



Iminodiacetic acid functionalized polypyrrole modified electrode as Pb(II) sensor: Synthesis and DPASV studies



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ABSTRACT

An electrochemical lead ion sensor has been developed by modification of carbon paste electrode (CPE) using polypyrrole functionalized with iminodiacetic acid (IDA-PPy) containing carboxyl group. The electrochemical response of Pb²⁺ ion on the IDA-PPy modified CPE has been evaluated and the controlling parameters have been optimized using differential pulse anodic stripping voltammetry (DPASV). The IDA-PPy modified CPE shows a linear correlation for Pb²⁺ concentrations in the range of 1×10^{-6} to 5×10^{-9} M and the lower detection limit of Pb²⁺ has been found to be 9.6×10^{-9} M concentration. Other tested metal ions, namely Cu²⁺, Cd²⁺, Co²⁺, Hg²⁺, Ni²⁺ and Zn²⁺, do not exhibit any voltammetric stripping response below 1×10^{-7} M concentration. However, the Pb²⁺ response is affected in the presence of molar equivalents or higher concentrations of Cu²⁺, Cd²⁺ and Co²⁺ ions in binary systems with Pb²⁺, consequent to their ability to bind with iminodiacetic acid, while Hg²⁺, Ni²⁺ and Zn²⁺ do not interfere at all. A good correlation has been observed between the lead concentrations as analyzed by DPASV using IDA-PPy modified CPE and atomic absorption spectrophotometry for a lead containing industrial effluent sample.

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1. Introduction

The development of carbon paste electrode (CPE) by mixing graphite powder with bromoform as the binder liquid was first reported by Adams in 1958 [1]. The CPE was initially intended to serve as a substitute for the dropping mercury electrode used in polarographic studies. Later, in 1964, the structure of the CPE was modified and its applicability extended such that it could be used as a solid state electrode for sensors and detectors [2]. This led to the development of a new class of surface modified electrodes with improved physiochemical properties and selectivity, which gained significant attention in pure and applied research. Electrodes of this type have been adapted for use in electrochemical sensors [3] and biological sensors [4] because of their ease of fabrication, low ohmic resistance [5], stable response, simple regeneration, low cost, and

immense potential for the immobilization of foreign molecules [6]. The utility of CPEs in electroanalytical chemistry has been critically reviewed and is well documented [7–10].

Conducting polymers have been regarded as one of the most promising materials to be used for the surface modification of CPEs. They are distinct from other compounds or polymers by virtue of their electron transport, redox characteristics, reduced overpotential, increased sensitivity, and increased reaction rates [11–13]. Instead of using conducting polymers in their native forms in the sensors, they are usually applied in a modified form as this is expected to improve their sensitivity. This can be achieved by functionalizing the polymer with receptor molecules to further enhance analyte interaction.

Electrochemical sensors for metal ions can be prepared by modification of the CPE using conducting polymers functionalized with coordinating ligands that can bind these specifically. There are several reports regarding the use of functionalized polymers and ligands for specific metal uptake studies [14–16]. Based on the complexing ability of the ligand, specificity of the metal ion sensor can be tuned for selective metal ion coordination. There are also many reports on the use of surface modified CPEs for metal ion sensing [17]. A well documented example is that by Goubert-Renaudin *et al.* [18] in which amide-cyclam-functionalized silica-modified

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CPE has been used for lead sensing. These authors achieved selective sensing of Pb^{2+} ion with a detection limit of 2.7×10^{-9} M concentration. In another study [19] a CPE was modified with a Schiff base molecule for Cu^{2+} determination in the concentration range of 1.0×10^{-8} to 1.0×10^{-1} M. Studies have also been carried out with other polymer modified CPEs for the detection of Pb^{2+} and other metal ions [20,21]. Iminodiacetic acid (IDA), as a selective metal coordinating ligand, has been used for remediation of lead [22] as well as for other kinds of sensing applications [23].

In the present investigation, a CPE has been modified with iminodiacetic acid functionalized polypyrrole (IDA-PPy) and evaluated for selective recognition of Pb^{2+} ion from aqueous media, using differential pulse anodic stripping voltammetry (DPASV) as the measuring technique. The pyrrole was initially pre-functionalized with iminodiacetic acid (IDA) and then chemically polymerized into IDA-PPy. The advantage of using polypyrrole as the supporting backbone is its inherent electron transport ability which improves the detection range of metal ions. Various parameters affecting the efficacy of IDA-PPy modified CPE, such as concentration of depositing solution, pH of depositing solution, deposition potential, deposition time, and scan rate, have been optimized to achieve maximum performance. The specificity of the IDA-PPy CPE for Pb^{2+} ions has been confirmed based on the comparison of the responses of individual solutions of different metal ions, namely Cu^{2+} , Cd^{2+} , Co^{2+} , Hg^{2+} , Ni^{2+} and Zn^{2+} , evaluated at or below 1×10^{-7} M concentration under identical conditions. Furthermore, the interference of these metal ions for Pb^{2+} ion sensing has been investigated from binary solutions of chosen concentrations. The practical efficacy of the developed lead ion sensor has been assessed using an industrial effluent sample.

