

Anodic Stripping Voltammetry Determination of Lead ions using Highly Sensitive Modified Electrodes Based on Multi-walled Carbon Nanotube

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Abstract

Two sensitive linear sweep and square wave anodic stripping voltammetry (LS- and SW-) AdASV methods were optimized for trace determination of Pb⁺² using carbon paste (CP) microelectrodes modified with mesoporous silica (SBA-15); mesoporous carbon (MC); and multi-walled carbon nanotube (MWCNT). Characterization of these modifiers were performed using XRD, TEM and BET. Lead (II) ion showed an anodic peak at -0.4 V in 0.1M HCl, using either bare or modified CP electrodes. A well-defined oxidation peak and high current response were observed using the MWCNT/CP electrode. Under optimal conditions (accumulation potential of -0.6 V for Ag/AgCl, and accumulation time of 15 min), a calibration curve ranging from 1x10⁻⁷ to 1x10⁻⁴ M was obtained for Pb⁺² determination. A limit of detection (LOD) of 3×10⁻⁸ M Pb⁺² was achieved using SW-AdASV at MWCNT/CP electrode. This (LOD) is much lower than that observed in most of the reported electrochemical methods. This method was successfully applied for trace determination of Pb⁺² in various water samples without interferences from various organic and inorganic species. The results were statistically comparable to ICP-AES.

Keywords: Lead (II) ion, Stripping voltammetry, Mesoporous silica, Mesoporous carbon, Multi-walled carbon nanotube

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1. Introduction

Environmental pollution is one of the most serious problems facing our recent world. Trace elements, especially heavy metals, are considered to be one of the main sources of pollution in the environment. Lead is one of the most dangerous environmental pollutants as it has a strong chemical toxic effect even in the presence of low concentrations. Lead is highly toxic to human and animal systems such as nervous, immune, reproductive and gastrointestinal. Lead-containing products such as gasoline, paint, painting inks, lead water pipes, lead glazed pottery and battery casings also contribute to the lead burden. Lead in contaminated soil and dust can find its way into food and water supply. So it is very important to find a very sensitive and selective method for the determination of trace levels of lead in the environment. Different techniques were used for trace lead analysis such as spectroscopic methods, especially graphite furnace atomic adsorption spectroscopy (GF-AAS), and inductively coupled plasma mass spectroscopy (ICP-MS), are used for trace analysis of lead [1-6]. These methods have excellent sensitivities and good selectivities; but they also have various drawbacks such as time consuming and high cost of instrument are required. On other hand electrochemical methods including stripping voltammetric techniques have been recognized as powerful tools for trace analysis. It has shown different advantages such as faster analysis, higher selectivity and sensitivity, low coast, easy operation and speciation analysis.

Different working electrodes are used in voltammetric determination of lead. These include hanging mercury drop electrode (HMDE) [7-12], mercury film electrode [13], gold electrode [14], gold screen printed electrode [15], Bismuth oxide screen printed electrode [16], and renovated silver ring electrode [17]. Adsorptive stripping voltammetry (AdSV) is commonly employed because of its wide linear dynamic range and low detection limit which are achieved as a result of a preconcentration step performed directly in the voltammetric cell, thus decreasing the sampling handling, risk of sample contamination, and multi element analysis. Additional advantages of AdSV over other methods include simplicity of the instrumentation, relative in expensiveness, small size, low electrical power consumption and portability for field usage. Also, the convenience of analyzing various samples without the need of a prior separation. Thus, adsorptive stripping analysis is becoming a widely accepted tool for trace amount measurements of heavy metal ions [18- 20]. The history, theoretical background and application of AdSV are given in references [21-24].

AdSV is widely used for individual and simultaneous determination of heavy metals and there are many reports on the application of AdSV for the determination of lead [25-28].

To increase the sensitivity of AdSV, chemically modified electrodes, which have been developed in the recent years can be used for the electrochemical determination of heavy metals due to various advantages such as ease of manufacture, absence of toxicity, renewability, fast response, high selectivity, low detection limit, stability in various solvents, longer life time and low cost. A number of chemically modified electrodes have been developed for the electrochemical determination of lead; examples include bismuth glassy carbon composite electrode [29]; hydroxylapatite modified carbon ionic liquid electrode [30]; cyclodextrin modified gold electrode [31]; kaolin modified platinum electrode [32]; cyclam-modified graphite felt electrodes [33]; hydroxylapatite modified platinum electrode [34]; 1-(2-pyridylazo)-2-naphthol modified screen printed carbon electrode [35]; calixarene modified screen printed carbon electrode [36]; anthraquinone improved Na-montmorillonite nanoparticles glassy carbon electrode [37]; Langmuir – Blodgett film of p-tert-butylthiacalix-4-arene modified glassy carbon electrode [38]; screen printed carbon electrode modified with bismuth oxide electrode [39]; and glassy carbon electrode modified with mercury [40].

