

FULL PAPER

Ultratrace determination of cadmium ion in petrochemical sample by a new modified carbon paste electrode as voltammetric sensor

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A novel chemically modified carbon paste electrode (CMCPE) impregnated with 4'-(4-chlorophenyl)-2,2':6',2''-terpyridine ligand was prepared and applied for voltammetric determination of Cd²⁺ ion in petrochemical samples. The effects of pH, ligand amount and supporting electrolyte on the selective adsorption properties for the Cd²⁺ ion were explored. The sensor displayed substantially good resistance against interfering agents. In the presence of a large excess of Na⁺, K⁺, Ca²⁺, Mg²⁺ and Pb²⁺, the adsorption capacity for Cd²⁺ was slightly changed, suggesting the high selectivity of CMCPE for Cd²⁺ ions. The parameters controlling the response of the electrode were investigated. The limit of detection (LOD) and relative standard deviation (n = 5) were obtained by 3.77 ng/L and 0.45%, respectively. The preconcentration procedure revealed a linear curve within the concentration range of 4 – 3000 ng/L and a good linearity with squared correlation coefficient of (R²) 0.9988 was achieved. The CV was run starting from –1.5 V to 0.0 V and back (Scan rate: 100 mV/s). The best ratio of the Cd²⁺-Ligand in carbon paste was 8% (w/w) for a good detection of Cd²⁺ ions. Optimum pH for maximum adsorption was 4.0 ± 0.2. All the instrumental parameters involved in the analytical procedure were optimized. The study was accomplished in Britton–Robinson (B-R) buffer solution of 2 ng/mL Cd²⁺ ions. The optimal values of scan rate, pulse amplitude, pulse time, voltage step, voltage step time, deposition potential and deposition time were obtained 100 mV/s, 0.20 V, 0.04 s, 0.005 V, 1.2 s, – 0.95 V and 150 s, respectively.

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KEYWORDS

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Introduction

Properties such as, corrosion and chemical resistance, high temperature tolerance, low melting point, good electrical conductivity and excellent metal Lewis acidity cause the cadmium ion to be used a lot in different industries. Some of the important consumptions of this element are in alloys [1], pigments [2], coatings [3], stabilizers [4], nickel-cadmium (Ni-Cd) batteries [5], solar cell manufacturing [6], and recently as solid

catalysts in petrochemical industries and production of biodiesel plants [7-9].

However, cadmium is a non-essential and toxic element for humans and unfortunately exists in some natural water resources, industrial waste matters, petrochemical samples, some other effluents and environmental samples. The airborne sources of cadmium in the environment are the burning of fossil fuels and municipal waste materials, and zinc, lead, or copper smelters emission. Cadmium levels in some foods can

be increased by the application of phosphate fertilizers or sewage sludge to farm fields. Smoking is another important source of cadmium exposure and smokers have about twice as much cadmium in their bodies as do nonsmokers [10]. It is toxic at ultra-trace amount and has harmful effects on health and the environment. The US Environmental Protection Agency (EPA) now classifies cadmium as a known human carcinogen, and it is recognized as a developmental toxicant and reproductive toxicant [11]. Thus, the determination of cadmium is considered highly important owing to its toxic characteristics. However, direct determination of trace amount of this element is challenging in these samples, because of the complexity of the matrix and extremely low concentrations of cadmium in real samples.

Various techniques including flame and graphite furnace atomic absorption spectrometry [12], inductively coupled plasma and various separation methods such as solvent extraction, cloud point extraction, solid-phase extraction, membrane filtration, electrodeposition, flotation, coprecipitation and ion exchange have been utilized for preconcentration of trace metals from natural aqueous samples [13-16]. The separation approaches such as liquid-liquid extraction and coprecipitation require large amounts of high purity hazardous organic solvents, and low selectivity is the major drawback of solid-phase extraction by stationary phase.

Voltammetric techniques have been utilized for metal ion determination due to their low cost, high selectivity and facile operation [17,18]. Recently, modified electrodes have been applied to improve the sensitivity and selectivity of these methods [19]. Chemically modified carbon paste electrodes (CMCPE) can be prepared by dispersing graphite powder in a non-conductive mineral oil as a binder and adding a specific reagent as a modifier [20-21]. The advantages of this electrode include high sensitivity and selectivity, low limit of

detection (LOD), nontoxicity and wide range of deposition potentials over the mercury electrode as well as other features required for voltammetric analysis [22-24].

