Int. J. Electrochem. Sci., 8 **(2013)** 2164 - 2181

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

A Novel Chitosan Nanoparticle-Schiff Base Modified Carbon Paste Electrode as a Sensor for the Determination of Pb(II) in Waste Water

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Received: 9 December 2012 / *Accepted:* 29 December 2012 / *Published:* 1 February 2013

This paper describes the preparation and electrochemical application of a modified carbon paste electrode with a new kind of chitosan nanoparticle-Schiff base for the determination of Pb(II) ions in waste water using differential pulse anodic stripping voltammetry (DPASV). Firstly a new kind of chitosan nanoparticle-Schiff base (CNSB) was synthesized by chitosan nanoparticle reaction with 2,4-dihydroxybenzaldehyde. CNSB structure was characterized by FT-IR spectroscopy, elemental analysis, particle size and zeta potential. Afterwards, a novel, simple and effective chemically modified carbon paste electrode with CNSB was prepared and characterized using scanning electronic microscopy (SEM-EDX) and anodic stripping voltammetry. The modified electrode showed only one oxidation peak in the anodic scan at -0.35 V (*vs.* Ag/AgCl) for the oxidation of Pb(II). The electrochemical properties and applications of the modified electrode, including the pH, supporting electrolyte, preconcentration time, reduction potential and time, and percentage of modifier were investigated. The best voltammetric response was observed for a paste composition of 73.7% (w/w) of graphite powder, 5.3% (w/w) of chitosan and 21% (w/w) of paraffin oil, with 0.2 mol L^{-1} NaAc solution at pH 6.0 as supporting electrolyte, preconcentration time of 600 s, a reduction potential of -0.1 V and reduction time of 10 s. The new electrode displays excellent response to Pb(II) which is linear in the range from 1×10^{-6} to 1×10^{-4} mol L^{-1}, with a correlation coefficient of 0.998 and a detection limit of 7.24×10^{-7} mol L^{-1}.

Keywords: Chitosan nanoparticles, Schiff base, Carbon paste electrode, Lead (II) sensor, Voltammetry

1. INTRODUCTION

Lead is widespread in the environment and has hazardous effects on human health at high levels [1,2]. It is a general metabolic poison and enzyme inhibitor [3] and continuous exposure to this element may cause serious disorders, such as anaemia, kidney disease and mental retardation. Detection of toxic traces of lead in the environment is a challenging analytical problem.

The most commonly used methods for the determination of various metal ions are atomic adsorption spectrometry (AAS) [4,5], atomic emission spectrometry (AES) [6] and mass spectrometry (MS). Although these methods are highly efficient, they require tedious sample pre-treatments, highly qualified technicians and sophisticated instruments. Moreover, these methods are also known to be expensive, time consuming and not suitable for analysis of multiple samples. In recent years, anodic stripping voltammetry (ASV) has played an increasing role in the determination of heavy metal ions because of high sensitivity, short analysis time and inexpensive equipment. The hanging mercury drop electrode (HDME) and mercury film electrode (MFE) are traditionally used as working electrodes for the simultaneous voltammetric determination of heavy metals since the invention of polarography. Recently, alternative working electrodes has been developed since the toxicity of mercury has been highlighted and its use is considered undesirable. The use of various mercury-free electrodes including bismuth film electrodes, gold-coated electrodes, silver electrodes, glassy carbon electrodes, carbon paste electrodes, carbon nanotube electrodes or screen-printed carbon electrodes has been described for sensitive metal determinations [7-11].

With the focus on modified carbon paste electrodes, the most sensitive detection limits were achieved using differential pulse anodic stripping voltammetry (DPASV) [12]. In recent years the construction and the application of modified electrodes have received great attention in relation to the enhancement of sensitivity and selectivity of electrochemical techniques mainly by electrochemical deposition [13,14,15]. Carbon paste electrodes (CPEs) and chemically modified electrodes (CMEs), have attracted great interest in recent years due to its ability to accumulate metal ions based on supramolecular interaction of these ions with a functional group on the electrode surface [16,17]. Nanocomposite based CPEs were used for voltammetric determination of metals as well [18]. CPEs can be readily prepared, renewed and modified by mixing with various reagents capable of supramolecular interactions. Moreover, they offer a renewable and modified surface as well as very low background current interferences [19].

Chitosan, a linear polymer of β-(1 $\rightarrow$ 4) linked 2-amino-deoxy-D-glucopyranese that is easily prepared from chitin by *N*-deacetylation, appears to be more useful than chitin because it has both hydroxyl and amino groups that can be modified easily [20]. Chitosan modified screen-printed carbon electrode was successfully used for sensitive determination of heavy metals [21] and CPE modified with chitosan was used for voltammetric determination of Pb(II) [22]. Chitosan is a biodegradable, biocompatible and bioadhesive polysaccharide capable of supramolecular interactions. It has been shown in a range of toxicity tests that chitosan is non-toxic and soft tissue compatible. Chitosan nanoparticles are obtained by the process of ionotropic gelation based on the interaction between the negative groups of sodium tripolyphosphate (TPP) and the positively charged amino groups of chitosan [23]. Generally, in this process chitosan nanoparticles are prepared by addition of TPP solution (pH 7–9) into an acidic solution (pH 4–6) of chitosan. The ratio between chitosan and TPP is critical, and highly dependent on pH of the solution [24]. The -NH_2 groups of chitosan can react with aldehydes or ketones to form imines (Schiff base). It was reported that chitosan Schiff bases have excellent chelation ability with heavy metal ions [25].

This work describes the preparation, characterization and analytical applications of a new environment friendly modified carbon paste electrode using newly synthesized chitosan nanoparticle-Schiff bases. Chitosan nanoparticles (CN) were formed by ionotropic gelation between positively charged amino groups of chitosan and negatively charged TPP. Then chitosan nanoparticle-Schiff bases (CNSB) were prepared and characterized by FT-IR, particle size, and zeta potential. Furthermore the synthesized nano-chitosan Schiff base was applied for the preparation of a modified electrode and used to determine lead (II) by using differential pulse anodic stripping voltammetry (DPASV).