Carbon paste electrode is one of the most popular chemically modified electrodes used with voltammetric techniques. This electrode is prepared by mixing a graphite powder with a suitable binder and a material known as a modifier that improves the selectivity of the prepared electrode. In literature survey some modifiers that has been used with carbon paste electrode for the electrochemical determination of lead, include zeolite [41]; hydroxyapatite [42]; SBA-15 nanostructured silica organofunctionalised with 2-benzothiazolethiol [43]; carbamoylphosphonic acid [44]; diacetyldioxime [45]; 1,4-bis(prop-2'-enyloxy)-9,10-anthraquinone [46]; and Chitosan [47]. Lead (II) ion complexes with sulfur donor atom ligands, have been studied actively during the last few decades due to their significant structural diversity and multiple applications [48]. Carbon nanotubes (CNTs), a new form of elementary carbon, are composed of graphitic sheets rolled into closed concentric cylinders with diameter of nanometers and length of micrometers. They have very interesting physicochemical properties, such as ordered structure with high aspect ratio, ultra-light weight, high mechanical strength, high electrical conductivity, high thermal conductivity, metallic or semi-metallic behavior and high surface area [49].

The facilitation of electron transfer between electroactive species and electrodes offers great promise for fabricating electrochemical sensors and biosensors. The combination of these characteristics make CNTs unique materials with the potential for diverse applications [50]. The present work is aimed to increasing both selectivity and sensitivity in the electrochemical determination of Pb^{+2} . MWCNT was selected for the modification of carbon paste microelectrode and for the determination of Pb^{+2} in different water samples. The obtained results were compared with the data obtained from ICP-AES.

2. Experimental

2.1. Chemicals

All reagents were of commercial grade materials and were used without further purification. Multi-walled carbon nanotube (MWCNT), Tetraethoxysilane ETOS (Shin-Etsu, Tokyo, Japan), Pluronic P123 (triblock copolymer of poly (ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide), $M_w = 5800$, $\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$, Aldrich, USA), Graphite powder, paraffin oil, lead (II) nitrate, Sucrose, HClO_4 , NaCl , H_2SO_4 , CH_3COOH , CH_3COONa , HCl aqueous solution, and HF were obtained from Wako, Japan. Double distilled water was used for the preparation of solutions.

2.2. Synthesis of Mesoporous SiO_2 Template (SBA-15)

SBA-15 was employed as a hard template for synthesizing CMK-5 type carbon. SBA-15 was synthesized according to the literature [51]. Briefly, TEOS (8.5 g), P123 (4 g), H_2O (105 ml) and HCl (20 ml) were mixed under stirring, to form a homogeneous solution. After reaction at $40\text{ }^\circ\text{C}$ for 4 h, the white milky solution was aged at $90\text{ }^\circ\text{C}$ for 48 h. The product was filtered off without washing, dried at $80\text{ }^\circ\text{C}$, and then calcined in air at $550\text{ }^\circ\text{C}$ for 6 h to remove the surfactant, P123.

2.3. Synthesis of MC

Calcined SBA-15 was impregnated with aqueous sucrose containing sulfuric acid and subsequent washing with NaOH or HF . Briefly, SBA-15 (1 g) was added to a solution of sucrose (1.25 g) and H_2SO_4 (0.14 g) in H_2O (5 ml). The mixture was heated to 373 K for 6 h, and then to 433 K for a further 6 h, during which the sample turned dark brown-black.

The silica sample contained partially polymerized and carbonized sucrose. Sucrose (0.8 g) and H_2SO_4 (0.09 g) in H_2O (5 ml) were added, and the solution was treated again at 373 and 433 K using the same procedure [52]. Carbonization was completed by pyrolysis at 1173 K under vacuum. The resulting carbon-silica composite was washed with HF (5 wt.%) at room temperature to remove the silica template. The template-free carbon product was collected by filtration, washed with ethanol, and dried at 393 K.

2.4. Preparation of CP Electrode

CP was prepared by thoroughly mixing graphite powder (5 g) with paraffin oil (1.8 ml) using a mortar and pestle. The CP was packed into a hole in the electrode body, and the electrode surface was smothered with clean paper until shiny. The CP electrode was immersed in a cell containing supporting electrolyte, and several sweeps were applied to obtain a low background current [53].