In this work, the 4'-(4-chlorophenyl)-2,2':6',2''-terpyridine (L) ligand (Figure 1) was employed as modifier to prepare a Cd²⁺ selective voltammetric sensor. The modifier can preconcentrate Cd²⁺ from sample solution to the surface of the modified electrode by forming complexes with these ions, and greatly increase the sensitivity of their determination. To the best of our knowledge, nanostructured Cd²⁺-L-MCPE has not been extensively explored as sensor for Cd²⁺ ion.

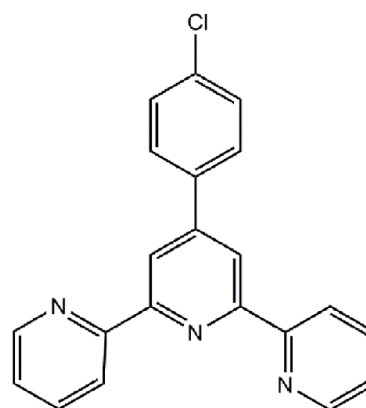


FIGURE 1 4'-(4-Chlorophenyl)-2,2':6',2''-terpyridine ligand (L)

The experiment

Reagents

All HPLC grade solvents and reagents hydrochloric acid, nitric acid, acetic acid, ammonium acetate 99.5%, toluene > 99.8%, ethanol 99.9%, analytical grade cadmium chloride min. 99.9%, paraffin oil, graphite powder (spectrum grade, size < 20 μm) were purchased from Merck (Germany) and utilized without any further purification. 4'-(4-chlorophenyl)-2,2':6',2''-terpyridine ligand (L) 97.0%, is commercially available from Sigma-Aldrich and is used without any changes. All the solutions were prepared with deionized water. Standard stock solutions (1000 μg/mL, traceable to SRM) of Fe²⁺, Co²⁺,

Ni^{2+} , Cu^{2+} , Zn^{2+} , Cr^{3+} , Au^{3+} , Pt^{2+} , Ag^+ , Pb^{2+} , Mn^{2+} , Hg^{2+} , Ca^{2+} , Mg^{2+} , Na^+ and K^+ ions in 2% HNO_3 were supplied from Merck. The fresh working solutions were prepared daily by diluting the stock solution in deionized water. The Britton–Robinson (B–R) buffer was used as supporting electrolyte.

Apparatus

Electrochemical experiments including cyclic voltammetry (CV) were carried out using a Autolab B. V., potentiostat - galvanostat (Nova 1.8 software). The voltammograms were acquired with a three-electrode system containing Ag/AgCl as the reference electrode, Pt wire as the auxiliary electrode, and CP as the working electrodes (unmodified or modified). Differential pulse voltammetry (DPV) was performed in an analytical system using a Metrohm 797 VA computerized, version 1.3.1. A Metrohm 713 pH meter was used for pH adjustments. All the electrochemical experiments were carried out at room temperature. The concentration of Cd^{2+} ion was determined utilizing a varian AA240FS fast sequential atomic absorption spectrometer too. Stirring of the solutions was accomplished by a Heidolph MR3001 magnetic stirrer (Germany).

Preparation of CMCPE

Modified carbon paste was prepared by complete mixing of high purity graphite powder (70 mg) with paraffin oil (30 mg), using a porcelain pestle and mortar. The suitable amounts of **L** were added in order to obtain a series of modified carbon pastes containing from 2 to 12% (w/w) **L**. Then a portion of the resulting paste (2 mm long) was packed firmly into one end of a tube and then a copper wire was inserted into the tube to provide electrical contact. A new surface on these working electrodes was obtained by pushing an excess of paste out of the tube and polishing it on a weighing paper [25].

Results and discussion

Electrochemical behavior of the CMCPE

X-ray diffraction study of Cd^{2+} -**L** complex by cadmium nitrate in aqueous medium reveals that the $[\text{Cd}(\text{L})(\text{NO}_3)_2(\text{H}_2\text{O})]$ is formed. Each cadmium atom is chelated by three nitrogen atoms of **L**, two oxygen atoms of bidentate nitrate, an oxygen atom of a monodentate nitrate, and water; thus, resulting coordination number of seven is augmented with CdN_3O_4 molecule core [26]. The cyclic voltammogram (CV) were carried out to assess the catalytic activity of **L** modified electrode toward Cd^{2+} ion. The cyclic voltammograms were obtained at freshly-prepared unmodified and modified CPE for Cd^{2+} ion as shown in Figure 2. Therefore, it is clear that the **L** - CMCPE has the greatest affinity for Cd^{2+} ion in comparison to CPE. The voltammetric response is apparently enhanced at **L** modified electrode, reflected by the enlargement of the peak currents (I_p) on both cathodic and anodic peaks. The presence of a small signal for CPE shows that carbon and binder slightly adsorb the Cd^{2+} ion. The CV was run starting from -1.5 V to 0.0 V and back (Scan rate: 100 mV/s).