2. MATERIALS AND METHODS

2.1. Apparatus and Chemicals

The FT-IR spectra of the newly synthetized derivatives were measured in the 4000-400 cm^{-1} regions using a Perkin Elmer Spectrum 100/ATR Sampling Accessory. Particle size was measured using a Zetasizer Nano-ZS-90 (Malvern Instruments). The analysis was performed at a scattering angle of 90^o at 25 ^oC. Zeta potential was measured using Zeta Potential Analyzer Ver. 3.54 (Brookhaven Instruments Corp.). Elemental analyses (C, H, N) were performed using a LECO CHNS 932 (Inonu University, Malatya, Turkey) elemental analyzer. SEM images were obtained on a scanning electron microscope (SEM-JSM 5600). Energy dispersive analysis of X-ray (EDX) was used to identify the elemental composition of the samples. It was performed with an EDX analyzer coupled to a scanning electron microscope. Differential pulse anodic stripping voltammetric (DPASV) curves for the determination of Pb(II) were recorded using CHI 600 D potentiostat employing a conventional three-electrode measuring cell with carbon paste electrode as a working electrode, an Ag/AgCI/ KCI_{sat} reference electrode and a platinum wire auxiliary electrode, respectively. Compared to other electrolytes, 0.2 mol L^{-1} NaAc gave the best voltammetric signals for Pb(II) using carbon paste working electrode. The voltammetric cell was rinsed every day before the measurements with supra pure concentrated HNO_3 to avoid accidental contamination. Pure nitrogen was bubbled through the sample solutions for 600 s before the measurements. The solutions were stirred with a Teflon-coated magnetic stirring bar in the electrolysis step.

The pH values of the solutions were determined with Orion 410A+ pH meter calibrated with potassium hydrogenephtalate (pH 4.13) and sodium bicarbonate (pH 8.20) buffer solutions. All aqueous solutions were prepared with ultra-pure water obtained from a Millipore Milli-Q Plus water purification system. A magnetic stirrer was used in preconcentration step. A Mettler balance (Toledo-AB104, Greifensee, Switzerland) was used for weighing the solid materials. A micropipetter (Eppendorf–Multipette® plus) was used for transferring the solutions throughout the experimental work. All the chemicals were of analytical or better grade and used as received. Chitosan of low molecular weight, sodium tripolyphosphate (TPP) and other chemicals were purchased from Fluka, Acros, Sigma-Aldrich and Merck Companies.

2.2. Preparation of chitosan nanoparticles (CN)

The chitosan nanoparticles were obtained using an ionotropic gelation interaction between positively charged chitosan and negatively charged TPP at room temperature [26-27]. A chitosan to TPP ratio of 5:1 was selected [28-29]. TPP was dissolved in deionized water and chitosan was dissolved in acetic acid (1 % v/v). CN were produced by drop wise addition of the TPP solution into a chitosan solution with a selective chitosan to TPP ratio of 5:1 (w/w) (e.g., 10 mL of 1.0 mg mL^{-1} chitosan solution was mixed with 2 mL of 1.0 mg mL^{-1} TPP solution). The gelation process was carried out under constant magnetic stirring followed by ultrasonication at room temperature. The nanoparticles were then separated by centrifugation at 16.000 rpm and 4 ^{o}C for 30 min. The supernatant was removed and the CN were rinsed with water followed by freeze drying. IR (ν_{max}, cm^{-1}): 2853 s, 3321 b, 1635 b, 1458 m, 1377 m, 1070 m.

2.3. Preparation of chitosan nanoparticles Schiff-base (CNSB)

Nano-chitosan Schiff base (CNSB) was prepared according to a method described in the literature [30,31,32]. 1 g of CN was added to 100 mL of methanol and the mixture was continuously stirred to produce homogeneous solution. Afterwards, an equimolar amount of 2,4-dihydroxybenzaldehyde relatively to that of nitrogen in CN was added to the mixture. The reaction mixture was refluxed for 48 h. CNSB formed was separated by centrifugation at 16 000 rpm and washed several times with ethanol. After drying in vacuum oven at 50^{o}C for 24 h, a yellow powder of CNSB was obtained with yield of 75%. The supposed structure of nano-chitosan is shown at Figure.1. IR (ν_{max}, cm^{-1}): 1629 s, 1460 m, 1274 s, 1151 m, 891 s, 753 s.

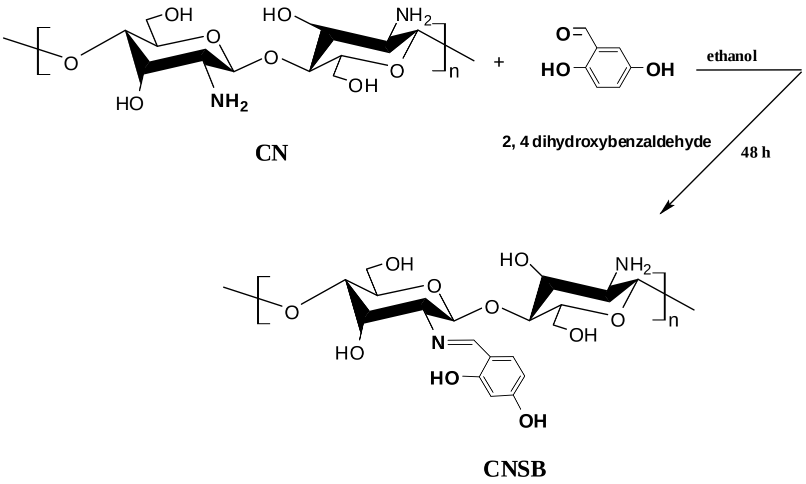

Figure 1. The schematic representation of the synthesis of chitosan nanoparticle Schiff base (CNSB).

2.4. Preparation of unmodified carbon paste electrode (CPE) and carbon paste modified by CNSB (CNSB-CPE)

Unmodified carbon paste electrode was prepared by careful mixing of 79% of graphite powder and 21% of paraffin oil. The modified carbon paste electrode (CNSB-CPE) was prepared by hand-mixing of 73.7% graphite powder with 5.3% CNSB followed by mixing with 21% of paraffin oil in a mortar for approximately 10 min to form the homogeneous modified carbon paste. After the homogenization of the mixture the paste was placed into the inner hole of the working electrode body (BAS MP 5023), the electrode surface was polished with a weight paper until the surface had a shiny appearance and it was used directly for voltammetric measurements without preconditioning. The electrodes were only washed with distillated water and stored in refrigerator at +4 °C when not in use.