2.5. Modification of CP Electrodes with SBA-15, MC and MWCNT

Modified CP electrodes were prepared by mixing fine graphite powder with MC or MWCNT (~4:1 w/w) in a carnelian mortar, with sufficient paraffin oil to give a homogenous CP. This mixture was pressed into the end cavity of a working electrode (3 mm diameter). The pressed CP paste surface was polished on smooth paper, and thoroughly rinsed with distilled water [54].

2.6. Physical Measurements

X-ray diffraction (XRD) patterns were recorded on an Ultima IV diffractometer (Rigaku, Tokyo, Japan) at 30 kV and 20 mA, with CuK_α radiation ($\lambda = 1.5406 \text{ \AA}$). Transmission electron microscopy (TEM) images were recorded using a JEM-2100F microscope (JEOL, Tokyo, Japan) at 200 kV. N_2 sorption isotherms were recorded using a TriStar II 3020 adsorption analyzer (Micromeritics, Norcross, USA), and surface areas were determined from the adsorption branch using the Brunauer–Emmett–Teller (BET) method; samples were degassed at 150 °C for 2 h under vacuum prior to measurement.

2.7. Electrochemical Measurements

Linear sweep voltammetry (LSV) and square wave voltammetry (SWV) were performed using a voltammetric analyzer (CV-50W, Bioanalytical Systems Inc. (BAS), West Lafayette (Lab. 1), controlled by a general-purpose electrochemical systems data processing program (GPES version 4.9, Eco Chemie, Metrohm Autolab), and an electrochemical test system (1260 A, Lab. 2, Solarton, UK). A three-electrode electrochemical cell was used. Bare or modified CP electrodes were used as working electrodes, Ag/AgCl/KCl_s as the reference electrode, and Pt wire as the counter electrode. The pH values were measured using a pH meter (TOA-DKK, Takadanobaba, Shinjuku-ku, Tokyo, Japan) with a combined glass electrode. Deionized water was used throughout the experiments.

2.8. Procedure

The general procedure adopted for obtaining adsorptive stripping voltammograms was as follows: The supporting electrolyte solution (10 ml 0.1M HCl) was transferred to the cell. An accumulation potential (-0.6 V vs. Ag/AgCl) was applied to MWCNT/CP electrode while the solution was stirred for 15 min and then the stirrer was switched off, and after 10 sec had elapsed to allow the solution to become quiescent, the potential was scanned in a positive direction from - 0.6 to 0.7 V using linear sweep and square wave adsorptive stripping Voltammetry. After background stripping voltammograms had been obtained, an aliquot of Pb⁺² standard was introduced into the cell, and following the above described procedure, the voltammogram was obtained. All measurements were carried out at room temperature.

3. Results and Discussions

3.1 Characterization of the SBA-15, MC and MWCNT

The XRD pattern of SBA-15 in Fig. 1 shows the characteristic broad peak of amorphous SiO₂ at ~23° 2θ. TEM image indicates that the template possess an ordered mesoporous structure, with a pore diameter of ~8 nm, as shown in Fig. 1. The BET surface area of SBA-15 calculated from the N₂ adsorption isotherm is 670 m²/g.

The crystal phase of the ordered MC was analyzed by XRD, as shown in Fig. 1. The characteristic peaks at 22.9 and 43.1° 2θ corresponded to the (002) and (100) reflections of MC, respectively. The broad diffraction peaks indicate that MC is amorphous, and has a small size [55]. Small size and amorphous state of electrode materials provides many superficial electroactive species to participate in faradic redox reaction. TEM image indicates that the MC morphology consists of rows of well-ordered carbon walls (width ~ 10 nm), accompanied by small carbon nanoparticles (Fig. 1). The well-ordered mesoporous structure provides a large MC surface area, and this favors diffusion of the redox couple in the electrolyte. The BET surface area of MC is 1421 m^2/g .

The crystal phase of the MWCNT was analyzed by XRD, as shown in Fig. 1. The characteristic peaks at 26.5 and 44.5° 2θ corresponded to the crystal structure of carbon nanotube. The sharp profile indicates that MWCNT was crystalline, and of small size. TEM image indicates that the MWCNT possess a nested structure, with no evidence of major in-plane structural changes (Fig. 1). The only breaks that occurred at bent corners, where in-plane defects occurred. Such defects can be caused by compressional stress along the elongated direction. The BET surface area of the MWCNT is 261 m^2/g .