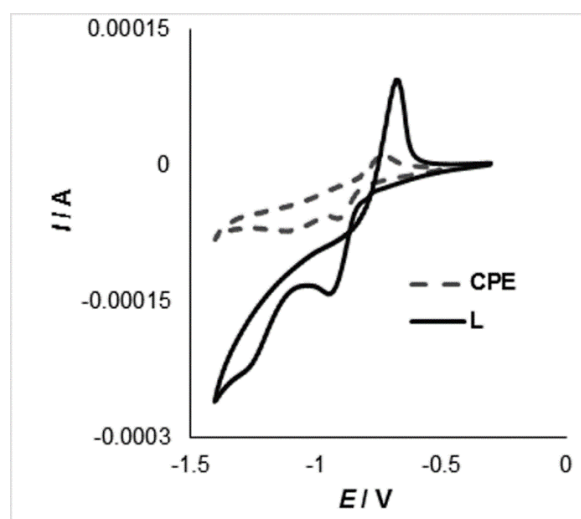
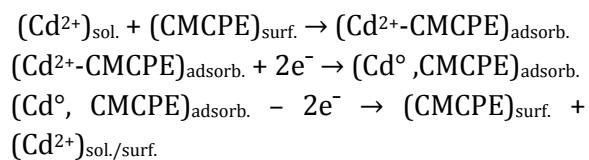


FIGURE 2 CV of Cd^{2+} ion (4×10^{-6} M concentration; B-R buffer solution 0.04 M supporting electrolyte, pH 4.0)

According to the results obtained on the electrochemical behavior of Cd^{2+} at the surface of **L** modified electrode, the following mechanism is proposed for the electrocatalytic oxidation of Cd^{2+} ion at the surface of **L** modified electrode:



Effect of **L** amount

Regarding optimization of the experimental conditions, some of the variables influencing

the peak current were studied. The accumulation of Cd^{2+} at the Cd^{2+} -**L**-CMCPE was based on the complex formation of CMCPE and Cd^{2+} and the voltammetric response was expected to influence mass loading of Cd^{2+} -**L** on the Cd^{2+} -**L**-CMCPE. Therefore, the relationship between the analytical signal and the Cd^{2+} -**L** amount in carbon paste was explored. The obtained results reveal that the voltammetric response reaches a maximum value by increasing Cd^{2+} -**L** to 8% (w/w). As illustrated in Figure 3, the best ratio of the Cd^{2+} -**L** in carbon paste was 8% (w/w) for a good detection of Cd^{2+} ions.

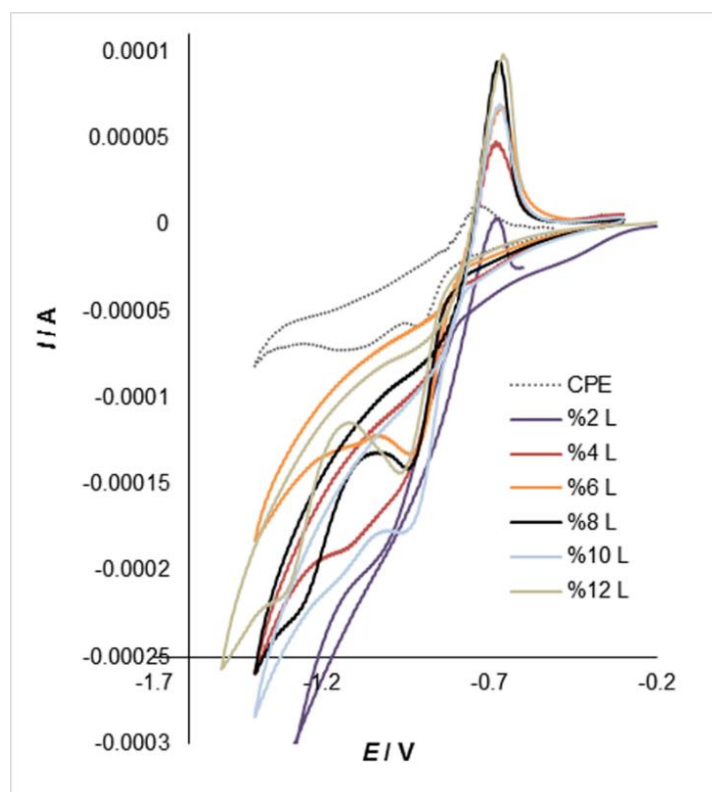


FIGURE 3 Percentage of **L** modifier effect on the sorption of Cd^{2+} ions using cyclic voltammetry

