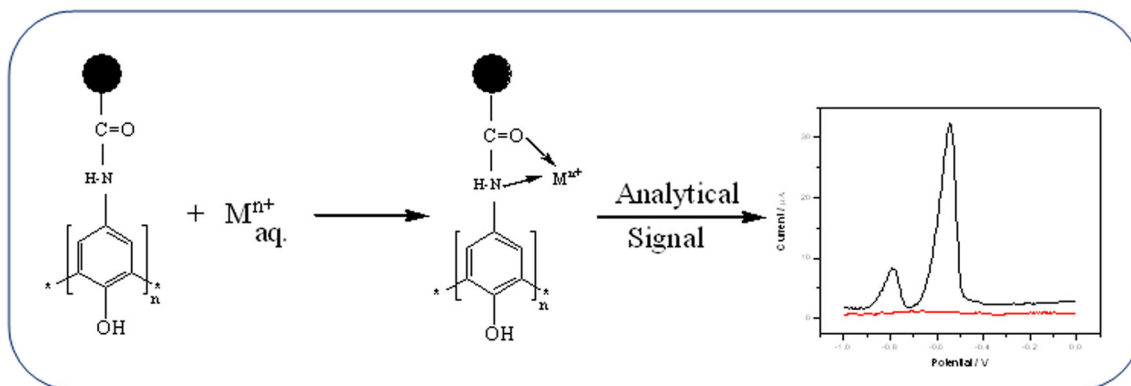


Fig. 6 Effect of pH on the anodic peak current observed for 1-mM concentration of each of Pb^{2+} and Cd^{2+} ions, preconcentration potential, -1.2 V; supporting electrolyte, 1 M KNO_3

non-availability of sites on the electrode surface for the accumulation of metal ions, indicating the electrode surface saturation [34]. Hence, an optimum preconcentration time of 5 min was used in all further studies.

Calibration plot

The differential pulse anodic stripping voltammograms with the above-optimized conditions at different concentrations of lead and cadmium ions in presence of CME showed a linearity in the concentration range 10–120 pM for Pb^{2+} and Cd^{2+} ions with detection limits of 3.3 and 3.5 pM, respectively. The experiments were repeated five times, and the concerned overlaid stripping voltammograms are shown in Fig. 7. The mathematical expressions for the calibration plots of target metal ions were found to be linear and given as lead ion $Y = (0.0054 \pm 0.0004) x + (1.02 \pm 0.03)$ $R^2 = 0.984$ and cadmium ion $Y = (0.0146 \pm 0.0012) x + (0.15 \pm 0.09)$ $R^2 = 0.983$. The



Scheme 4 Schematic representation of binding and complexation mode of modifier with analyte

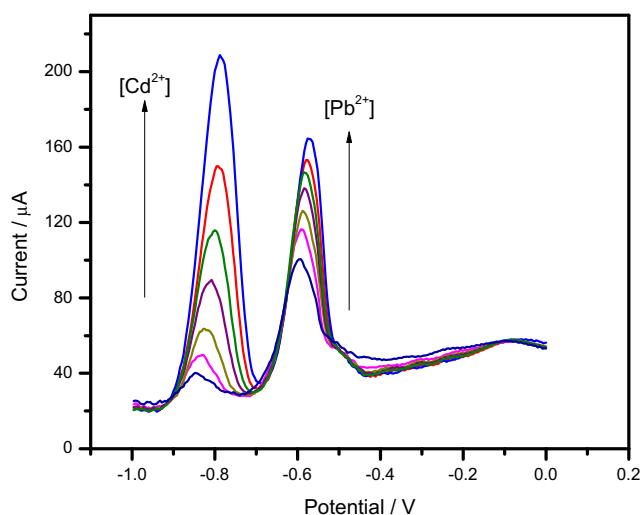


Fig. 7 Overlaid stripping voltammograms of the modified electrode in presence of different concentrations of Pb^{2+} and Cd^{2+} after a deposition time of 300 s at -1.20 V, respectively

regression coefficients of the above equations indicate the linearity and standard deviations in the slope (Table 3ESI).