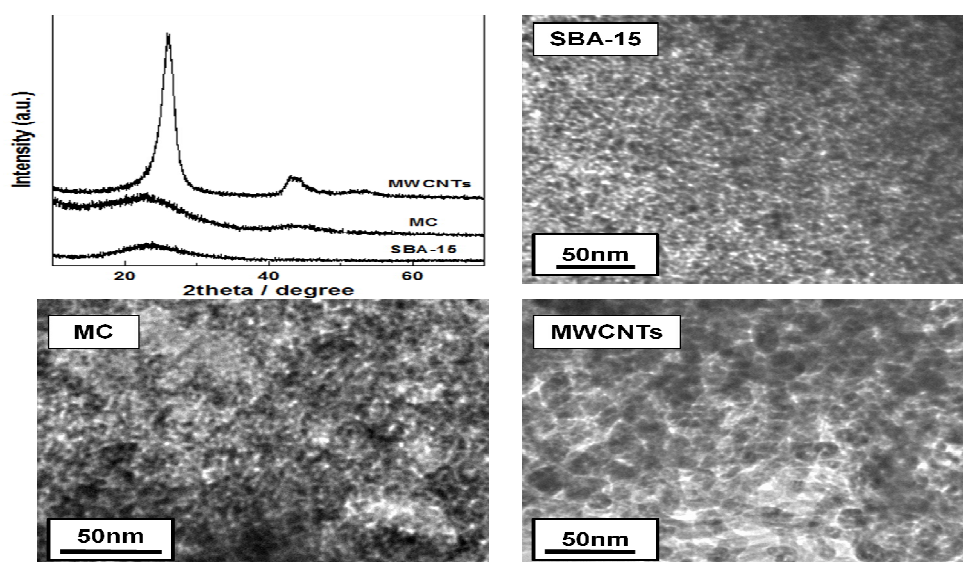


Fig. 1: XRD patterns and TEM images of SBA-15 after calcination at 550°C , MC after heating at 900°C under vacuum, and MWCNT.

3.2. Stripping Voltammetric Methods

Linear sweep and square-wave voltammograms of Pb^{+2} showed a single irreversible anodic peak at -0.4V using either bare or modified electrodes. The optimum operational conditions for analytical determination of Pb^{+2} using (LS-AdASV, and SW-AdASV) were obtained by studying the effect of pH of the medium, accumulations parameters (potential E_{acc} and time t_{acc}) and instrumental parameters (scan rate ν and pulse-height a , scan increment ΔE_s and frequency f) on the voltammetric peak current (i_p) magnitude.

3.2.1. Effect of Type of Working Electrode.

Fig. 2 shows the square wave voltammograms for Pb^{+2} using (a) a bare CP; (b) SBA15/CP; (c) MC/CP; and (d) MWCNT/CP electrodes. It is clear that the anodic i_p for Pb^{+2} using modified electrodes (MEs) are much higher than the i_p of Pb^{+2} for a bare CP electrode. This enhancement in the oxidation i_p is due to increased Pb^{+2} concentration on the electrodes surfaces, by the adsorption of Pb^{+2} according to Scheme 1. The current increases as the adsorption of Pb^{+2} on MEs surface increases. The trend of current intensity increment, for the different MEs is as follows; SBA15 < MC < MWCNT. The best and sharpest peak morphology was obtained using MWCNT/CP electrode, which was chosen for the rest of the analytical study.

$(\text{Pb}^{2+})_{\text{solution}} + (\text{CPME})_{\text{surface}} = (\text{Pb}^{2+} - \text{CPME})_{\text{adsorption}}$

$(\text{Pb}^{2+} - \text{CPME})_{\text{adsorption}} + 2e^- = (\text{Pb} - \text{CPME})_{\text{adsorption}}$,

$(\text{Pb} - \text{CPME})_{\text{adsorption}} = (\text{Pb}^{2+})_{\text{solution}} + (\text{CPME})_{\text{surface}} + 2e^-$

Scheme 1.

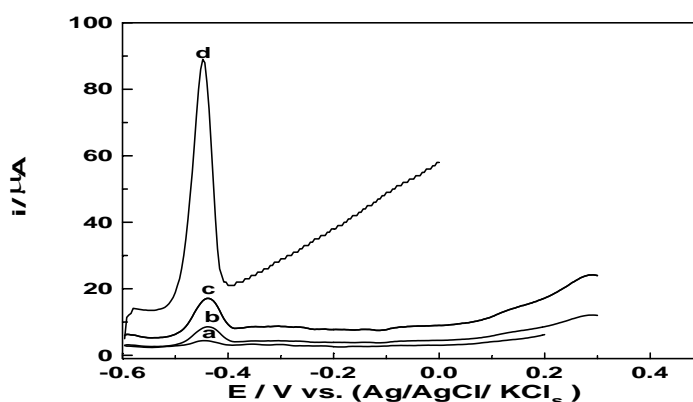


Fig. 2: Representative SW-AdAS voltammograms for Pb^{+2} using (a) a bare CP, (b) SBA15/CP, (c) MC/CP, and (d) MWCNT/CP electrodes, in 0.1 M HCl.