Effect of pH

The effect of pH in the range of 2.0–10.0 on the determination of the Cd^{2+} ion is shown in Figure 4. Among the investigated parameters, pH is the most important factor for adsorption of Cd^{2+} ion on the MCPE. At pH 4.0, the peak current reached a maximum for Cd^{2+} ion and the decrease in the currents of lower responses at a relative acid electrolyte can be

attributed to the competition between proton ion and the metal ions for binding to the donating atoms of the modifier at the surface of CMCPE. At higher pHs, the hydrolysis of Cd^{2+} ion could be the reason for the decrease in the peak current. Therefore, high concentration of the hydrogen ions interferes with the rebinding of the metal ion to the cavity as the hydrogen ions also bind with the cavity,

whereas a low concentration of hydrogen ions and existence of OH^- usually leads to the formation of precipitates with ligands [27].

Therefore, all the samples were buffered to $\text{pH } 4.0 \pm 0.2$ by adding B-R buffer, for further studies.

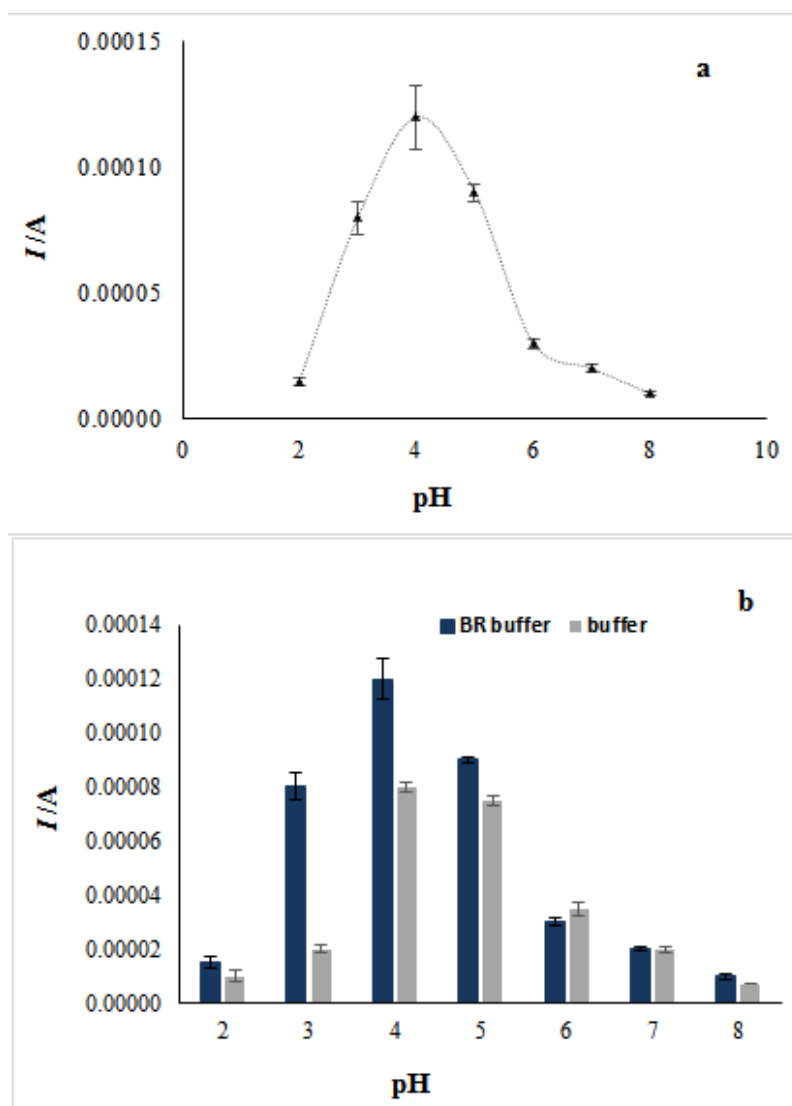


FIGURE 4 The pH effect (a), B-R buffer effect: (b) on the sorption of Cd^{2+} ions using L-CMCPE

Optimized parameters

The variation of the potential scan rate demonstrated that the anodic and cathodic peak current increased linearly with the scan rate in the range of 10–150 mV/s. Figure 5 displays that the anodic and cathodic peak currents of the oxidation and reduction of cadmium ions changed linearly with the square root of the potential sweep rate ($V^{1/2}$) with good correlation ($R^2 = 0.9922$ and 0.9833 for anodic and cathodic peak currents, respectively). Catalytic adsorption mechanism

can control the electron transfer owing to the improvement of mass-transfer rates of the metal ions to the electrode surface. All the instrumental parameters involved in the analytical procedure were optimized. The study was accomplished in B-R buffer solution of 2 ng/mL Cd^{2+} ions. The optimal values of scan rate, pulse amplitude, pulse time, voltage step, voltage step time, deposition potential and deposition time were obtained 100 mV/s, 0.20 V, 0.04 s, 0.005 V, 1.2 s, -0.95 V and 150 s, respectively (Figure 6).