2.5. Analytical Procedure

The freshly prepared modified electrode CNSB-CPE was first activated in sodium acetate (0.2 mol L^{-1}) solution (6.0 mL) by successive sweep in DPASV mode until the reproducible background voltammograms were obtained in the supporting electrolyte. The potential range was set from -1.2 to 0 V vs. Ag/AgCl electrode with the scan in the anodic direction. In the case of ASV, the electrode was rinsed with water and then immersed in a 100 mL of the solution containing the analyte which was preconcentrated in the stirred solution for a given period of time (The electrode was held at starting potential for 10 seconds). The electrode was removed, rinsed with water, connected to the potentiostat and then quickly placed into the measurement cell containing the supporting electrolyte. A reduction potential of -1.0 V was applied for 10 seconds, and then an anodic potential scan was registered. Afterwards, the electrode surface was renewed by applying the end potential (0.4 V) of the scan for a given period of time. The electrochemical behavior of CNSB-CPE was examined by differential pulse anodic stripping voltammetry (DPASV). A series of standard solutions of Pb(II) was measured by DPASV under the optimized working conditions describe above. The recovery studies were realized with a synthetic sample solution with known concentration of Pb(II). The influence of some inorganic cations was investigated and evaluated. The same procedure was applied to waste water sample and the results were compared with the reference method.

3. RESULTS AND DISCUSSION

3.1. Characterization of CN and CNSB

3.1.1. FT-IR and elemental analysis

The FT-IR spectrum of CN shows the characteristic absorption peak of –OH and $–NH_2$ at 2853-3321 cm^{-1}. The characteristic absorption peaks of N–H angular deformation, CH_3 symmetrical angular deformation, and the second hydroxyl absorption peak (–OH) appear at 1635, 1458, 1377, and 1070 cm^{-1}, respectively. The FT-IR spectra of the chitosan nanoparticle Schiff-base show a strong absorption at 1629 cm^{-1} which is attributed to the strong stretching vibration of imine (C=N). In addition, the characteristic absorption peaks of the phenyl and phenolic groups (phenolic-OH) can be seen at about 1460, 1274, 1151, 891 and 753 cm^{-1}. These results indicate that CNSB contains C=N groups at the N-position in nano-chitosan [31-33, 34].

The results of elemental analysis are as follwos: (wt %): CN (C: 34.77, H 6.04, N: 6.14); CNSB (C: 52.73, H: 5.97, N: 4.63). The nitrogen content of CNSB was lower than that of CN because of the high percent of carbon containing 2,4-dihydroxybenzaldehyde. The degree of substitution of CNSB was calculated from the C/N value of elemental analysis on the basis of the formula:

$$C_1/ N_1(1-x) + C_2/ N_2 (x) = C_3/ N_3 . 0.790$$

C1/N1 is a value calculated from the formula of the nonsubstitued chitosan and C2/N2 from the CNSB. C3/N3 is a found value of the sample by elemental analysis. X (0.640) is a substitution degree of CNSB. Deacetylation degree of chitosan is 0.790 [20].

3.1.2. Particle Size and Zeta Potential

Afterwards, CN and CNSB particle size and zeta potential were measured. Table 1 presents the particle size and zeta potential of CN and CNSB. The particle sizes of CN and CNSB were found to be 33 nm and 36 nm, respectively (Figure 2). There is no remarkable change in the size of the chitosan nanoparticles after reaction with 2,4-dihydroxybenzaldehyde [35]. The CN have a positive zeta potential because the amino and hydroxyl groups forms hydrogen bonds with the hydroxyl groups or oxygen atoms of water [36-37]. Figure 3 shows the zeta potential curve of CN and CNSB. The potential distribution has a single peak, indicating excellent uniformity [38]. The zeta potential of CNSB is lower than that of CN. This decrease may result from the consumption of the amine groups of the CN in the Schiff base reaction [35].

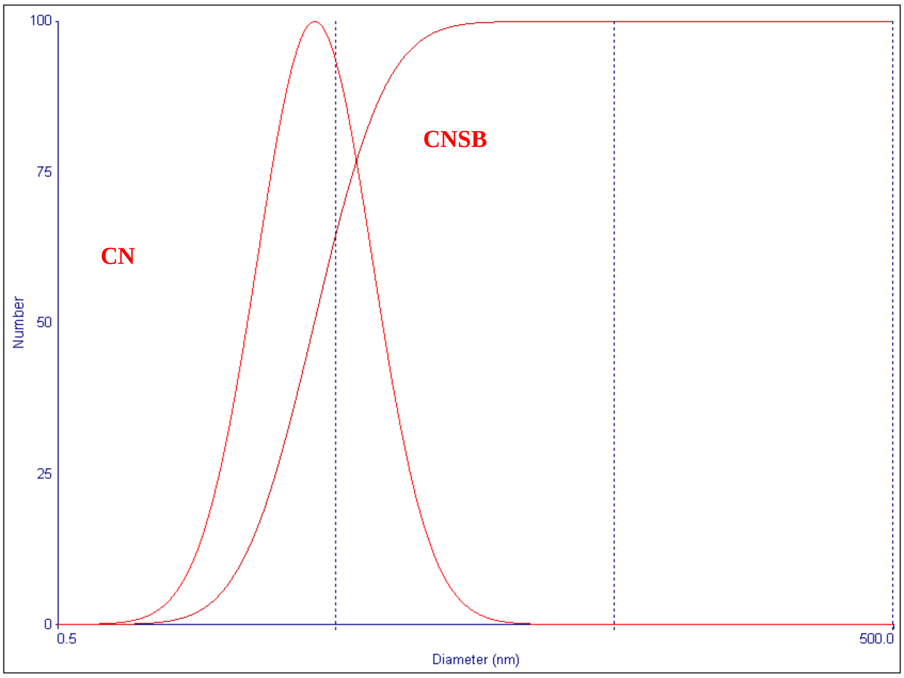

Figure 2. The size distribution of CN and CNSB .