2. Experimental

2.1. Chemicals, reagents and other materials

All the chemicals were analytical grade reagents and purchased from local suppliers and used as such. These included iminodiacetic acid (Merck Ltd., India), epichlorohydrin (Sisco Research Laboratories Pvt. Ltd., India), tetrabutyl ammonium hydrogen sulfate, ethanol, and potassium hydroxide (s d Fine-chem Ltd., India). Pyrrole (Spectrochem Pvt. Ltd., India) was dried over potassium hydroxide and purified by distillation under vacuum prior to use. High purity analytical grade acetic acid and sodium acetate (Sigma Aldrich) were used for buffer solution preparation. Potassium nitrate of analytical grade (s d Fine-chem Ltd., India) was used as supporting electrolyte. Graphite powder of average grains size $100 \mu\text{m}$ and light-weight paraffin oil (s d Fine-chem Ltd., India) were used for making the electrodes. Deionized (D.I.) water (Milli-Q system, $> 15 \text{ M}\Omega \text{ cm}$) was used for all experiments, and all reactions were carried out under inert argon atmosphere.

2.2. Characterization techniques

All the synthesized products were characterized after each step using NMR and GCMS techniques. NMR spectra were recorded using a Bruker 400 MHz instrument and GCMS data using a Thermo Trace GC Ultra instrument. Fourier transform infrared (FTIR) spectra were recorded in a Thermo-Nicolet 6700 instrument using the KBr pellet technique. Thermogravimetric analysis was carried out under ultrapure argon atmosphere using a Netzsch STA 409 instrument at a heating rate of $10^\circ\text{C min}^{-1}$. The crucible was preheated and the base line was corrected before the analysis of each sample. Atomic absorption spectrophotometric analysis of the chosen metal ion samples was carried out using a Thermo Electron Corporation Series AA spectrometer adopting standard procedures.

2.3. Synthesis procedures

2.3.1. Synthesis of diethyliminodiacetate (1)

About 11 g of iminodiacetic acid (0.0826 mol) was dispersed in 75 ml of absolute ethanol. To this 6 ml of concentrated sulfuric acid was added dropwise over time and the reaction mixture was refluxed for 24 h. Then the mixture was allowed to cool down to room temperature and the excess acid was neutralized with 1 M sodium hydroxide. The organic layer was collected by filtration and the filtrate was diluted with 200 ml of dichloromethane. This was then washed three times with 50 ml brine solution in each step. The organic layer was evaporated under vacuum to get a yellowish liquid. Yield: 9.04 g. NMR (DMSO-d_6 , 400 MHz): δ 4.19 (4H, q), 3.45 (4H, s), 2.13 (NH, s), 1.26 (6H, m). HRMS: 212 (M+Na). The NMR spectrum is shown in Fig. S1 (Supporting Information).

2.3.2. Synthesis of *N*-glycidyl pyrrole (EPy) (2)

About 100 g of potassium hydroxide was dissolved in 150 ml of D.I. water and cooled to 0°C in an ice bath. To this 4.2 g of tetrabutyl ammonium hydrogen sulfate was added followed by dropwise addition of 45.1 ml of epichlorohydrin (0.58 mol). This mixture was allowed to form a homogeneous solution by vigorous stirring for 5 min. 20 ml of pyrrole (0.29 mol) was then added dropwise over 20 min while keeping the temperature below 5°C whereafter stirring was continued for another 6 h at 0°C . The reaction mixture was poured into an excess of D.I. water and the organic layer was extracted with diethylether, washed with three batches of brine solution of 150 ml each, and dried over Na_2SO_4 . The solvent was evaporated under reduced pressure and the residue was purified by vacuum distillation using a short-neck distillation apparatus under high vacuum at 250°C to get EPy. The distillate was collected in portions and the last fraction yielded a colorless liquid, which turned yellowish upon long exposure to atmosphere. To prevent this, the last batch distillate was stored in a refrigerator under dark conditions prior to use in subsequent experiments. GCMS: 122.77 (retention time 10.15 s). NMR (CDCl_3 , 400 MHz): δ 6.79 (1H, t), 6.08 (1H, t), 4.21 (1H, dd), 3.91 (1H, dd), 3.2 (1H, p), 2.78 (1H, q), 2.53 (1H, m). The NMR spectrum also showed the presence of unreacted epichlorohydrin in small fractions. The NMR spectrum and the GCMS results are shown in Fig. S2 (Supporting Information).

2.3.3. Synthesis of 1-*N,N'*-diacetylacetate-2-hydroxy-3-*N*-pyrrolyl propane (3)

About 8.2 g of EPy (colorless, 0.0667 mol) and 15.2 g of diethyliminodiacetate (0.0805 mol) were mixed with 3 ml of absolute ethanol and stirred for 24 h at 70°C in an inert atmosphere. The solution was purified by column chromatography (100–200 silica gel, 25% ethyl acetate/petroleum ether) to get a yellowish viscous liquid. Yield: 3.82 g. GCMS: 311.87 (retention time 22.76 s). NMR (CDCl_3 , 400 MHz): δ 6.8 (2H, s), 5.9 (2H, s), 4.83 (1H, s), 4.1 (4H, q), 3.79 (2H, d), 3.55 (4H, s), 2.6 (2H, s), 1.2 (6H, t). The NMR and GCMS results are shown in Fig. S3 (Supporting Information).

