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Electropolymerization characterization of paraphenylenediamine using exfoliated graphite doped carbon paste electrode

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ABSTRACT

A sensor based on conducting polymer paraphenylenediamine was developed for the voltammetric determination of Pb(II) and Cd(II). The electropolymerization of the incorporated phenylendiamine was carried out in acidic medium by cyclic voltammetry between -0.40 V and 0.90 V and under constant potential. The conducting polymerfor exfoliated graphite doped cpeexhibited a significantly increased sensitivity and selectivity towards Pb(II) and Cd(II)compared with carbon paste electrode. Cadmium and lead were preconcentrated at – 1.1 V on the modified electrode. The measurements were carried out using a square wave voltammetry in an acidic medium. Under the optimum conditions, a linear range was obtained in the concentration range 0.6-15nmol/L with a correlation coefficient of 0.998. The detection limit were 0.5 and 0.52nmol/L and relative standard deviation for 9 successive determinations of 10.5nmol/L were 2.5% and 2.78% for Pb(II) and Cd(II) respectively. Interference from metal ions was also studied, and the method was applied to the direct determination of lead and cadmium in tap water.

KEYWORDS

Paraphenylenediamine;
Electropolymerization;
Exfoliated graphite;
Carbon paste electrode;
Lead;
Cadmium.

INTRODUCTION

Paraphenylenediamine (p-PD) (Figure 1.) is an aromatic diaminecompound derived of the aniline used in the manufacture of dyestuffs, as hair dye and as adjuvant of henna, as well as that of wood and leather[1]. Paraphenylenediamine is commonly used in several industries, dyeing furs, photochemical processes, cosmetic and fabrication of household goods[2,3]. Recently, the electrochemical properties of phenylenediamines (PDs) have been investigated in biocatalyst[4,5]. (Liu et al., 2012; Yuqing et al., 2006), and in adsorption[6]. The synthesis, characterization and the polymerization were reported by several groups[7-11]. Poly (phenylenediamine) and its derivatives represent an important class of conducting polymers and have been attracted great attention since their discovery, owing to their molecular electrical, optical and magnetical properties[12-14]. Poly-PDs have also variety of potential applications in the fields of sensors[15-18], corrosion protection[19], nanocomposite, composite[20,21] and in the electroanalytical purposes[22]. At the same time, several voltammetry methods especially coupled with chemically modified electrodes (CME) have been developed. Our group employed carbon paste electrode modified by poly paraphenylenediamine for the detection of some heavy metals[23].

Nowadays, considerable interest is focused on chemically modified electrodes for different sensor applications due to their inherent advantages over conventional electrodes. Electrochemical sensors based on graphene, carbon nanotube, carbon black and exfoliated graphite represents a new and interesting alternative for different analytes. Since their discovery, exfoliated graphite "graphene" has been used beneficially in electrochemical sensor[24-26], and determination of metals as a copper and a lead[27-29], because it is easy to manufacture at lower costs. Eventually, a graphite derivative calledexpanded graphite, or "exfoliated" graphite could be abeneficial filler for producing conductive polymers. Exfoliatedgraphite is usually obtained by rapid heating of agraphite intercalation compound (GIC), and has a good affinity for both organiccompounds and polymers, therefore some monomers andpolymers can be absorbed into the pores and galleries ofexfoliated graphite[30]. This paper describes a novel electrochemical sensor that was fabricated with exfoliated graphite doped p-PD modified carbon paste electrode (EX-G doped pPD modified CPE), and the electrochemical property of the sensor was investigated. It can be used for ultrasensitive determination of lead and cadmium in tap water using square-wave voltammetry (SWV) technique. The results show that an exfoliated graphite doped p-PD modified CPE exhibits excellent performance for detecting lead and cadmium.