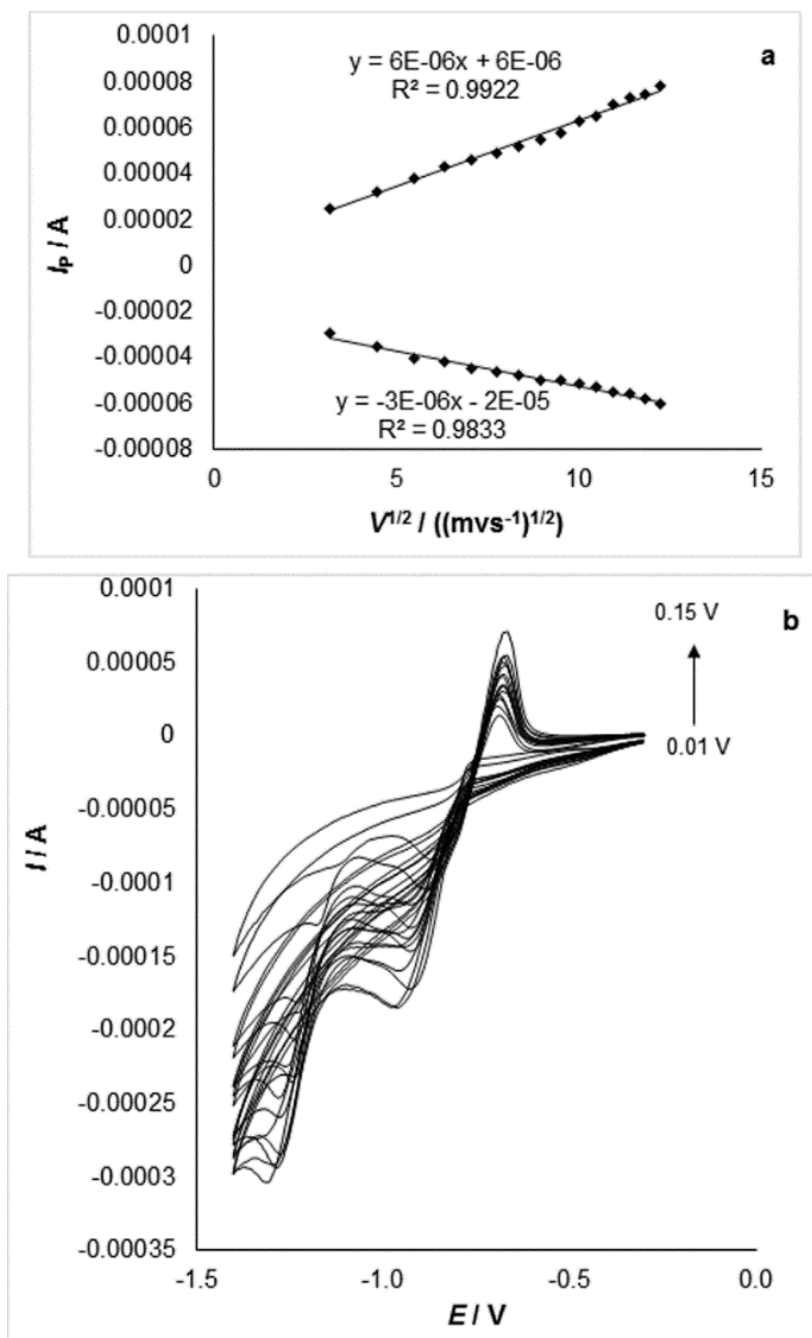


FIGURE 5 (a) Effect of varying scan rates for L-CMCPe; (b) cyclic voltammograms of varying scan rates (0.01-0.15 V)