2.3.4. Polymerization of 1-*N,N'*-diacetylacetate-2-hydroxy-3-*N*-pyrrolyl propane

5.15 g of the synthesized compound (3) (0.0193 mol) was mixed with a 1:1 mixture of conc. HCl and D.I. water and refluxed for 12 h. 5.74 g of ammonium persulfate (0.0251 mol) in 20 ml of D.I. water was added dropwise and stirred for 24 h. The solution turned dark brown in color. The pH was adjusted to 2.5 by the slow addition of dilute NaOH solution to initiate the precipitation process. The solution was then kept in a refrigerator overnight to precipitate out the polymer, which was later washed with D.I. water and decanted many times until the washings became colorless. The black residue

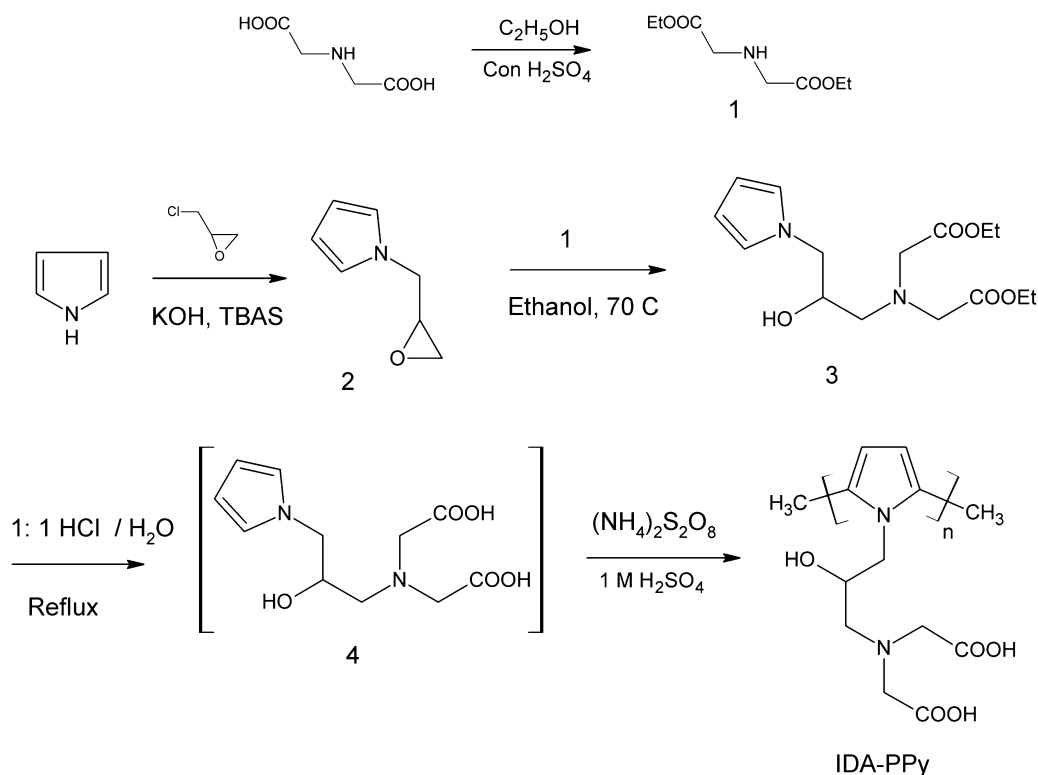


Fig. 1. Systematic synthesis route of IDA-PPy starting from pyrrole and diethyliminodiacetic acid.

collected was dried in a vacuum oven to obtain the iminodiacetic acid functionalized polypyrrole (IDA-PPy). Yield: ~800 mg.

2.4. Preparation and modification of carbon paste electrode with IDA-PPy

A carbon paste electrode (CPE) was prepared from a blend of graphite powder and paraffin oil in 4:1 ratio in a glass tube of 4 mm inner diameter. A copper wire was inserted for electrical contact. The CPE surface was later polished on a woolen cloth to get a smooth finish. The synthesized IDA-PPy was used to modify the electrode surface by the drop-casting method. For this, an aqueous solution of IDA-PPy was prepared by dissolving 25 mg of IDA-PPy in 10 ml of 1 M HCl and this was used for coating the CPE. Thereafter the CPE was allowed to dry at ambient conditions for 24 h.

2.5. Differential pulse anodic stripping voltammetry (DPASV): analysis of lead

All the electrochemical measurements were performed using a 660D Analyzer from CH-Instruments with a cell consisting of three electrodes. The IDA-PPy modified CPE was used as the working electrode, a calomel electrode was used as a reference electrode, and a platinum wire of 1.5 mm diameter was used as a counter electrode. All measurements were performed in triplicate and the standard deviation was estimated.