EXPERIMENTAL

Apparatus

Electrochemical experiments were carried out with an autolab (Metrohm-Autolab, Utrecht Netherlands) PGSTAT302N potentiostat/galvanostat controlled by GPES 4.9 software. A three-electrode electrochemical cell was employed for all electrochemical measurements. Carbon paste electrode (4 mm diameter) served as the working electrode, a platinum plate as counter electrode, and saturated electrode calomel (SEC) as reference electrode.

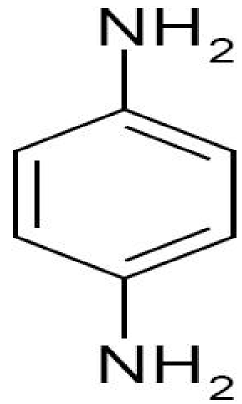

Figure 1 : Chemical structure of paraphenylenediamine.

Reagents

Graphite and all chemicals were of analytical reagentgrade. O-phenylenediamine, p-phenylenediamine and m-phenylendiamine were from Sigma,exfoliated graphite was prepared in house[30]. Lead and cadmium sulfate were obtained from Riedel-de häen, Solution were prepared with distilled water. Standard Pb(II) and Cd(II) stock solution were prepared by dissolving $Pb(NO_3)_2$ and $Cd(NO_3)_2$ in water. Acidic solution served as the supporting electrolyte. Tape water sample were collected from our laboratory.

Preparation of the electrodes

The modified carbon paste electrodes were prepared by thoroughly mixing weighed amounts of monomer 5 mg of p-PD, dissolved in a small quantity of acetonitrile, with 0.5mg of exfoliated graphite, the mixture was then mixedwith 0.5 g of graphite powder and 0.15 mL of paraffin oil until a uniformly wetted paste was obtained.

Electropolymerization at monomer modified electrode

The electropolymerization for p-PD modified CPE and exfoliated graphite doped p-PD modified CPEwere carried out in 0.1 mol/L HCl solutions by cyclic voltammetry. For preparative purposes, electropolymerization was also performed at a constant potential of 0.7 V for 1 min and cycling voltammetry for 5 scans between -0.4 and 0.9 V.

Cadmium and lead determination

After the formation of the films, the electrode was removed from the solution, rinsed with water and placed in the measurement cell containing a selected concentration of $Pb(NO_3)_2$ and $Cd(NO_3)_2$ in 0.1 MHCl. An initial potential of-1.1 V (vs. ECS) was applied for 120s. Following the preconcentration step, the rotation of the electrode was stopped and the solution was left to equilibrate for 30 s. The electrode potential is stepped reversibly between -1.1 V to -0.3 V vs. Ag/AgCl at 50 mV s^{-1}using square wave voltammetry. The parameters used were a potential step height of 5 mV, pulse amplitude of 50 mV and frequency of 10 Hz.

RESULTS AND DISCUSSION

Characterization of CPE and exfoliated graphite doped CPE

Preliminary studies consist of studying both electrodes by cyclic voltammetry in 0.1 M HCl, at a potential scan rate of 50 mV s^{-1}. The first results indicatethat electrode modified with exfoliated graphite behave similar to carbon paste electrode and the background currents are very low as shown in Figure 2. Neverthelessa small shift in reduction current was observed.

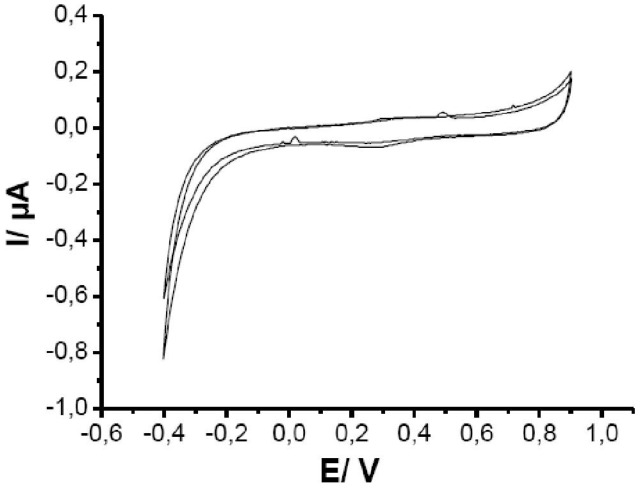

Figure 2 : CVs of the CPE and exfoliated graphite doped CPE, in 0.1 M HCl at a scan rate of 50 mV.s^{-1}, between -0.4 and 0.9 V.