Table 1. Particle size and zeta potential of CN and CNSB

Nanoparticles	Particle size (nm)	Zeta Potential (mV)
CN	33	+65.10
CNSB	36	+57.74

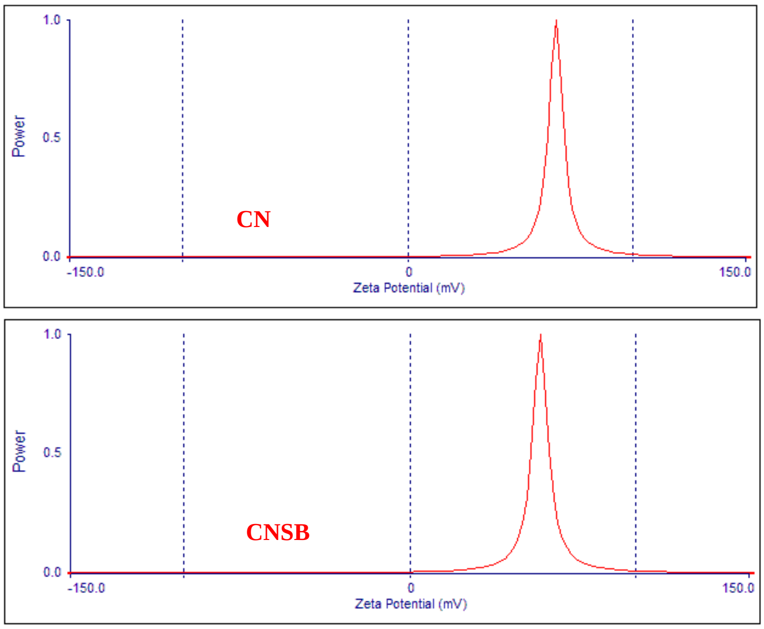

Figure 3. The zeta potential distribution of CN and CNSB

3.2. Characterization of carbon paste electrode

Scanning electron microscopy (SEM) was used to characterize the morphology of the bare carbon paste electrode and carbon paste electrode modified with CNSB. Figure 4 (A) represents the SEM morphology of the prepared electrode. The SEM image of the bare carbon paste electrode showed a microstructure with a discontinuous grain growth with a large unclear crystal structure. The surface structure of the bare carbon paste electrode also shows that the graphite particles are covered by a very thin film of paraffin oil. Figure 4 (B) shows that the surface of the carbon paste electrode modified with CNSB is relatively homogeneous and smother than the bare carbon paste. However, any difference between the surface properties of the modified and unmodified electrode was not clearly visible [37]. In addition, the energy dispersive X-ray (EDX) spectra of the modified carbon paste (Figure 4 C and D) confirmed the presence of nitrogen in the CHNS-CPE.

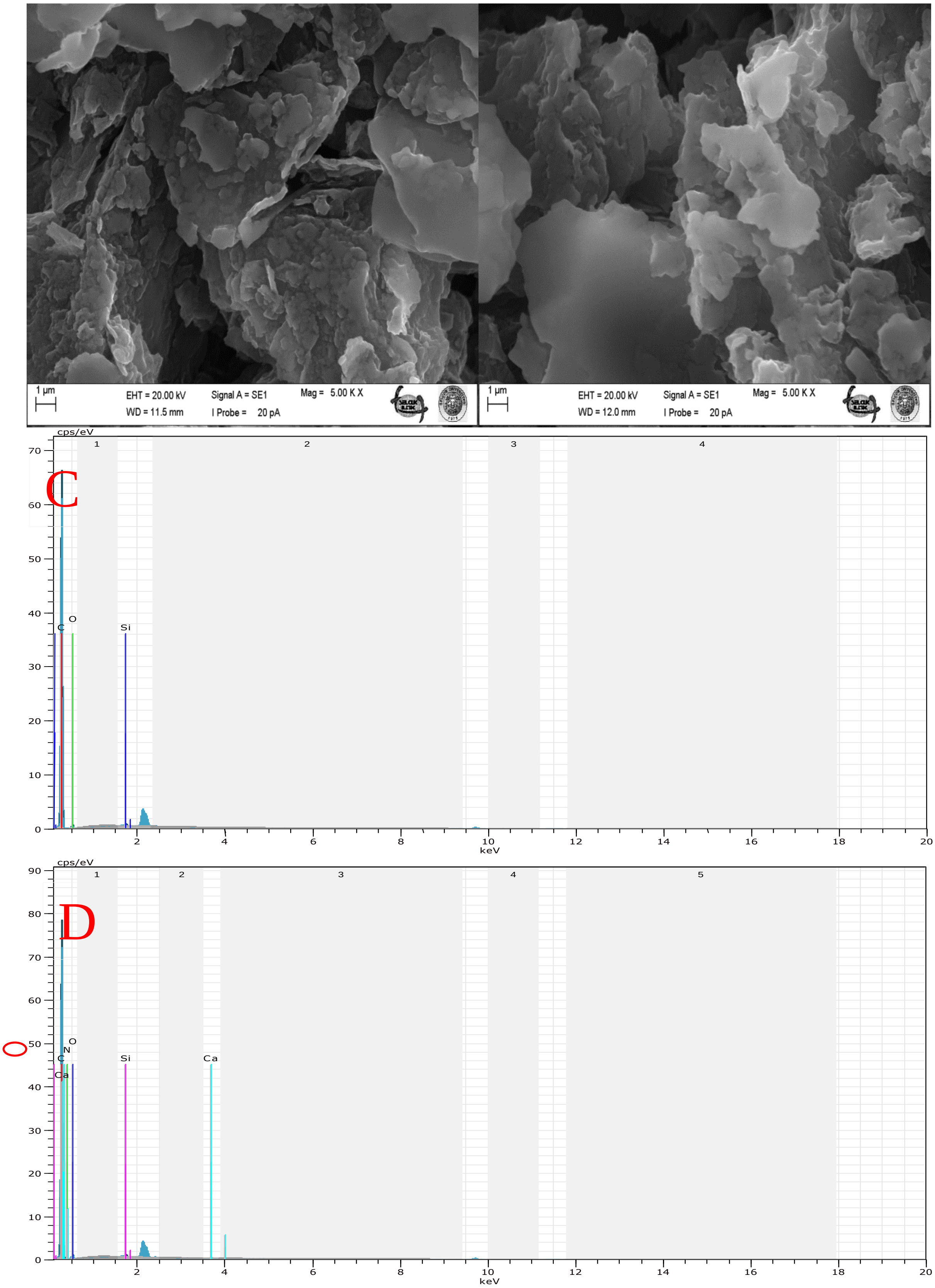

Figure 4. SEM images of bare carbon paste and carbon paste modified with CNSB (A and B). EDX spectra obtained from bare CPE and modified CNSB-CPEwith CNSB structure shown in (C and D). Note the nitrogen peaks coming from CNSB highlighted by red (D).

3.3. Electrochemical behavior of Pb(II) on the surface of modified electrode

The performance of the freshly prepared CNSB modified carbon paste electrode is based on the preconcentration of Pb(II) from aqueous solution on the surface of the modified electrode by forming complexes with the modifier [39].

DPASV was used to study the electrochemical behavior of the bare carbon paste electrode and carbon paste electrode modified with CNSB. The electrochemical behavior of the prepared electrode was examined in a potential range from 0 to -1.2 V (vs. Ag/AgCl) using a potential scan rate of 100 mV s^{-1}. Figure 5 shows the stripping voltammograms for a bare carbon paste electrode and carbon paste electrode modified with CNSB using sodium acetate (NaAc) pH 6.0 in the presence of 1.0×10^{-5} mol L^{-1} Pb(II). Stripping peak of Pb(II) was observed at the CNSB modified carbon paste electrode, whereas no peaks were seen at the bare carbon paste electrode. The results show that the carbon paste electrode modified with CNSB is efficient sensor for the sensitive determination Pb(II) ions.