DPASV was carried out in two steps. The initial pre-concentration of Pb²⁺ ions on the electrode surface was carried out from 10 ml of a Pb(NO₃)₂ solution of desired concentration. The pH of the solution was controlled using acetate buffer containing 0.1 M KNO₃ as supporting electrolyte and the solution was kept stirred using a magnetic stirrer. The subsequent stripping step was carried out in 0.1 M acetic acid solution containing 0.1 M KNO₃ as supporting electrolyte. The polarization potential was swept from a high to a low value and the solution was kept stagnant. Prior to each

experiment the solution was de-aerated by purging high purity argon gas for 5 min, and each measurement was carried out using freshly prepared electrodes. The pulse potential parameters were maintained constant for all experiments, namely amplitude of 0.025 V, pulse width of 0.05 s, pulse period of 0.4 s, and sampling width of 0.025 s.

3. Results and discussion

3.1. Synthesis and properties of IDA-PPy

Iminodiacetic acid functionalized polypyrrole (IDA-PPy) was synthesized by first N-functionalizing the pyrrole with iminodiacetic acid (IDA) and then chemically polymerizing the pyrrole. Fig. 1 shows the systematic synthesis route followed for the synthesis of IDA-PPy polymer. In the first step, esterification of iminodiacetic acid was carried out by refluxing with absolute ethanol in the presence of conc. H₂SO₄ to obtain diethyliminodiacetate (1). Pyrrole was then subjected to N-functionalization using epichlorohydrin to obtain N-glycidyl pyrrole (2). This was followed by glycidyl ring opening using diethyliminodiacetate (1) to produce monomer 1-N,N'-diacetylacetate-2-hydroxy-3N-pyrrolyl propane (3). This resulting compound (3) was in ester form and was directly hydrolyzed using hydrochloric acid as catalyst to obtain the deprotected form (4). This was finally chemically polymerized using ammonium persulfate to yield IDA-PPy.

The functionalized polypyrrole (IDA-PPy) was characterized using FTIR spectroscopy to determine its chemical structure. As a control experiment, a non-functionalized polypyrrole (PPy) was synthesized under identical conditions in order to be able to identify the peaks pertaining to the polypyrrole backbone structure of the functionalized polymer (IDA-PPy). The FTIR spectrum of IDA-PPy along with that of PPy is shown in Fig. 2. The characteristic vibrational peaks observed for PPy (Fig. 2A) are as follows: 3108 cm⁻¹ (N-H stretching vibration), broad peak centered at

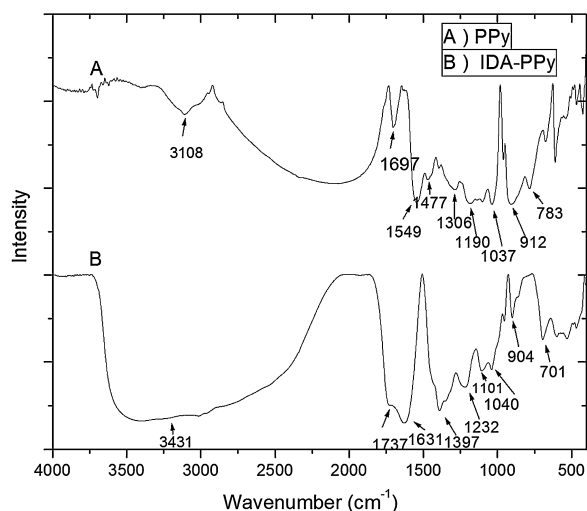


Fig. 2. FTIR spectra of A) PPy and B) IDA-PPy.

2300 cm^{-1} (C-H stretching vibration), 1306 cm^{-1} (C-N stretching vibration), 1549 cm^{-1} (fundamental ring vibration), 1477 cm^{-1} (N-H stretching vibration in the ring), 1190 cm^{-1} (C-H in-plane deformation), 1037 cm^{-1} (N-H in-plane deformation vibration), 912 cm^{-1} (C-H out-of-plane vibration) and 783 cm^{-1} (C-H out-of-plane ring deformation). The observed peaks are all in good agreement with those reported by other workers [24–26]. The FTIR spectrum of IDA-PPy shows dominant changes vis-à-vis the spectrum of PPy. In addition to the characteristic peaks of the polypyrrole backbone observed at 1040 and 904 cm^{-1} , the FTIR spectrum of IDA-PPy shows the peaks of the IDA moiety at 3431 and 1737 cm^{-1} (Fig. 2B) which are due to the stretching of the hydroxyl group and the stretching of the carboxyl group present in the IDA, respectively. Additionally, other characteristic peaks due to IDA appear at 1631 and 1397 cm^{-1} which can be attributed to the asymmetric and symmetric stretching vibrations of the COOH group, respectively [27,28].