Electropolymerization of paraphenylenediamine

After characterization of the electrodes, the monomer p-PD was added to CPE and to exfoliated graphite doped CPE as described in paragraph 2.3. The polymerization of p-PD film was conducted on the surface of electrode by cycling a potential between -0.4 and 0.9 V vs. Ag/AgCl electrode at a sweep rate of 50 mV/s for 120 scans in 0.1 mol/ L HCl. Figure 3 shows typical cyclic voltammograms recorded during the electrochemical growth of the polymer on exfoliated graphite doped CPE and CPE. During the first scan, at CPEan anodic peak was observed at 0.6 V, this peak was attributed to the oxidation of monomer, and two reduction peaks were observed, the first one at 0.45 V and the second at 0.25 V as reported by adraoui[23], with the currents of anodic was 5 µA and cathodic were 3 and 4 µA. At EX-G doped CPE the same peaks are observed but the anodic peak was about 0.6 V and cathodic peaks are 0.4 V and 0.2 V, with the currents anodic and cathodic were 22, 10 and 11 µA respectively. At the one hundred twenty scans, and upon further cycling, both cathodic and anodic currents increase, indicating continuous polymerization but for CPE, stable voltammograms were observed while permanent increase for EX-Gdoped CPE was observed. The oxidation current of polymers recorded on CPE and EX-G doped CPEwere 50 and 150 µA after 120 scans respectively. This indicates that the film formed by EX-G doped CPE has good properties[30].

Electrochemical characterization of exfoliated graphite

A comparative study was conducted using 1 mM $[Fe(CN)_6]^{3-/4-}$ as an electrochemical probe in HCl at a potential scan rate of 50 mVs^{-1}. Figure 4 shows the CV curves of the CPE, exfoliated graphite doped carbon paste electrode, poly (p-PD) modified cpeand exfoliated graphitedopedpoly (p-PD) modified CPE in presence of 1mM $[Fe(CN)_6]^{3-/4-}$. A pair of poor redox peaks was observed at polymer of CPE which might be ascribed to the low conductivity of graphite (b). While the EX-GdopedCPE exhibited well-defined peaks with a peak potential separation (ΔE) of 0.12 V, suggesting the dramatic increase in the electron transfer rate due to the high conductivity of exfoliated graphite (b).

Electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy(EIS) is further used for the investigation on the modified electrode, which can exhibit the impedance changes of the modification processes using1 mM $[Fe(CN)_6]^{3-/4}$. The