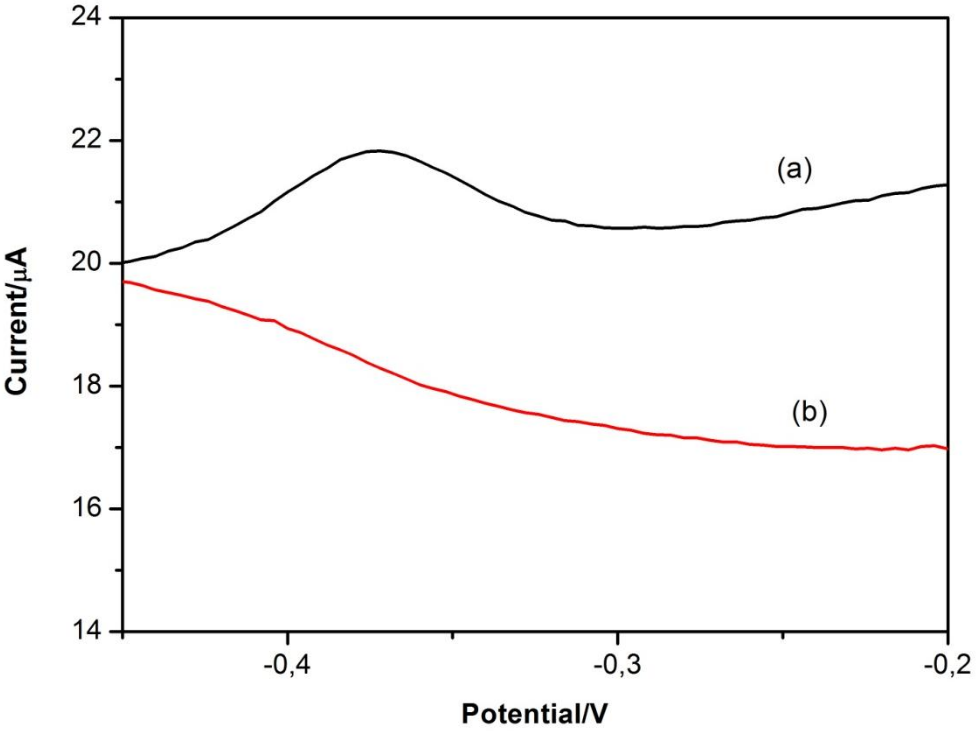

Figure 5. Stripping voltammogram of 1×10^{-5} mol L^{-1} Pb(II) in 0.2 mol L^{-1} acetate buffer at different carbon paste electrodes: (a) CNSB modified carbon paste electrode, (b) bare carbon paste electrode. Conditions: preconcentration time: 600 s; reduction potential: −1.0 V; reduction time: 10 s; scan rate: 100 mVs^{-1}; CNSB/ graphite powder: 7.1%

The electrode process can be explained as follows ("aqueous" or "surface" subscript means compound is in aqueous solution or at the electrode surface) [40]

Preconcentration of Pb(II)

$$Pb^{2+}_{(aqueous)} + CHNS_{(surface)} \rightarrow Pb^{2+}\text{–}CNSB_{(surface)} \quad \text{(open circuit)}$$

Reduction of accumulated Pb(II) in acetate buffer

$$Pb^{2+}\text{–}CNSB_{(surface)} + 2e^{-} \rightarrow Pb^{0}_{(surface)} + CNSB_{(surface)} \quad \text{(at –1.2 V)}$$

Stripping of reduced lead in acetate buffer

$$Pb^{0}_{(surface)} + CNSB_{(surface)} \rightarrow Pb^{2+}_{(aqueous)} + CNSB_{(surface)} + 2e^{-} \quad \text{(scan from–1.2 to + 0 V)}$$

3.3. Optimization of analytical conditions

In order to obtain the optimum experimental conditions, some variables affecting the peak current i.e. supporting electrolyte, pH, the amount of modifier, preconcentration time, reduction potential and time for a 1.0×10^{-5} mol L^{-1} Pb(II) solution were studied.

3.3.1. Effect of pH and supporting electrolyte

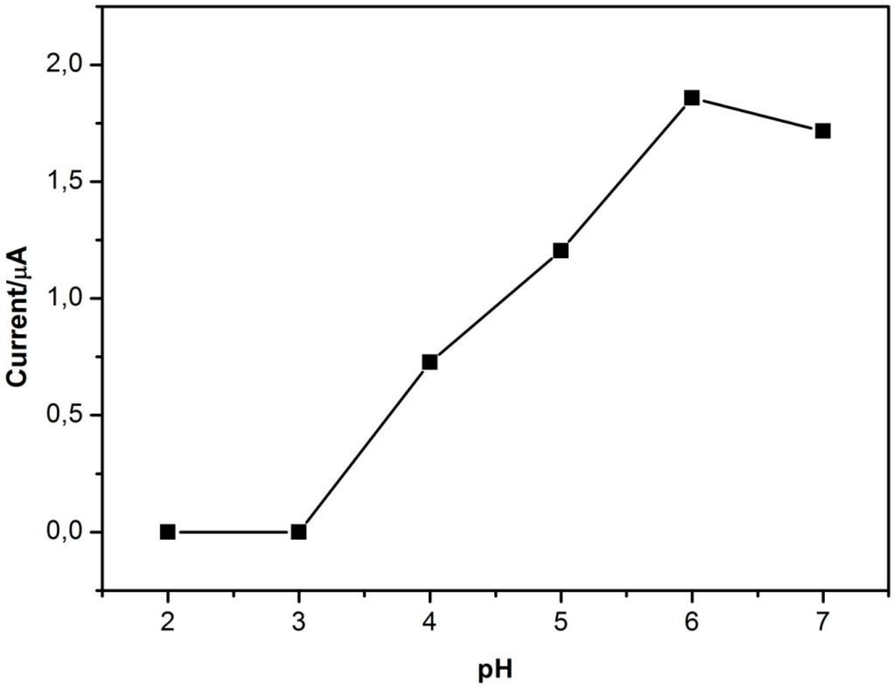

Figure 6. The effect of pH on the DPASV peak current at CNSB-CPE. Preconcentration time:600 s; reduction potential:–1.0V; reduction time:10 sec; Pb(II) concentration: 1.5×10^{-5} mol L^{-1}.