The thermograms of PPy and IDA-PPy in the temperature range of 30 to 800 $^{\circ}\text{C}$ were recorded using a thermogravimetric analyzer at a scan speed of 10 $^{\circ}\text{C min}^{-1}$. The TGA scans of PPy and IDA-PPy are portrayed in Fig. 3. PPy shows a decrease of mass in the range of 30 to 150 $^{\circ}\text{C}$ (Fig. 3A) which is mainly due to volatile moisture residues present in it [29], followed by a gradual decrease from 300 $^{\circ}\text{C}$ which results from thermal decomposition of the polymer [30]. IDA-PPy shows a continuous decrease in mass (Fig. 3B) due

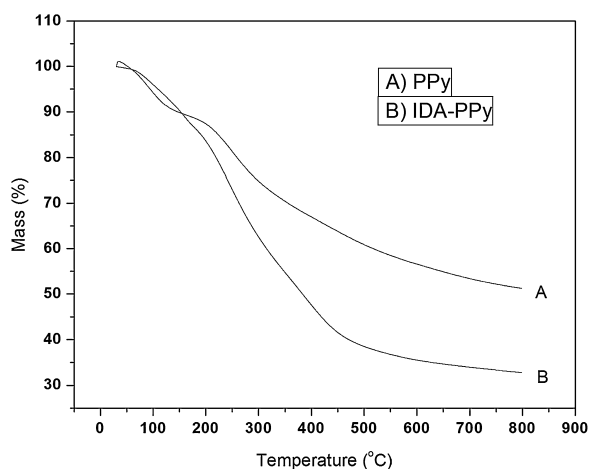


Fig. 3. Thermograms of A) PPy and B) IDA-PPy under inert atmosphere.

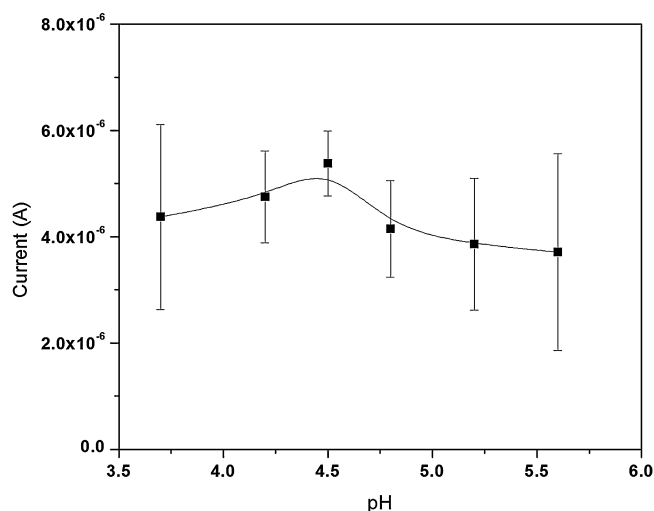


Fig. 4. Effect of pH on the anodic stripping current of Pb^{2+} ion.

to thermal decomposition of its hydroxyl and carboxyl functional groups, which causes an additional loss of 18% by mass for IDA-PPy compared with PPy. At 450 $^{\circ}\text{C}$ complete degradation occurs and only the carbonaceous material of both polymers remains (Fig. 3A and 3B).

3.2. Optimization studies of the IDA-PPy modified CPE

The optimization of IDA-PPy modified CPE was carried out using DPASV in an acetate buffer of 0.1 M concentration. The various parameters governing the sensing ability of the IDA-PPy modified electrode are thickness of the coated polymer layer on the electrode surface, pH of depositing solution, deposition potential, deposition time, and scan rate.

Initially, the effect of thickness of the IDA-PPy coating was studied by varying the solution volume used for drop casting and measuring the stripping current. The underlying principle involved is that the higher the concentration of complexing functional groups on the electrode surface, the more will be the pre-concentration of lead ions on the electrode surface. The volume of IDA-PPy solution used for coating was varied from 10 to 60 μl and the anodic stripping current for each of these coated electrodes was determined. A deposition time of 4 min from a 1×10^{-5} M Pb^{2+} solution in acetate buffer of pH 5 was maintained. A reduction potential of -1.4 V was applied on the working electrode for the pre-concentration step. This was followed by stripping into 0.1 M acetic acid solution. The measured stripping current was plotted against the volume of the polymer solution (Fig. S4 of Supporting Information). It was observed that the anodic stripping current increases with the increase in the volume of the polymer solution up to 20 μl and decreases thereafter. Evidently, above 20 μl the thickness of the polymer coating increases beyond an optimum limit, which then reduces the electrochemical response on the electrode surface and thereby the stripping current. The optimum thickness achieved with 20 μl addition was subsequently used in further analyses.

Another parameter which governs the anodic stripping current is the pH of the Pb^{2+} depositing solution. The pH of the solution was varied from 3.7 to 5.6 and the optimum pH was determined from the highest anodic stripping current obtained by DPASV analysis. Fig. 4 shows the variation of anodic stripping current observed for Pb^{2+} as a function of the pH of the solution. The tested pH values were restricted toward the acidic region, as above pH 6 precipitation of the Pb^{2+} ions would take place [31]. It can be seen that the anodic stripping current increases with increasing pH of the solution and reaches a maximum at pH 4.5 and reduces thereafter.