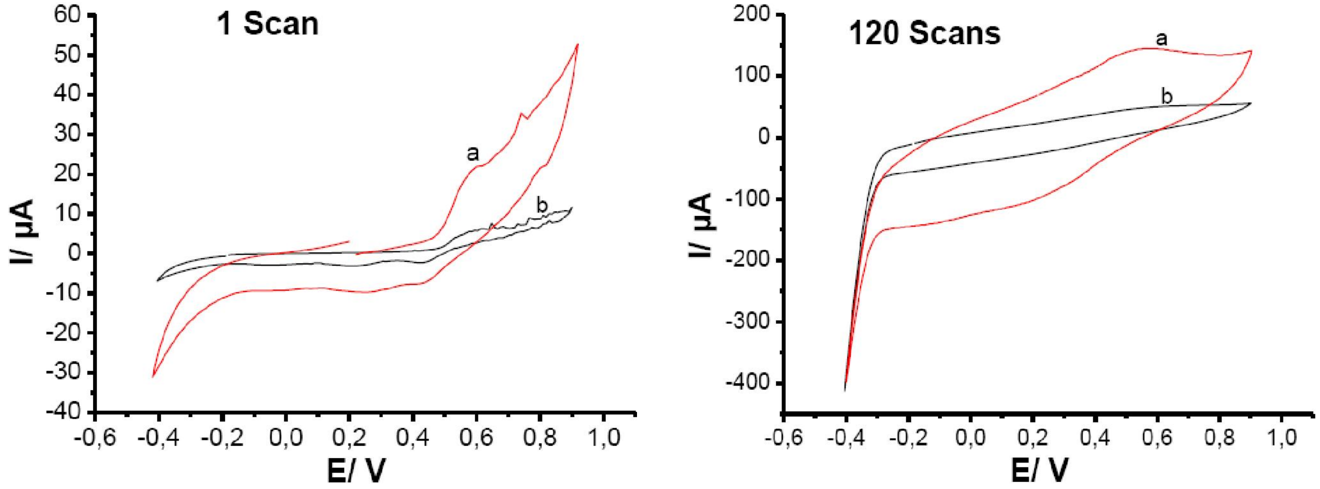

Figure 3 : CVs of the conducting polymers after polymerization for (a) exfoliated graphite doped p-PD modified CPE and (b) p-PD modified CPE, in 0.1 M HCl at a scan rate of 50 mV.s^{-1}.

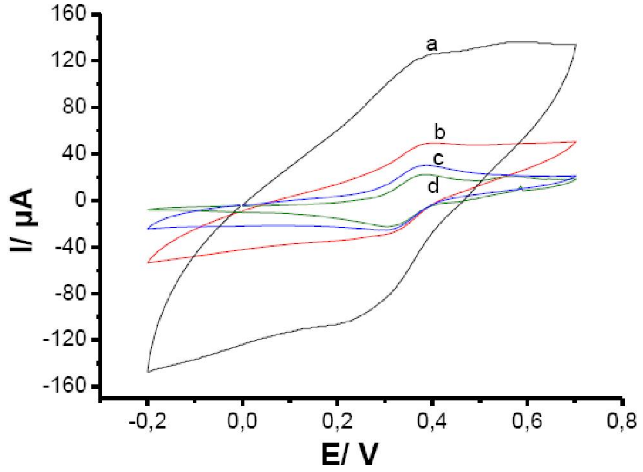

Figure 4 : CVs for 1 mM $[Fe(CN)_6]^{3-/4-}$ on different electrodes; (a) exfoliated graphite doped Poly (p-PD) modified CPE, (b) Poly (p-PD) modified CPE, (c) exfoliated graphite doped p-PD modified CPE and (d) p-PD modified CPE scan rate 50 mV s^{-1}.

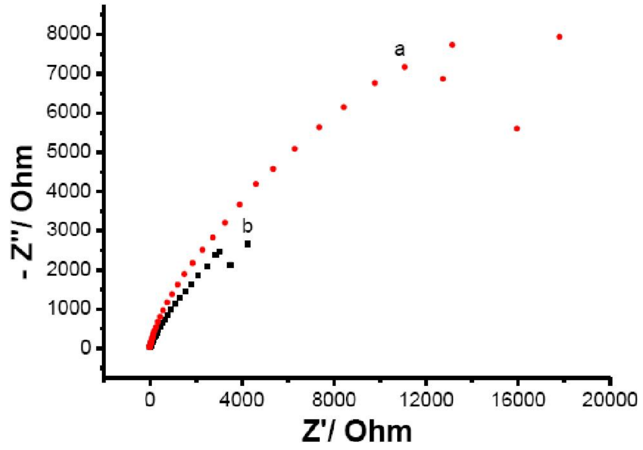

Figure 5 : EIS for (a) Poly (p-PD) modified CPE and (b) exfoliated graphite doped Poly (p-PD) modified CPE in 1 mM $[Fe(CN)_6]^{3-/4}$.