Interference study

In order to check the selectivity of the proposed sensor, the effect of interfering ions was studied. Common cations and anions were added into the electrolyte in addition to the analyte species, and the impact of these ions on the analytical signal intensity was studied. The developed sensor showed least interference from most of the common cations and anions due to specific interaction between the moieties of the modifier molecule and the target analytes, i.e., lead and cadmium ions. The effect of interfering ions on the anodic peak

current response in presence of 60 pM each of Pb^{2+} and Cd^{2+} ions was investigated (Table 1ESI).

Repeatability and long-term storage stability

The simultaneous measurements of lead and cadmium ions in presence of 60 pM each of these ions were studied five times using the CME following the proposed protocol. The relative standard deviation in the peak current response was found to be 3.1 and 3.5 %, respectively. The stripping voltammograms of the modified electrode in presence of metal ions were studied for a period of 3 months, and the deviation in the peak currents obtained was 4.7 and 5 %, respectively, for lead and cadmium. These results revealed that the proposed electrode interface could be used repeatedly over a period of time and posses good stability; hence, it can be used for repeated measurements at trace-level concentration.

Application study

The proposed sensor has been successfully applied to quantify Pb^{2+} and Cd^{2+} ions present in battery effluents, wood's alloy, and wastewater samples. Battery effluents and alloy samples were collected from different sources and filtered to remove any colloidal matter present in it. Ten milliliters of real samples was diluted to 100 mL by adjusting the pH to 6, and this solution was added into the electrochemical cell containing modified glassy carbon electrode. The stripping peak currents were measured, and the concentrations were correlated through the standard calibration plots (Table 2 ESI). The real samples were also analyzed by the atomic absorption spectroscopy (AAS) method for comparison purpose. The results obtained by the proposed protocol are in good agreement with

Table 1 Comparison table with other existing sensors

Electrode	Metal ions	Deposition time (s)	Linear range ($\mu\text{g L}^{-1}$)	Limit of detection LOD ($\mu\text{g L}^{-1}$)	Ref.
Bi-CPE	Pb^{2+}	300	10–100	0.9	[49]
	Cd^{2+}		10–100	1.2	
Bi-BDD	Pb^{2+}	120	1–20	1.9	[50]
	Cd^{2+}		1–20	2.3	
EPPG electrode	Pb^{2+}	240	2–200	0.2	[51]
	Cd^{2+}		20–200	0.3	
Nafion-BHP-CPE	Pb^{2+}	300	2–10.4	0.62	[52]
	Cd^{2+}		1–5.6	0.17	
Bi/PANI-MES/GCE	Pb^{2+}	300	0.1–30	0.05	[53]
	Cd^{2+}		0.1–20	0.04	
Calixarene-GCE	Pb^{2+}	300	10–120 ng L^{-1}	3.3 ng L^{-1}	Present work
	Cd^{2+}		10–120 ng L^{-1}	3.5 ng L^{-1}	

Bi-CPE bismuth carbon paste electrode, *Bi-BDD* bismuth boron-doped diamond, *EPPG* edge plane pyrolytic graphite, *Nafion-BHP-CPE* Nafion–barium hydrogen phosphate–carbon paste electrode, *Bi/PANI-MES/GCE* Bi, Nafion and 2-mercaptoethanesulfonate (MES)-tethered polyaniline (PANI)/glassy carbon electrode

the AAS method. Known aliquots of standards were added to the real samples, and its recovery was also studied. The analytical performance of the proposed sensor has been compared with other existing similar protocols (Table 1). The present method showed much better detection limit (ng L^{-1}) than all other methods in which the limit of detection is in the order of microgram per liter. The obtained superior detection limits in the present protocol could be due to complexation between the hydroxyl groups in the lower rim and amide groups in the upper rim of the calixarene and metal ions during the stripping study.

Conclusions

A novel amino-calixarene-graphite composite material has been used as a modified electrode for the detection of ultra trace Pb^{2+} and Cd^{2+} ions by the DPASV technique. The composite material has been easily prepared by microwave irradiation of graphitic carbon in presence of amino-calixarene as a modifier molecule. The chemically modified graphitic carbon has been immobilized on glassy carbon electrode by the drop-casting method and used as a novel electrochemical interface in the measurement of lead and cadmium ions simultaneously. The proposed sensor has shown very low detection limits, respectively, for lead and cadmium ions. The proposed sensor has been successfully applied to measure lead and cadmium ions at trace level from battery effluents, wastewater, and alloy sample matrices. The results obtained by the proposed sensor are in good agreement with the results of the standard protocols.

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