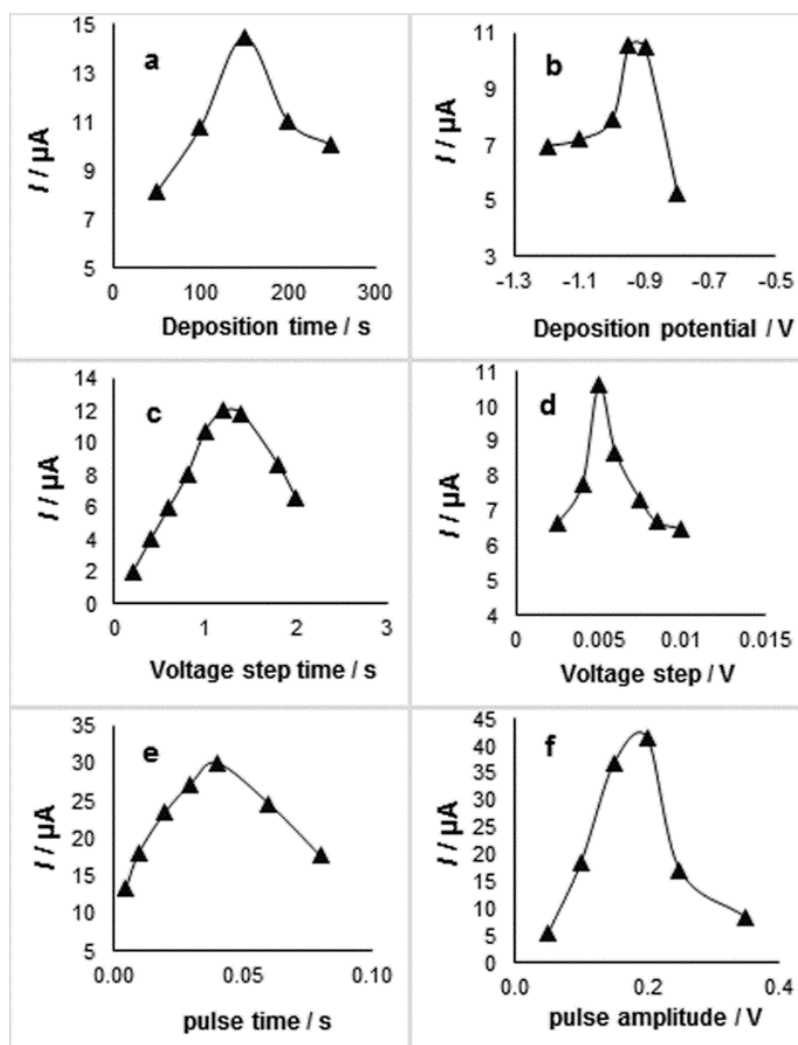


FIGURE 6 Optimized parameters of (a) deposition time, (b) deposition potential, (c) Voltage step time, (d) Voltage step, (e) Pulse time and (f) Pulse amplitude

Calibration curve

To obtain the calibration curve, the effect of different Cd^{2+} concentrations was investigated and the results are presented in Figure 7. The proposed DPV method with optimal conditions has been thus employed for determination of Cd^{2+} by using L- MCPE.

The DPV peak currents revealed a good linear relationship with the concentration of Cd^{2+} ions. The limit of detection, defined as $\text{LOD} = 3S_b m^{-1}$, where LOD, S_b and m are respectively the limit of detection, standard deviation of the blank and the slope of the calibration curve are exhibited in Figure 7. The

S_b was estimated by 5 replicate determinations of the blank signals. The precision of the method for five standard solutions containing 2 ng/mL of Cd^{2+} ion was assessed by determining the relative standard deviation, and was found to be 0.45%. It is clear that this method has a good precision for the analysis of trace Cd^{2+} ions in aqueous samples. The detection limit was determined to be 3.77 ng/L. The preconcentration procedure showed a linear curve within the concentration range 4 to 3000 ng/L. A good linearity with squared correlation coefficient (R^2) 0.9988 was achieved.

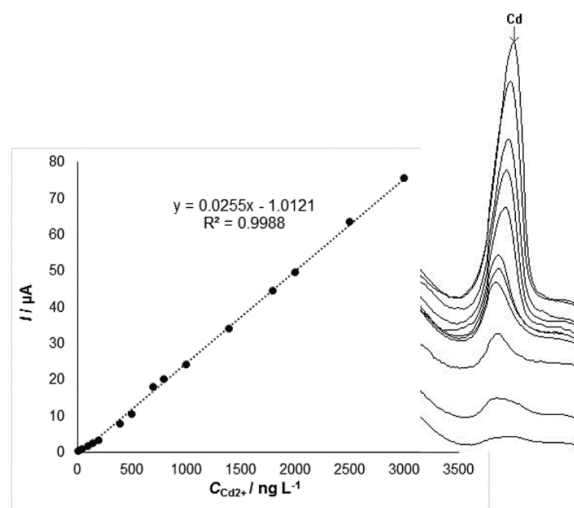


FIGURE 7 Calibration curve and DPV voltammograms of L-CMCPE for Cd²⁺ ion detection