EIS spectra are recorded at the potential applied of the 0.6 V in the frequency range of 10 kHz to 50 mHz. As can be seen in Figure. 5 an almost semicircle is observed at the polymer modified CPE (a) and a small circle at the polymer doped EX-Gmodified CPE (b). On the other hand the electrochemical impedance spectrum at polymer doped exfoliated graphite modified CPE has a low resistance indicating that the EX-G on the electrode surface facilitated the electron transfer kinetics offering very less impedance to the electron transfer process compared to that at the polymer modified CPE (TABLE 1). The observations made in the EIS study are in good agreement with those of CV studies. The same result was observed using graphene with polyaniline modified glassy carbon[31] and graphene modified carbon ionic liquid[32].

Electropolymerization by a fixed potential

Since our aim is to develop a sensor for detection of lead and cadmium the parameter time is very important. The time of polymerization and analysis must be reduced, so the polymerization of EX-G doped p-PD modified CPEwas investigate at fixed potential toprepare the polymer film on electrode. The polymer synthesized at a fixed potential of 0.7 V during 1 min and cycling voltammetry for 5 scans was compared with the repetitive 40 cycles. The best result was obtained with a fixed potential. The difference observed in currents, show the efficiency of fixed potential and the advantage to reduce the time.

Determination of cadmium and lead

TABLE 1 : Polymer resistance of two electrodes

	Rs/ ohm	Rp/ Kohm	CPE/ μF
Exfoliated graphite doped poly (p-PD) modified CPE	29.89	18.08	248.70
poly(p-PD) modified CPE	44.03	27.90	413.85

Rs. solution resistance; Rp. electrontransfer resistance; CPE.Constant-phase element

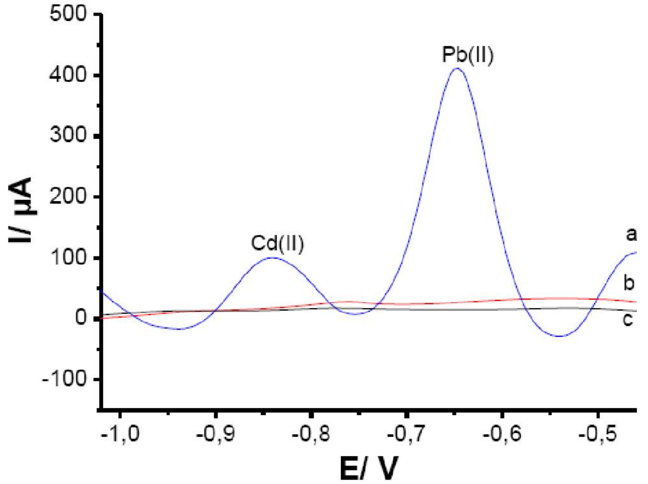

Figure 6 : Comparison between the results obtained by SWV for determination of 6 nM of lead and cadmium after 120 scans used (a) exfoliated graphite doped poly (p-PD) modified CPE and (c) poly (p-PD) modified CPE (b), and by fixed potential used exfoliated graphite doped poly (p-PD) modified CPE (a), $E_{deposition}$= -1.1 V, $t_{deposition=}$ 60 s, pH= 12.