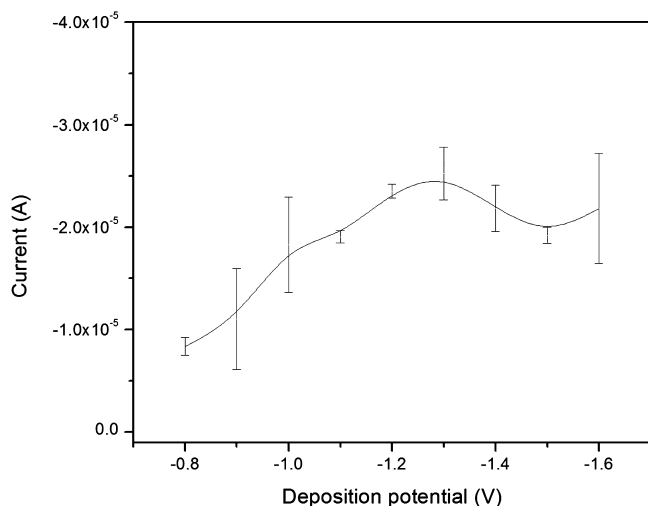


Fig. 5. Effect of deposition potential on the anodic stripping current of Pb^{2+} ion.

It is plausible that at this particular pH the functional groups are liable to chelate a maximum amount of Pb^{2+} ions, which facilitates the enhanced pre-concentration of Pb^{2+} ions on the electrode surface.

The deposition potential of lead was next optimized in a similar manner. Fig. 5 shows the effect of deposition potential on the anodic stripping current. It was observed that as the potential is varied from -0.8 to -1.6 V, the anodic stripping current increases steadily and attains a maximum at the deposition potential of -1.3 V and thereafter decreases. This potential of -1.3 V was thus chosen as the optimum deposition potential for all further experiments. Adopting a similar protocol, the optimum deposition time and scan rate were determined and found to be 11 min and 8 mV s^{-1} , respectively (Figs. S5 and S6 of Supporting Information).

Table 1 summarizes the experimental ranges chosen for the optimization tests and the optimum values observed for each of the above parameters, based on the maximum stripping current obtained.

Based on the optimum values obtained for the various parameters, IDA-PPy modified CPEs were prepared and tested for the analysis of $1 \times 10^{-6} \text{ M}$ Pb^{2+} concentration. From Fig. 6 it is evident that, under identical conditions, the anodic stripping current of IDA-PPy modified electrode for lead (Fig. 6A) is significantly higher than that of the bare CPE (Fig. 6B). It is pertinent to note that the oxidation potential during the stripping of lead is found to be -0.56 V in the case of both the IDA-PPy modified CPE and the bare CPE. This confirms that the stripping occurs from the carbon electrode surface and not through IDA-PPy complexed lead ions. Based on the experimental observations, the mechanism of lead complexation on the IDA-PPy electrode surface and its subsequent stripping may be explained as follows. It is expected that the buildup of Pb^{2+} ion on the electrode surface is facilitated by the presence of IDA-PPy

Table 1

The experimental conditions used and the optimum values arrived at for IDA-PPy modified CPE.

Parameter	Range of experimental values	Optimized value
Volume of IDA-PPy solution (2.5 g l^{-1})	10 to 50 μl	20 μl
Deposition pH	3.6 to 5.4	4.5
Deposition potential	-0.8 to -1.4 V	-1.3 V
Deposition time	0.5 to 15 min	11 min
Scan rate	1 to 16 mV s^{-1}	8 mV s^{-1}

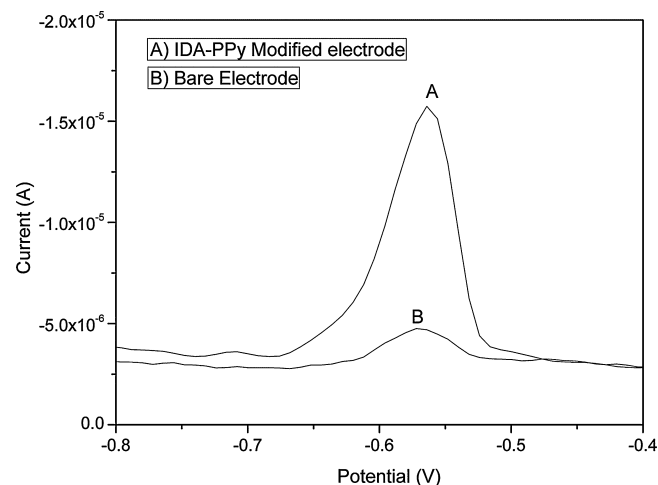
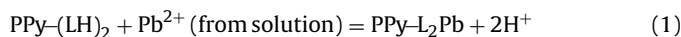
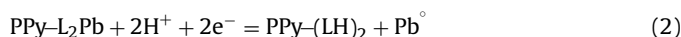


Fig. 6. Anodic stripping current of Pb^{2+} ion as a function of applied potential at A) IDA-PPy modified and B) bare CPE.

via metal ion complexation with the carboxyl group present on the IDA-PPy, as shown in Eq. (1).



where L represents the $-\text{COO}^-$ group of the IDA and PPy is the polypyrrole backbone. The lead complexed on the electrode surface is then reduced to its metallic form at the applied reduction potential, as represented in Eq. (2).



This step is followed by the stripping of the reduced metal from the electrode surface to the bulk solution, as shown in Eq. (3). This involves the oxidation of Pb^0 at an applied potential sweep from a higher to a lower reduction potential, yielding the anodic stripping current.



The better response of the IDA-PPy electrode for lead sensing vis-à-vis the bare CPE is clearly borne out by the results shown in Fig. 6, which indicates a more than sevenfold increase in sensitivity.