The influence of pH of the preconcentration solutions on the Pb(II) signal was investigated in the range of 2.0-7.0 in the presence of 1.0×10^{-5} mol L^{-1} Pb(II) (Figure 6). The peak increased with the increase of pH from 4 to 6 and decreased from pH 7. At lower pH (pH<4), the modifier loses its ability to complex with Pb(II) and the peak current decreases because the degradation of CNSB took place and it lost its ability to immobilize Pb(II) . Also, Zhang et al.[40] reported that at pH < 2.5, in the presence of Cl^{-}, the species such Pb(II) precipitates in the form of chloride. Furthermore, at higher pHs, the peak current decreased and the peak shape was deformed due to the hydrolysis of Pb(II) in basic solution [32]. The peak current reached a maximum value around pH of 6.0. To achieve maximum sensitivity, the pH 6.0 was used in all subsequent experiments.

The supporting electrolyte can greatly affect voltammetric response of the sensor. The effect of various supporting electrolytes including HCl, $NaNO_3$, KNO_3, NaAc, BR and Na_3PO_4 solutions (each one 0.2 mol L^{-1}) on the stripping peak currents of Pb(II) was investigated at pH 6.0; preconcentration time, 600 s; reduction potential, -1.0V; reduction time, 30 s. The best voltammetric results were obtained in 0.2 mol L^{-1} NaAc solution.

3.3.2. Effect of percentage of modifier

The effect of the amount of CNSB within the carbon paste electrode on the voltammetric response was evaluated by changing mass ratio of CNSB to graphite powder in the carbon paste (Figure 7). The stripping peak current of Pb(II) increases with the increasing of amount of modifier because the concentration of CNSB on the surface of the modified electrode increases correspondingly. However, when the amount of CNSB reaches 5.3% (w/w) in (CNSB/ carbon paste), the peak current reaches its maximum. After this point, any continuing increase in the amount of modifier causes a decrease in the peak current, due to the decrease of the conductivity of the modified electrode [41]. Thus electrode composition of 5.3 % (w/w) CNSB, 73.7 % (w/w) graphite powder and 21% (w/w) paraffin oil was used for further experiments.

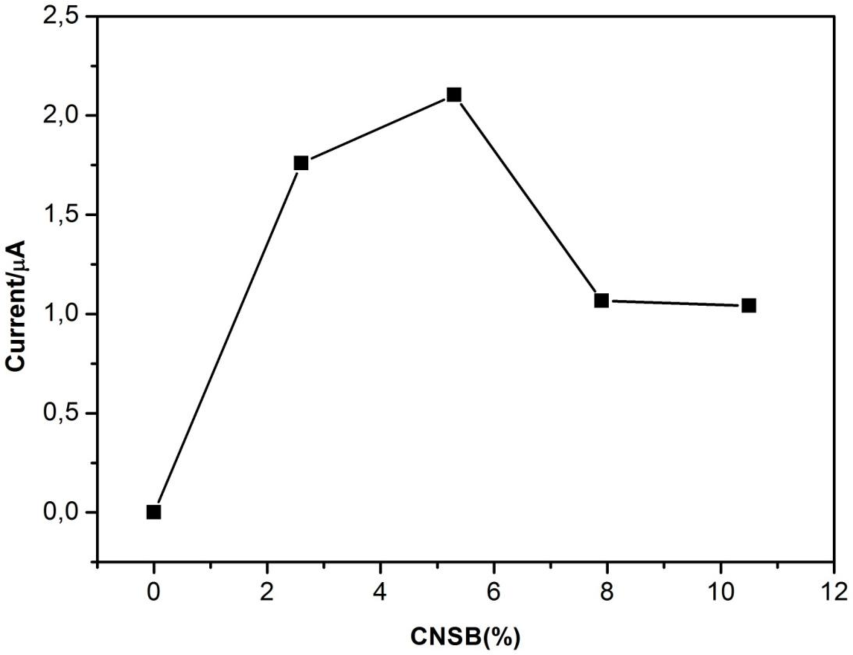

Figure 7. The effect of percentage of modifier on the peak current at CNSB-CPE in 0.20 mol L^{-1} NaAc, pH 6.0. Preconcentration time: 600 s; reduction potential: –1.0V; reduction time: 10 s; Pb(II) concentration: 1.5×10^{-5} mol L^{-1}.

3.3.3. Effect of preconcentration time, reduction potential and time

Preconcentration time can apparently influence the determination of Pb(II). The stripping peak currents were proportional to the preconcentration time up to ten minutes. For longer times observed currents increased, but surface of the modified electrode was completely covered by Pb(II) which resulted in distortions of observed peaks. Taking into account sensitivity, repeatability and efficiency, accumulation time 10 min was used in all following experiments.

The influence of the reduction potential on the peak current of Pb(II) over the range from -1.2 to -0.6 V was also investigated (Figure 8). The negative shift of reduction potential can improve the reduction of the metal ions onto the surface of the modified electrode and enhance the peak currents [42], but other metal ions can interfere at potentials more negative than -1.0 V. The results obtained for the peak current using different reduction potential values showed that at -1.0 V the maximum peak current was obtained. Therefore, in all further experiments a reduction potential of -1.0 V was employed and it was used throughout the following analytical study.

The effect of the reduction time on the peak current was also examined in the range between 5 - 60 s and 10 s was chosen as an optimum. All optimized parameters used to determine Pb(II) with CNSB modified carbon paste electrode are summarized in Table 2.