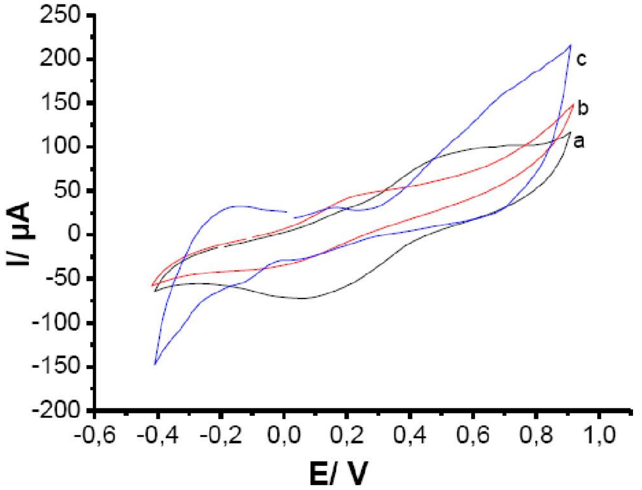

Figure 7 : Polymer synthesized at a fixed potential of 0.7 V for 1 mn and 5 scans, (a) p-PD, (b) o-PD and (c) m-PD.

In the first step, preliminary studies of lead and cadmium accumulation were performed with the monomer after polymerization by repetitive cycles, on carbon paste electrode and on exfoliatedgraphite doped carbon paste electrode. Figure 6 shows square wave voltammetry for 6nM of Cd(II) and Pb(II) in a 0.1 M HCl. The peaks currents were observed at the EX-Gdopedpoly (p-PD) modified CPE (b) of 20 and 8 μA and at poly (p-PD) modified graphite (c) of 6 and 3 μA for lead and cadmium respectively. This indicates that exfoliated graphite plays an important role in the accumulation process of Cd(II) and Pb(II) on the electrode surface and significantly increases the sensitivity of determining Pb(II) and Cd(II).

In the second step, and in order to reduce the time of analysis, the polymer was tested in the same solution of lead and cadmium. The polymer synthesized at a fixed potential of 0.7 V during 1 mn and cycling voltammetry for 5 scans to the EX-G doped poly (p-PD) modified CPE (a) was tested for its efficiency to preconcentrate 6 nM Pb(II) and Cd(II). An increase anodic peaks currents observed at lead (284 μA) and cadmium (44μA). For the remaining study the polymer was synthesized using fixed potential.

Electropolymerization of phenylenediamines compounds

Comparison of phenylenediamines compounds

The polymerization of EX-G doped phenylenediamine (p-PD, o-PD and m-PD) modifiedCPE were studied by fixed potential at a scan rate of 50 mV/s in 0.1 mol/ L HCl (Figure 7). The current of oxidation and reduction peaks ofp-PD (a) increased after 5 scans compared with o-PD (b) and m-PD (c). This indicates that the film obtained withp-PD are good benefit for continuous in our working.

Determination of lead and cadmium

The phenylenediamines after polymerization were tested for its efficiency to preconcentratePb(II) and Cd(II) on EX-G doped CPE. The square wave voltammetry for Cd(II) and Pb(II) of polymers synthesized at a fixed potential of 0.7 V to the exfoliated graphite doped PDs modified CPE in a 0.1 M HCl was used (Figure not shown). Two well-defined peaks were observed at the p-PD (a), while a small peaks appear at the o-PD (b) and no response were observed to m-PD

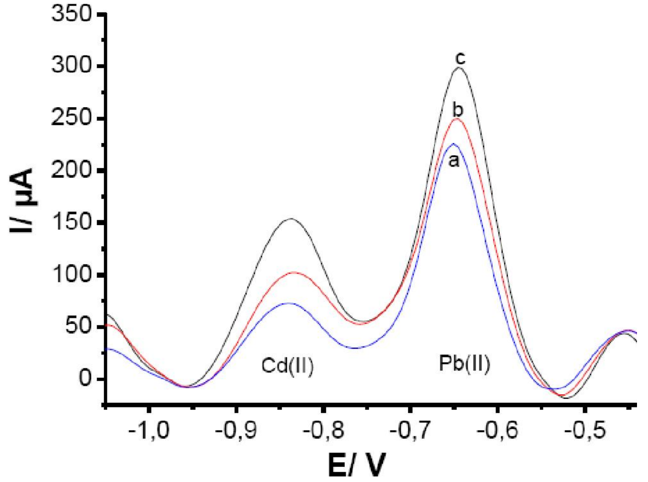

Figure 8 : The effect of fixed potential (P), 6 nM of Cd(II) and Pb(II), a) 0.5; b) 0.7 and c) 0.6 V, t= 1 mn; V=50 mV/s, E_{dep}= -1.1 V,t_{dep}= 60 s, pH= 12.