3.2.2. Effect of pH and Supporting Electrolyte

The effect of pH on the electrochemical behavior of Pb^{+2} using MWCNT/CP electrode was studied using (LS- and SW-) AdAS techniques in the pH range of 2.0 to 7.0. The oxidation peak of Pb^{+2} showed high i_p at pH 2.0 B-R buffer. 0.1 M of different supporting electrolytes HClO_4 , NaCl , H_2SO_4 and HCl , were examined. The best oxidation peaks were obtained using HClO_4 and HCl solutions. The highest i_p and the best peak morphology was observed using 0.1 M HCl solution. Hence for subsequent 0.1 M HCl solution was used as the supporting electrolyte.

3.2.3. Linear-Sweep Voltammetric Studies

Effect of E_{acc} on the i_p magnitude was studied over the potential range of (−0.5 to −0.8 V) using 1×10^{-5} M Pb^{+2} solutions, following its preconcentration onto the modified electrode for 3min. A much developed i_p magnitude was achieved at a potential of −0.6 V, and this was used for the rest of the analytical study. The dependence of the LS-AdASV i_p of 1×10^{-5} M and 3×10^{-6} M Pb^{+2} , in 0.1M HCl , on the t_{acc} at $E_{\text{acc}} = -0.6$ V using MWCNT/CP electrode was studied using different times ranging from 0 to 20 min. For 1×10^{-5} M bulk Pb^{+2} , the response was linear up to 15 min, and then leveled off. The later behavior may be attributed to the complete coverage of the MWCNT/CP electrode surface with adsorbed analyte species until a maximum level and after that some of the outer adsorbed ions with a weak adsorption to the electrode leave the surface until an equilibrium is reached. While for 3×10^{-6} M bulk Pb^{+2} , as the t_{acc} was increased, linearity was prevailed over the tested accumulation time. Thus, the t_{acc} of choice will be dictated by the sensitivity needed. Effect of scan rate ν (10 – 100 mVs^{-1}) was also studied and an optimal scan rate of 100 mV s^{-1} for a well developed i_p was obtained. The influence of the rest time was also studied and an optimal time period of 10 s was obtained. Accordingly, the optimum operational conditions were: 0.1M HCl as a supporting electrolyte, $E_{\text{acc}} = -0.6$ V, $t_{\text{acc}} \leq 15$ min, $\nu = 100 \text{ mVs}^{-1}$, and rest time = 10 s.

A linear calibration graph (fig.3) was obtained over the concentration range 3×10^{-7} to 1×10^{-5} M Pb^{+2} , with a corresponding regression equation: $i_p (\mu\text{A}) = 24.9927 C (\mu\text{M}) + -17.2699$ ($r = 0.995$ and $n = 12$). Limits of quantification (LOQ) and detection (LOD) of 3×10^{-7} M and 9×10^{-8} M Pb^{+2} respectively, were achieved [56] by means of the described LS-AdASV method.