The selectivity studies

Petrochemical samples commonly contain other alkaline, alkaline earth and transition metal cations, which may compete with Cd²⁺ for the active adsorption sites. Thus, the possible interferences of Na⁺, K⁺, Ca²⁺, Mg²⁺, Pb²⁺ and some transition metal cations on the Cd²⁺ adsorption capacity of the CMCPE were also investigated. The interfering metal ions for this study were selected considering the similarity of the ionic radius and chemical features of the metal cations and target analyte. The influence of other ions present in the analyte solution on the current response of Cd²⁺ is given in Table 1. The interference is

referred to in terms of percentage current change, although peak potentials were unchanged. At the coexisting ion concentration that affected the DPV peak current of Cd²⁺, only a 5% change of peak current is allowed [28]. In the presence of a large excess of Na⁺, K⁺, Ca²⁺, Mg²⁺ and Pb²⁺, the adsorption capacity for Cd²⁺ slightly changed, suggesting the high selectivity of L-CMCPE for Cd²⁺ ions. Several ions such as Ni²⁺, Hg²⁺, Pt²⁺ and Au³⁺ have only insignificant effect on the determination of Cd²⁺ ions. As seen in Table 1, it is evident that the extraction efficiency of Cd²⁺ has no interference with the L-CMCPE in the presence of metal cations.

TABLE 1 The result of interferences of some metal ions on the determination of 2.0 ng/mL Cd²⁺

| Interfering ion | Concentration (ng mL ⁻¹) | Peak current change (%) |
|------------------|--------------------------------------|-------------------------|
| Co ²⁺ | 100 | +5.0 |
| Fe ²⁺ | 100 | +1.85 |
| Cu ²⁺ | 100 | -0.84 |
| Zn ²⁺ | 100 | +2.25 |
| Cr ³⁺ | 100 | +4.5 |
| Pt ²⁺ | 50 | +3.44 |
| Ag ⁺ | 100 | -1.92 |
| Au ³⁺ | 50 | +2.01 |
| Mn ²⁺ | 100 | +1.06 |
| Hg ²⁺ | 50 | +2.46 |
| Ni ²⁺ | 50 | -3.63 |
| Pb ²⁺ | 1000 | +0.10 |
| Ca ²⁺ | 1000 | +2.85 |
| Mg ²⁺ | 1000 | +0.72 |
| Na ⁺ | 1000 | +4.84 |
| K ⁺ | 1000 | +0.94 |

Real sample analysis

The feasibility of the L-CMCPE for the determination of Cd²⁺ ion in real samples was verified by the analysis of 08N-10X-0.5 inorganic standard. Standard addition method was employed for determining the concentrations of Cd²⁺ ion. The amount of Cd²⁺ ion in 08N-10X-0.5 (according to package label) is 10000 µg/mL, and we determined 10000.15 µg/mL. As seen, the obtained results of standard material analysis show that the

Cd²⁺ ion recovery is quantitative. The results for determination of Cd²⁺ in two petrochemical samples, Karaj river water, a tobacco sample, a cigarette sample and a pesticide sample are summarized in Table 2. The results obtained by this method are well matched with those acquired by ICP spectrophotometry, indicating applicability of the proposed method for precise and accurate determination of the Cd²⁺ ion in a wide variety of real samples with different complex matrices.

TABLE 2 Cd²⁺ ion recovery of different samples by DPV and ICP by standard addition method (N = 3).

| Sample | Cd ²⁺ ion content (ng/L) | | Recovery (%) | AAS method (ng/L) |
|------------------------|-------------------------------------|-------------|--------------|-------------------|
| | Added | Found | | |
| Petrochemical sample 1 | 0 | 55.45±0.32 | - | 53.27±0.88 |
| | 20 | 75.66±0.54 | 100.27 | 74.36±0.46 |
| Petrochemical sample 2 | 0 | 39.08±0.21 | - | 40.19±0.25 |
| | 20 | 58.69±0.24 | 99.34 | 57.21±0.32 |
| Karaj river | 0 | 7.59±0.45 | - | 8.07±0.43 |
| | 20 | 26.48±0.58 | 95.97 | 27.12±0.40 |
| Tobacco | 0 | 141.46±0.77 | - | 143.50±0.38 |
| | 20 | 159.93±0.84 | 99.05 | 171.50±0.55 |
| Cigarette | 0 | 122.94±0.50 | - | 120.20±0.69 |
| | 20 | 138.22±0.77 | 96.69 | 136.81±0.47 |
| pesticide | 0 | 13.93±0.25 | - | 13.00±0.85 |
| | 20 | 30.97±0.38 | 91.27 | 35.10±0.73 |

Reusability

To examine the stability of the Cd²⁺-L-CMCPE, several sorption and desorption operation cycles were carried out. Sorption studies of reused Cd²⁺-L-CMCPE showed that the L-CMCPE can be utilized again in the process

after being washed with water (pH 7.0) for 20 s and being polished on a weighing paper. The L-CMCPE was relatively stable up to at least hundred determinations without a distinguishable decrease in the current. The lifetime of L-CMCPE is shown in Figure 8 and was about within 12 weeks.