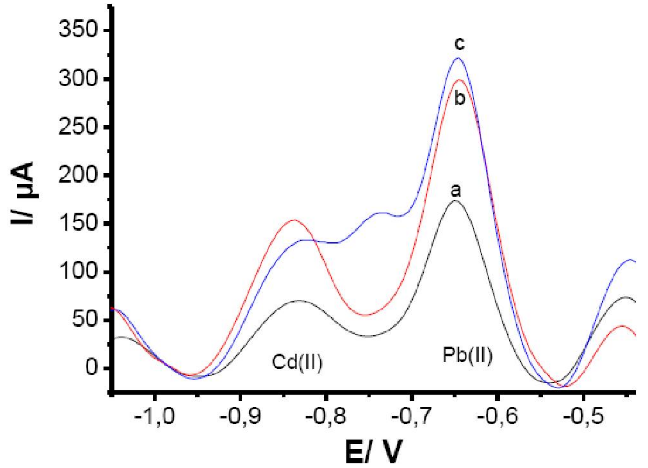

Figure 9 : The effect of the time for fixed potential, 6 nM of Cd(II) and Pb(II), a) 5 mn; b) 1 mn and c) 2 mn, P= 0.6 V, V= 50 mV/s, P_{dep}= -1.1 V, t_{dep}= 60 s, pH= 12.

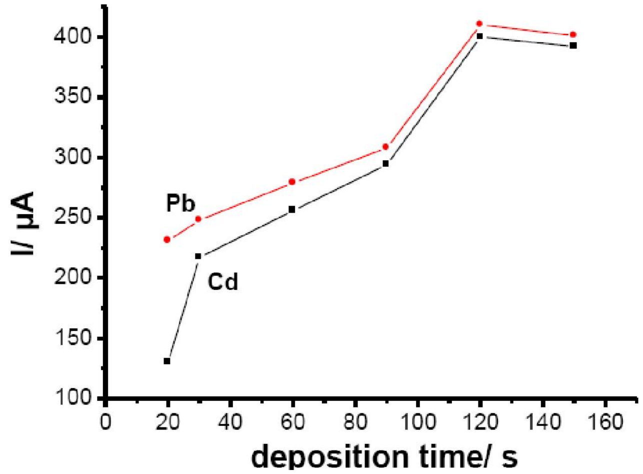

Figure 10 : Effect of accumulation time on the peak current of 6 nmol/L of Cd(II) and Pb(II), t= 1 mn, P= 0.6 V, E_{dep}= -1.1 V, V= 50 mV/s, pH= 12.

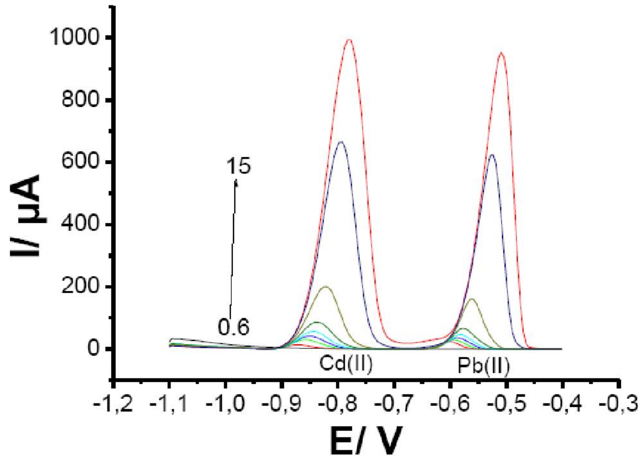

Figure 11 : Calibration plot 0. 6- - - - -15 nM, of Pb(II) and Cd(II), t= 1 mn, P= 0.6 V, P_{dep}= -1.1 V, t_{dep}= 120 s, V= 50 mV/s, pH= 12.