3.3. IDA-PPy modified CPE as a lead ion sensor: construction of calibration plot and evaluation of detection limit of Pb^{2+}

The anodic stripping current for a range of concentrations of Pb^{2+} ions was determined using 0.1 M acetic acid as the lixiviant. The corresponding calibration plot is shown in Fig. 7. The proportionality between the logarithm of diffusion current and that of concentration of lead ion was found to follow a linear relationship ranging from nanomolar to micromolar concentrations ($R^2 = 0.9772$). The region of the linear relationship observed corresponds to the useful working range where the IDA-PPy electrode could be utilized for the determination of lead with a high degree of accuracy. The limit of detection (LOD) has been calculated using the relation $\text{LOD} = 3S_a/b$ [32], where S_a is the standard deviation of the measurement and b is the slope of the linear regression. LOD of the Pb^{2+} ion was found to be $9.6 \times 10^{-9} \text{ M}$.

3.4. DPASV studies on individual metal ions and binary systems with lead using the IDA-PPy modified CPE

DPASV studies were carried out to examine the response of other metal ions in the observed working concentration range of lead. It has been reported that iminodiacetic acid is likely to bind to a range

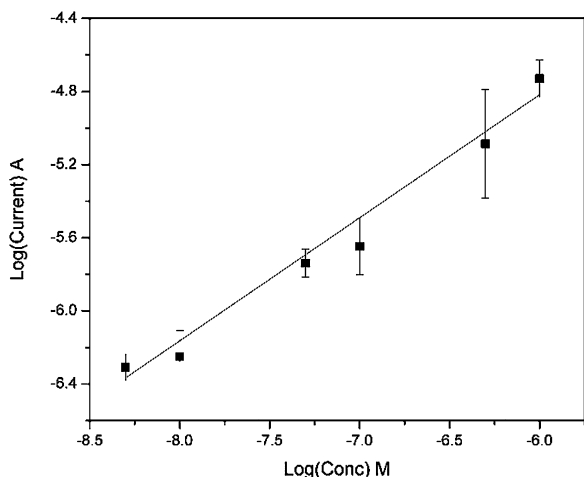


Fig. 7. DPASV calibration plot for Pb^{2+} ion concentrations ranging from 1×10^{-6} to 1×10^{-9} M.

of other divalent metal ions [28,33–35]. The IDA-PPy coated electrode was hence tested by DPASV analysis for some other divalent metal ion systems, such as CuCl_2 , $\text{Cd}(\text{NO}_3)_2$, CoCl_2 , $\text{Hg}(\text{NO}_3)_2$, NiCl_2 and ZnCl_2 , using solutions of 1×10^{-6} M concentration and below in all cases. From the experiments it is observed that Cu^{2+} and Cd^{2+} are responsive to the IDA-PPy modified CPE. The response of Cd^{2+} is limited to 1×10^{-6} M, while for Cu^{2+} the limit is 1×10^{-7} M. Reports indicate that iminodiacetic acid has a higher stability constant for Cu^{2+} than any other divalent metal ion which explains this peculiar behavior [36,37]. However, the other chosen metal ions do not respond in the concentration range of interest. It is noteworthy that the response limit of Pb^{2+} ions is two to three orders of magnitude lower than that observed for Cu^{2+} and Cd^{2+} ions. The respective stripping voltammograms for all the metal ions including Cu^{2+} and Cd^{2+} are shown in Fig. S7 (Supporting Information).

The competitive coordination of other metal ions with iminodiacetic acid could also influence the sensing ability of lead. In order to study this, binary solutions were prepared that contained Pb^{2+} ions and a second metal ion, and the stripping voltammograms were recorded. These tests were carried out keeping the Pb^{2+} concentration as 1×10^{-6} M while the concentration of the other metal ions was varied from 1×10^{-5} to 1×10^{-7} M, using CuCl_2 , $\text{Cd}(\text{NO}_3)_2$, CoCl_2 , $\text{Hg}(\text{NO}_3)_2$, NiCl_2 and ZnCl_2 . The stripping analyses were carried out under conditions identical to those used earlier.

Fig. 8 shows the resultant anodic stripping currents for Pb^{2+} at 1×10^{-6} M concentration as well as for Pb^{2+} at the same concentration in the presence of 1×10^{-5} M concentration of Cu^{2+} , Cd^{2+} , Co^{2+} , Hg^{2+} , Ni^{2+} and Zn^{2+} , respectively. It is evident that Cu^{2+} , Cd^{2+} and Co^{2+} at 1×10^{-5} M strongly interfere with Pb^{2+} in that the stripping current values of Pb^{2+} in combination with these ions are significantly reduced vis-à-vis Pb^{2+} alone. This could be due to the moderate coordination of these metal ions by the iminodiacetic acid. The anodic stripping currents of Pb^{2+} in the presence of Ni^{2+} and Zn^{2+} are more or less the same as that of Pb^{2+} alone, while the stripping current of Pb^{2+} in the presence of Hg^{2+} has increased in comparison with that of Pb^{2+} alone. This enhancement of the Pb^{2+} stripping current in the presence of Hg^{2+} is presumably due to the formation of amalgam [38] which aids the deposition of Pb^{2+} ion [39] on the electrode surface.