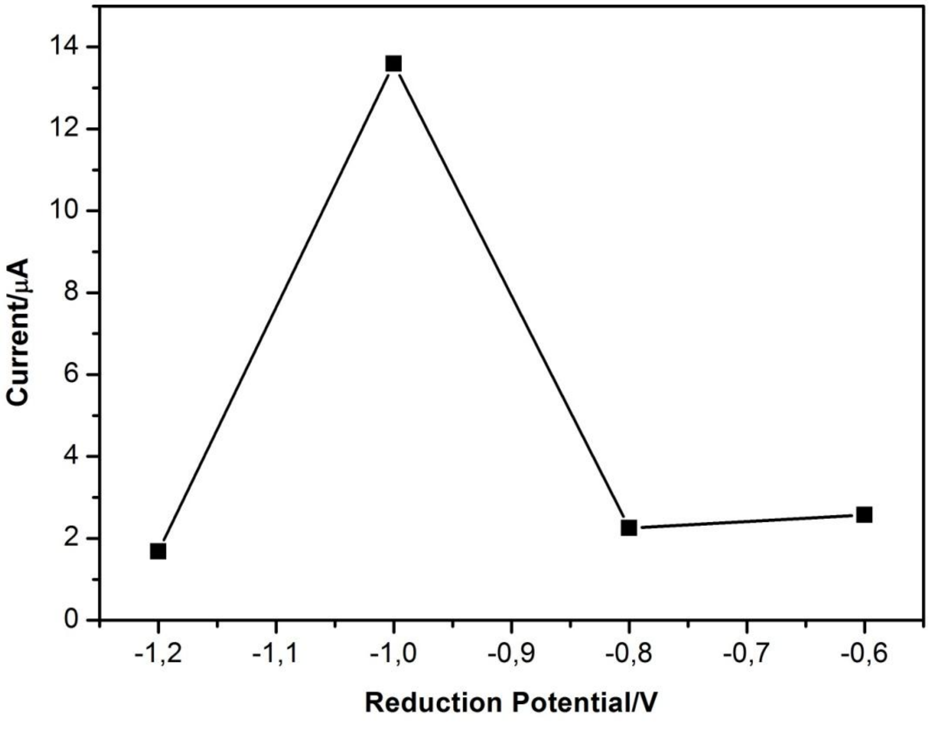

Figure 8. The effect of reduction potential on the peak current of Pb(II) at CNSB-CPE in 0.20 mol L^{-1} NaAc, pH 6.0. Preconcentration time: 600 s; reduction time: 10 s; Pb(II) concentration: 1.5×10^{-5} mol L^{-1}.

Table 2. Optimum parameters for determination of Pb(II) with CNSB modified carbon paste electrode by differential pulse anodic stripping voltammetry

Parameter	Optimised Value
Supporting electrolyte	0.2 mol L^{-1} NaAc (pH 6.00)
pH..	6.0
Preconcentration time	600 sec
Reduction potential	-1.0 V
Reduction time	10 sec
Electrode composition..................	5.3 % CNSB, 73.7 graphite powder, 21% paraffin oil
Scan rate	0.1 Vs^{-1}
Pulse amplitude	0.05 V

3.4. Analytical curves, detection limits and recovery in synthetic samples

The differential pulse anodic stripping voltammograms of a series of concentration of the Pb(II) is presented in Figure 9 under the optimized working conditions resumed in Table 2.

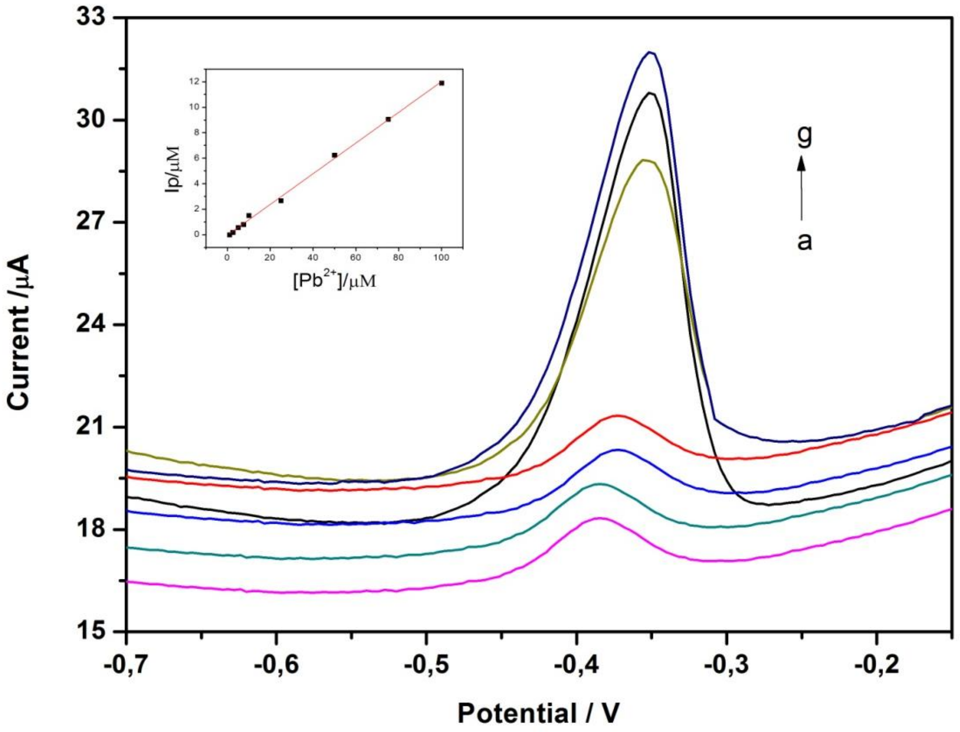

Figure 9. DPSAV curves of different concentration of Pb(II) (a-g; 1, 2.5, 5, 7.5, 10, 25, 50, 75, 100 µM) at CNSB-CPE in 0.20 mol L^{-1} NaAc, pH 6.0. Preconcentration time, 600 s; reduction potential, -1.0V; reduction time, 10 s.

The stripping peak current (Ip) is related to Pb(II) concentration over the range of 1×10^{-6} - 1×10^{-4} mol L^{-1} with correlation equation: Ip(μA) = 0.12052C Pb(II) (mol L^{-1}) - 3.391×10^{-8} . The results are shown in Table 3. The limits of detection (LOD) and quantitation (LOQ) of Pb(II) by the newly developed DPASV method under the optimized conditions were calculated using the equation: k.δ / s , where k=3,3 for LOD and k=10 for LOQ. δ is the standard deviation of blank and s is slope of the calibration curve [43]. The limits of detection and quantitation of Pb(II) ($7{,}24\times10^{-7}$ mol L^{-1} and $2{,}20\times10^{-6}$ mol L^{-1}) indicated the high sensitivity of the described method using new CNSB modified CPE under the optimum conditions.

Table 3. Validation data of calibration graph for removal of Pb(II) at CNSB-CPE in 0.20 mol L^{-1} NaAc, pH 6.0. Preconcentration time, 600 s; reduction potential, -1.0V; reduction time, 10 s.