(c). The film formed by poly (p-PD) was used for further work.

Optimization of parameters

Potential of polymerization

Figure 8 shows the effect of fixed potential on the peaks currents determination at 0.6 V, 0.5 V and 0.7 V. The best response was obtained with 0.6 V. Therefore, this potential was selected for further investigations.

Potential time of polymerization

The effect of time on the peak current of fixed potential was examined. Figure 9 shows the effect of time on the peak current. The better response of peak current was 60 s and 120 s. So, for further experiments, a time of 60 s will be used to reduce time of analysis.

Accumulation time

Figure : 10 shows the effect of the accumulation time on the peak current of 6nmol/L. The peak current increases with the increasing of accumulation time up to 120 s and become stable. The better response of peak current was 120 s. So, for further experiments, an accumulation time of 120 s will be used to reduce time of analysis.

Calibration plot

Under the parameters optimization studies a calibration graph for the determination of Cd(II) and Pb(II) was constructed for a concentration range 0.3–15nmol/

TABLE 2 : Interference of others metal ions with the determination of 1.5 nmol/L of Cd(II) and Pb(II)

Cations, change in peak currents, %	Pb	Cd
Pb	100	- 119
Cd	54.33	100
Fe	- 58.82	-247.82
Cu	24.26	-65.86
Hg	72.05	38.80
Zn	NF	NF

TABLE 3 : Recovery analysis of Cd(II) and Pb(II) in tap water sample.

Cations	Added, nmol/L	Found, nmol/L	Recovery (%)
Pb	3	2.08	104
	6	3.79	94.75
Cd	3	1.94	97
	6	3.64	91

L. A linear range was obtained in the concentration range 0.6-15nmol/L with thefollowing regressions equations I_{pa} (μA) = - 19.08 + 65.80 C (μM) (R^2= 0.998) for lead and I_{pa} (μA) = - 9.20 + 68.15 C (μM) (R^2= 0.998) for cadmium (Figure 11.). The detection limit were 0.5 and 0.52nmol/L for Pb(II) and Cd(II) respectively and relative standard deviation for 9 successive determinations of 10.5nmol/L were 2.5% and 2.78% for Pb(II) and Cd(II) respectively.

Interference

The possible influence of several ions on the reduction signal of 1.5nM lead and cadmium was considered. Voltammetric responses resulting from the presence of some interfering ions such asZn(II), Cu(II), Fe(II), Hg(II)were carried out under the optimized conditions. In TABLE 2, the results obtained show that 10.5nM of interfering ion of Fe (II) affect on Cd(II) and Pb(II), also interfering ion of Cu(II) affect only the Cd(II) determinations. Can be explained by the competition of interfering ions with Cd(II) and Pb(II) for complexes formation with poly (p-PD). To avoid possible interference with others metals, the choice of deposition potential is very important.

Analytical application

The method for the determination of lead and cadmium was applied to tap water sample. The standard addition method was applied, the Recovery analysis of Pb(II) and Cd(II) in tap water sample showed good recovery. Consequently, that is a good accuracy for Pb(II) and Cd(II) determinations in the samples matrix studies. The results were summarized in TABLE 3.

CONCLUSION

The carbon paste electrode (CPE) modified with exfoliated graphite doped p-phenylenediamine showed a sensitive, precise and accurate response for Pb(II) and Cd(II). The electropolymerization could be performed in acidic medium, and the developed electrode can be easily prepared. Under optimized conditions, the electrode showed excellent performance in terms of detection limit, linearity range, selectivity, repeatability and recovery values. The developed method was applied for the determination of Pb(II) and Cd(II) in real sample analysis.

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