Additional studies have been carried out to investigate the interferences of Cu^{2+} , Cd^{2+} and Co^{2+} on Pb^{2+} at 1×10^{-6} M by adding the chosen interfering ions at concentrations of 1×10^{-6} or 1×10^{-7} M. The anodic stripping current for each of these cases has been studied under identical conditions and the results are shown in Fig. 9. It can be observed that the anodic stripping current of Pb^{2+} is not

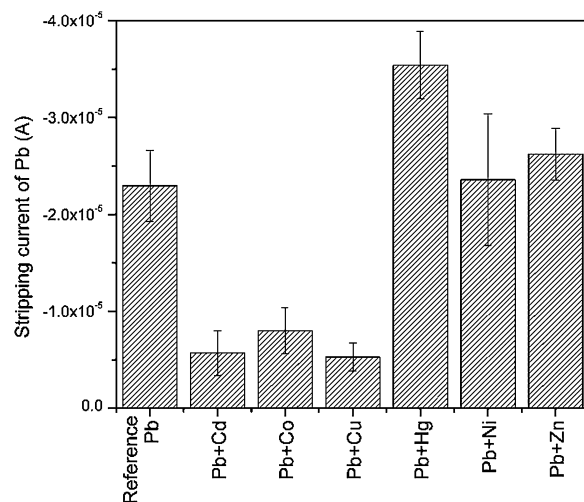


Fig. 8. Anodic stripping current of Pb^{2+} ion (at 10^{-6} M concentration) in the presence of other metal ions (at 10^{-5} M concentration).

altered in the presence of Cu^{2+} ions at both concentrations tested. On the contrary, in the case of binary combinations of Pb^{2+} with equimolar concentrations of Cd^{2+} and Co^{2+} , the anodic stripping current values of Pb^{2+} are appreciably diminished. However, when the concentrations of Cd^{2+} and Co^{2+} are reduced to one tenth that of Pb^{2+} , the stripping current values are nearly identical to that of Pb^{2+} alone.

3.5. Analysis of lead in an untreated industrial effluent sample using the IDA-PPy modified CPE

An untreated lead containing effluent obtained from a lead acid battery manufacturing industry was analyzed for the presence of Pb^{2+} ions. The sample was centrifuged to remove solid colloids prior to analysis with the IDA-PPy modified CPE. The sample was then adjusted to pH 4.5 using acetate buffer and a ten-fold dilution was carried out. The stripping analysis was carried out using the same conditions as before and the corresponding concentration of Pb^{2+} in the untreated effluent sample was determined from the calibration curve. The concentration was determined to be $6.38 (\pm 0.47) \times 10^{-6}$ M. The concentration of Pb^{2+} was independently analyzed by atomic absorption spectrophotometry and was determined to

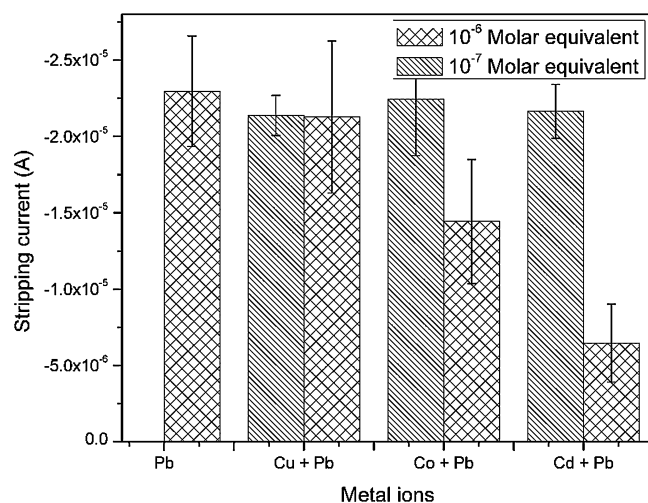


Fig. 9. Anodic stripping current of Pb^{2+} ion (at 10^{-6} M concentration) in the presence of Cu^{2+} , Cd^{2+} and Co^{2+} ions (at 10^{-6} and 10^{-7} M concentration).

be $8.46 (\pm 0.29) \times 10^{-6}$ M. There is good agreement of the results obtained by both methods.

4. Conclusions

Iminodiacetic acid functionalized polypyrrole (IDA-PPy) has been synthesized and used for carbon paste electrode (CPE) modification. The various parameters affecting the electrode response have been optimized. The working window region for the detection of the Pb^{2+} ion has been found to be within the concentration range of 1×10^{-6} to 5×10^{-9} M at pH 4.5. The effects of other metal ions have been studied and Cu^{2+} , Cd^{2+} and Co^{2+} were found to be interfering with the Pb^{2+} ion. A good correlation has been achieved for the analysis of lead from an industrial effluent sample using the IDA-PPy modified CPE and atomic absorption spectrophotometry. The developed IDA-PPy Pb^{2+} ion sensor has a high sensitivity and is capable of detecting very low concentrations, which is a limitation for other analytical instruments.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.electacta.2014.06.040>.

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