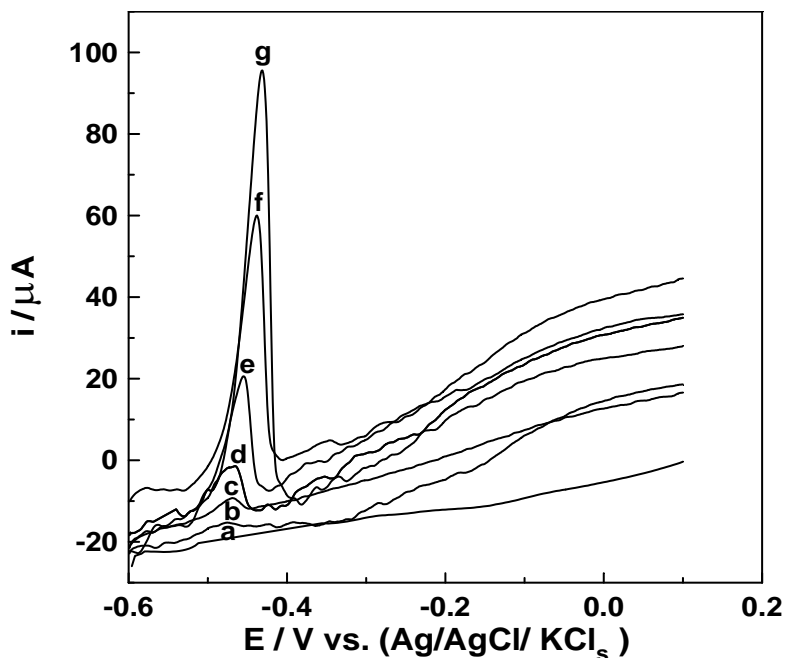


Fig. 3: LS-AdAS voltammograms for different Pb^{+2} concentrations at the optimum conditions (0.1 M HCl , $E_{\text{acc}} = -0.6 \text{ V}$, $t_{\text{acc}} = 15 \text{ min}$, $\nu = 100 \text{ mVs}^{-1}$, and rest time = 10 s) onto MWCNT/CP electrode: (a) Background, (b) $3 \times 10^{-7} \text{ M}$, (c) $1 \times 10^{-6} \text{ M}$, (d) $1.2 \times 10^{-6} \text{ M}$, (e) $2 \times 10^{-6} \text{ M}$, (f) $3.5 \times 10^{-6} \text{ M}$, (g) $4 \times 10^{-6} \text{ M}$.

3.2.4. Square Wave Voltammetric Studies.

3.2.4.1. Effect of Square Wave Instrumental Parameters

The effect of different square wave voltammetric parameters were studied on the i_p using $1 \times 10^{-5} \text{ M Pb}^{+2}$. This involved different square wave frequency (f) with value ranging from 10 to 120 Hz. By increasing the frequency, the i_p increased. An optimal frequency of 120 Hz was obtained and thus selected for further investigations. The effect of square wave pulse amplitude (a) on the i_p using $1 \times 10^{-5} \text{ M Pb}^{+2}$ with $f = 120 \text{ Hz}$ was also studied. The i_p increased linearly within the range of 5.0 to 25 mV. Therefore, 25 mV was taken as the optimum pulse amplitude height. Step potential effect was also studied using the following conditions: $1 \times 10^{-5} \text{ M Pb}^{+2}$; $f = 120 \text{ Hz}$; and $a = 25 \text{ mV}$. The peak height increased linearly, up to 3 mV, with increasing step potential. No pronounced increase in peak height was observed after 3 mV. Hence, a step potential of 3 mV was selected as optimum value for further studies.

3.2.4.2. Effect of E_{acc}

The effect of E_{acc} on the i_p height was studied using a potential range of -0.5 V to -0.8 V under the following conditions 5×10^{-6} M Pb^{+2} ; 0.1M HCl; $f = 120$ Hz; $a = 25$ mV; 3 mV step potential; and $t_{acc} = 2$ min onto MWCNT/CP electrode. As shown from Fig.6, by increasing the E_{acc} to more negative values, the i_p increased to reach a maximum value at -6.0 V after which it decreased. So, -6.0 V was selected as an accumulation potential for further studies.

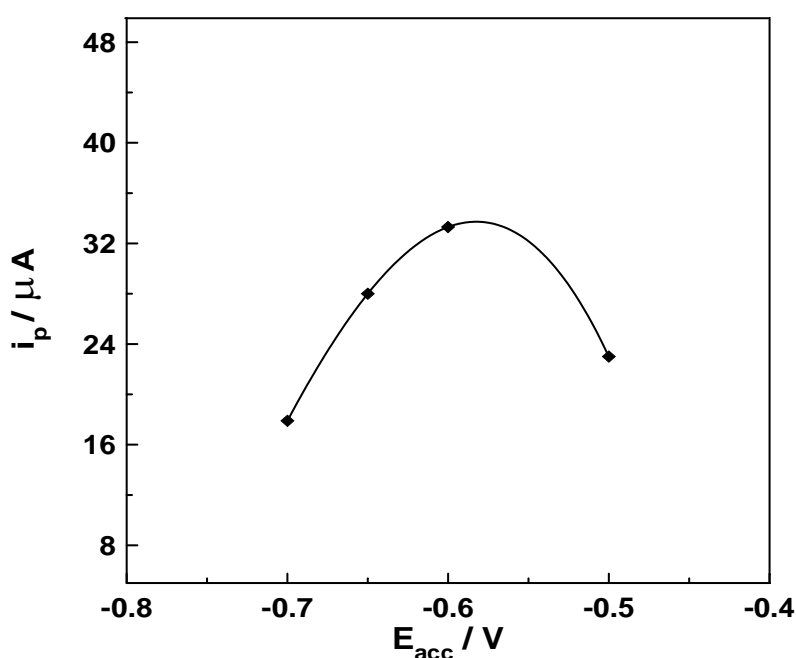


Fig. 4: Plot of E_{acc} with i_p height for 5×10^{-6} M Pb^{+2} using SW-AdASV under the following conditions; 0.1 M HCl; $f = 120$ Hz; $a = 25$ mV; 3 mV step potential; and $t_{acc} = 2$ min onto MWCNT/CP electrode.