Number of Points	**9**
Equation	y=a+bx
R^2	0,9977
Intercept	-0,0339
Standard error of intercept	0,09476
Slope	0,1205
Standard error of slope	0,0021

The DPASV method with the modified carbon paste electrode (CNSB-CPE) was applied for the removal of lead from different synthetic samples. The accuracy and validity of the proposed method were also evaluated by performing removal studies. The percentages of removal were determined by comparing the peak area obtained from the standard and from the spiked matrix. Each assay was carried out five times and the average calculated removals ranged between 94.7% and 100.8% . The results are shown in Table 4**.**

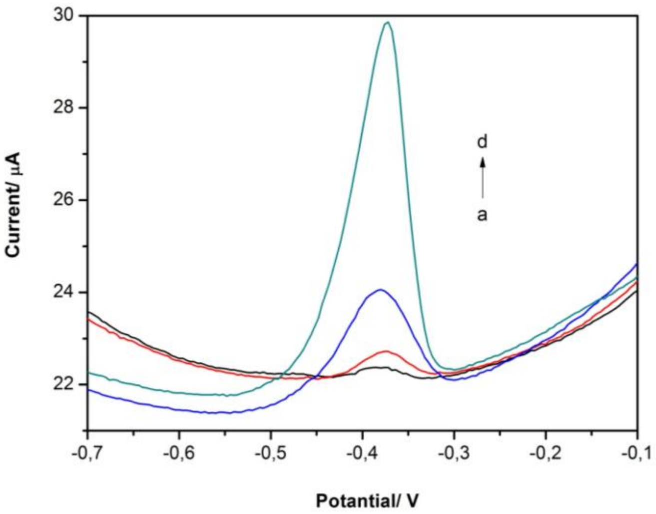

Figure 10. DPSAV curves of synthetic samples (a-d; 1, 2, 4, 8 mg g^{-1} Pb(II)) at CNSB-CPE in 0.20 mol L^{-1} NaAc, pH 6.0. Preconcentration time, 600 s; reduction potential, -1.0V; reduction time, 10s.

Table 4. Results obtained with DPASV method in laboratory-made synthetic samples

SAMPLE	TAKEN (mg g^{-1})	FOUND (mg g^{-1})	REMOVAL(%)
1	1,000	0,947	94,7
2	2,000	1,980	98,8
3	4,000	3,970	99,2
4	8,000	8,070	100,8
		MEAN:	98,4
		SD:	2,6

3.5. Interferences

The interference of Cd(II) and Cu(II) which can compete for free sites on CNSB-CPE were tested under the conditions optimized for the determination of Pb(II). The interference studies were carried out by using different interfering ion/ Pb(II) ratios. The effect of interfering ion on Pb(II) peak current is shown in Table 5. In the presence of high concentrations of Cd(II) and Cu(II) , the peak current of Pb(II) decrease, which is ascribed to the fact that Cd(II) and Cu(II) can compete with Pb(II) for complexing sites at CNSB modified electrode resulting in the decrease of peak current of Pb(II). However, the presence of interfering ions in the concentrations one hundred times smaller than Pb(II) has only little effect on the Pb(II) peak current, causing a decrease smaller than 5.0 % in the peak currents [12].

Table 5. The effect of interfering ion on the Pb(II) peak current

Interfering ion	Interfering ion/ Pb(II)	Relative signal (%)
Cd^{2+}	0.01	97,67
	0.1	75,32
	1.0	40,70
	10.0	7,60
Cu^{2+}	0.01	97,07
	0.1	82,63
	1.0	12,68
	10.0	4,71

3.6. Analysis of lead in waste water

To test the newly developed method, CNSB-CPE was applied to determine Pb(II) in waste water. The concentration of Pb(II) in the water sample was determined by the standard addition method to compensate the matrix effect from the sample. Four measurements were made for each addition. The results obtained (RSD and percentage recovery) are presented in Table 6. Recovery experiments were also carried out in order to evaluate the interference of matrix effects of the water samples on the detection of Pb(II) on CNSB-CPE. As shown in the table, the recoveries and RSD were satisfactory. The recovery percentage obtained was satisfactory thus indicating the suitability of the proposed method for the application in water samples. In addition, to investigate the accuracy of this method, the results obtained by CNSB-CPE were compared with those obtained by ICP. Recovery was between 98.3% and 101.2%.

Table 6. Determination of Pb(II) in waste water using the proposed CNSB-CPE method and comparative method.

	Proposed method			*Comparative method		
Taken ($\mu g\ mL^{-1}$)	**Found ($\mu g\ mL^{-1}$)**	**RSD%**	**Recovery (%)**	**Found ($\mu g\ mL^{-1}$)**	**RSD%**	**Recovery (%)**
1.320	1.305	0.305	99.00	1.287	0.372	97.50
1.637	1.662	0.321	101.16	1.670	0.210	102.02
1.540	1.514	0.360	98.31	1.492	0.337	96.88
1.470	1.482	0.267	100.82	1.489	0.402	101.30

* ICP

F test was applied to determine if there is a significant difference between the precision of DPASV and ICP methods. For comparison, calculated F values [44] were compared with F critic values. Values of F and F_{critic} are shown in Table 7. As can be seen from the table, F values are less than the critical F value (6.39) where $n_1 = 4$ and $n_2 = 4$ at 95% confidence level.

Table 7. Statistical treatment of data obtained for the determination of Pb(II) using proposed DPASV method with CNSB-CPE electrode in samples in comparison with the comparative (ICP) method.

Sample	**(ICP) %**	**DPASV method (CNSB-CPE electrode) %**	**F-test**	**t-test**
	99.4	99.8	0.28	0.40

Tabulated t = 8.61.
Tabulated F = 6.39.

Consequently, no meaningful difference between the precision of these methods in the confidence limit of 95% was observed. Furthermore, t-test was carried out to investigate if there is a difference between the accuracy of the two methods and the t values found were smaller than the theoretical t value (8.61) in the confidence limit of 99.9%. Therefore, there is no meaningful difference between the accuracy of these methods. The method applying the modified electrode does not exhibit significant differences in comparison with the ICP method which reflects the accuracy and precision of this method.

4. CONCLUSION

A simple, fast, reproducible and direct procedure was used for the preparation of a modified carbon paste electrode. Newly synthesized chitosan nanoparticle- Schiff base as the effective modifier material was used to fabricate modified electrode for the determination of Pb(II). Nano-chitosan bound Schiff bases of 2,5- dihydroxybenzaldehyde were then prepared and characterized by FT-IR, elemental analysis, zeta potential and particle size. A novel and efficient carbon paste modified electrode was prepared that enables sensing of Pb(II). The modified electrode showed an excellent selectivity and stability for Pb(II) determinations and for accelerated electron transfer between the electrode and the analyte. It was characterized by SEM and the electrode was successfully used for selective preconcentration and sensitive determination of Pb(II) in both synthetic and real samples. Selectivity and sensitivity can be enhanced by altering the some experimental and instrumental conditions as commonly used for multicomponent samples. The above results indicate that the carbon paste electrode modified with CNSB is a chemical sensor of high reproducibility and sensitivity for determination of Pb(II) in waste water samples.

ACKNOWLEDGEMENT

Financial support for this research from the Selcuk University Scientific Research Project and Charles University in Prague project (project UNCE 2012/44 “Supramolecular Chemistry”) is gratefully acknowledged.

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