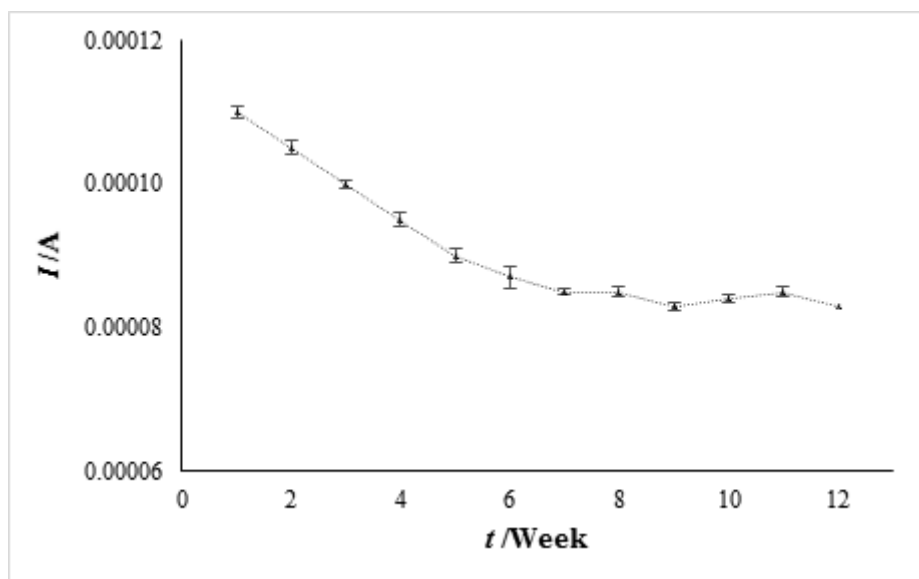


FIGURE 8 Lifetime of L-MCPE within 12 weeks

Comparison with other methods

Some of voltammetric determination of Cd²⁺ ions by various working electrodes with

TABLE 3 Data from previously reported working electrode for Cd²⁺ ion separation

| Working electrode | RSD (%) | LOD (ng/mL) | LR (ng/mL) | References |
|-------------------|---------|-------------|------------|------------|
| CPE- MWCNT | 2.3 | 0.74 | 1 –1200 | 29 |
| CPE-M- Cd-IIP | 2.1 | 0.31 | 2 –200 | 30 |
| CPE | 1.8 | 6.6 | 1 –2000 | 31 |
| CPE-IIP | 3.3 | 0.058 | 0.11 –56 | 32 |
| L-MCPE | 0.45 | 0.003 | 0.004 –3 | This work |

Conclusion

To sum up, a new electrochemical sensor was prepared for the determination of Cd²⁺ ion at trace levels. The application of 4'-(4-chlorophenyl)-2,2':6',2''-terpyridine ligand (**L**) as a novel modifying agent in the carbon paste electrode made it very selective for Cd²⁺ determination in the presence of common potential interferers. The **L** used in the carbon paste composition acted as both the selective chemical interface of the sensor and a preconcentration agent. The cyclic voltammogram (CV) was carried out to assess the catalytic activity of **L** modified electrode toward Cd²⁺ ion. The obtained results reveal that the voltammetric response reached a maximum value by increasing Cd²⁺-**L** to 8%

different related standard deviation (RSD), limit of detection (LOD) and linear range (LR) are reported and summarized in Table 3.

(w/w). The lifetime of L-CMCPE was about within 12 weeks. The interfering metal ions for this study were selected considering similarity of the ionic radius and chemical features of the metal cations and target analyte. In the presence of a large excess of interfering agents, the adsorption capacity for Cd²⁺ slightly changed, suggesting the high selectivity of L-CMCPE for Cd²⁺ ions. The proposed sensor affords higher sensitivity, lower limit of detection, wider linear range and higher selectivity compared to the other reported electrodes. Moreover, the preparation procedure of the modified electrode is simple, fast and reproducible.

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