3.2.4.3. Effect of t_{acc}

The effect of t_{acc} (0 to 20 min) on the i_p was studied using 3×10^{-6} M and 1×10^{-5} M Pb^{+2} ; using $E_{acc} = -0.6$ V; 0.1M HCl and onto the MWCNT/CP electrode (Fig. 5). For 1×10^{-5} M bulk Pb^{+2} , the response was linear up to 15 min, and then leveled off.

The later behavior may be attributed to the complete coverage of the MWCNT/CP electrode surface with the analyte species until a maximum adsorbed amount is reached, and after that some of the outer adsorbed ions, with a weak adsorption to the electrode, leave the surface until an equilibrium is reached. While for 3×10^{-6} M bulk Pb^{+2} , as the t_{acc} was increased, linearity prevailed over the tested preconcentration time. Thus, the t_{acc} of choice will be dictated by the sensitivity needed. In the present analytical investigations, t_{acc} of 15 min was used for further studies.

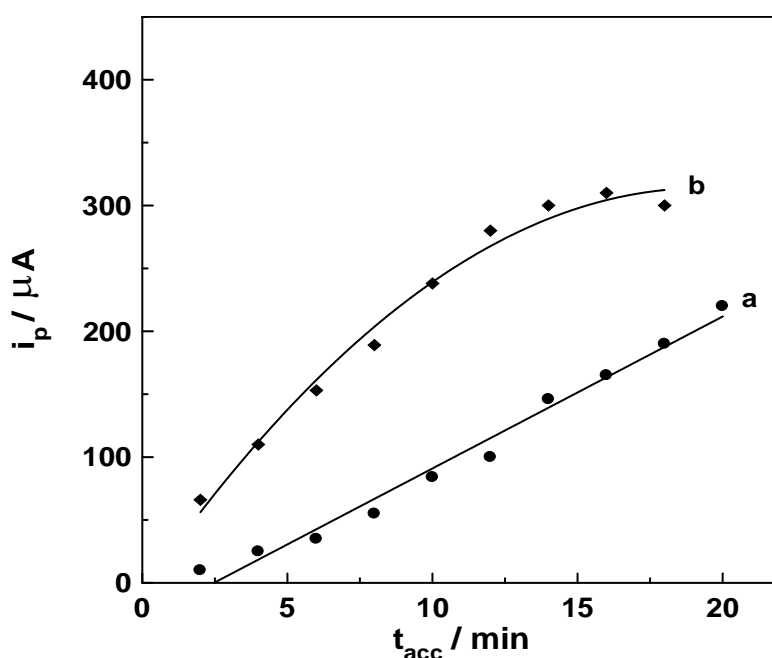


Fig. 5: Effect of accumulation time (t_{acc}) on SW-AdASV i_p height of (a) 3×10^{-6} , (b) 1×10^{-5} M Pb^{+2} under the following conditions; **0.1 M HCl; $f = 120$ Hz; $a = 25$ mV; 3 mV step potential; and $E_{\text{acc}} = -0.6$ V at MWCNT/CP electrode.**

3.2.4.4. Calibration Curve and Detection Limit

The effect of concentration on the i_p of Pb^{+2} was examined at the optimum conditions obtained. The resulting calibration curve showed a linear range from 1×10^{-7} to 1×10^{-4} M (Fig. 6) with a correlation coefficient of 0.999 and a relative standard deviation (RSD) of 1.83×10^{-5} .

The lower detection limit for Pb^{+2} was calculated based on three signal to noise ratio to obtain 3×10^{-8} M [56]. The obtained value for lower detection limit in this method was compared with the values from the different electrochemical methods sited in literature and the data is given in Table 1.

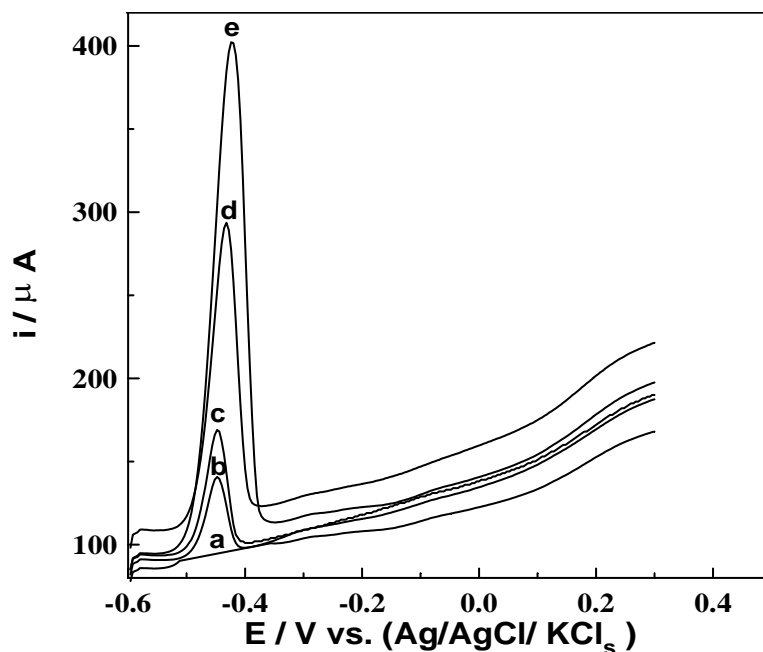


Fig. 6: SW-AdAS voltammograms for different Pb^{+2} concentrations at the optimum conditions (0.1 M HCl, $E_{\text{acc}} = -0.6$ V, $t_{\text{acc}} = 15$ min, $a = 25$ mV, $f = 120$ Hz and $\Delta E_s = 10$ mV) on **MWCNT/CP** electrode: (a) Background, (b) 2×10^{-7} M, (c) 5×10^{-7} M, (d) 1.5×10^{-6} M, and (e) 2×10^{-6} M.

Table 1: Detection limits (LOD) of Pb^{+2} using the Proposed Method and the Methods from Literature

Technique	LOD	Reference
Square wave voltammetry	3.0×10^{-8} M	The present work
Differential pulse stripping voltammetry	8.0×10^{-9} M	[27]
Square wave voltammetry	7.7×10^{-9} M	[31]
Differential pulse stripping voltammetry	4.0×10^{-8} M	[32]
Differential pulse stripping voltammetry	8.0×10^{-7} g/L	[37]

3.3. Methods Validation

3.3.1. Reproducibility

To examine the reproducibility [57], of the prepared electrode under investigation the obtained i_p value for 5×10^{-6} M Pb^{+2} using the optimum conditions mentioned above, five successive measurements were studied. An RSD of 3.65% was obtained, and this value indicates that this method gives a good reproducibility for the obtained results.

3.3.2. Robustness

The robustness [57] of the described LS-AdASV and SW-AdASV methods were examined by studying the effect of variation of some of the operational conditions such as pH (1 to 2); E_{acc} (-0.55 to -0.65 V); and t_{acc} (13 to 15min) on mean percentage recovery (% R) and relative standard deviation (% RSD) of different concentrations (5×10^{-7} – 5×10^{-6} M) of Pb^{+2} . The obtained results (98.55 ± 0.17 to 101.02 ± 0.08) were insignificantly affected within the studied range of variation of the operational conditions, and consequently the described methods can be considered robust.

3.3.3. Effect of Interferences

The effect of some metal ions, such as Fe^{+3} , Ca^{+2} , Ni^{+2} , Cu^{+2} , Cd^{+2} and Zn^{+2} regarded as the most interfering ions in the electrochemical determination Pb^{+2} was examined. Different concentrations (1×10^{-6} - 1×10^{-5} M) of Fe^{+3} , Ca^{+2} , Ni^{+2} and Cu^{+2} were added to 5×10^{-6} M of Pb^{+2} . No effect on the i_p of 5×10^{-6} M Pb^{+2} was observed; and no signals for these ions were observed either. While 1×10^{-4} M Cu^{+2} showed a small signal around -0.15 V, it however had no effect on i_p of Pb^{+2} . Addition of different concentrations of Cd^{+2} ranging from 1×10^{-6} to 1×10^{-4} M showed no effect on the i_p of 5×10^{-6} M Pb^{+2} . However 5×10^{-4} M of Cd^{+2} decreased the i_p of 5×10^{-6} M Pb^{+2} by 0.32 %. Addition of Zn^{+2} within a concentration range of 1×10^{-6} to 1×10^{-4} M showed no effect on the i_p of 5×10^{-6} M Pb^{+2} .

3.3.4. Analytical Applications

In order to test the validity of the prepared MWCNT/CP electrode, this proposed method was applied for the electrochemical determination of Pb^{+2} in different water samples. The samples were prepared by addition of different concentrations of Pb^{+2} from a standard to drinking water samples. Using the optimum conditions and calibration curve (analytical equation: $y = 2.829 \times 10^{-5} C + 1.847$) the obtained results are presented in Table 2. The recoveries ranges between 98.67-106.11%. The obtained results were compared with the data obtained from the ICP-AES (Table 2). From Table 2, the obtained results from the prepared modified electrode compared favorably with those obtained from ICP-AES.

Table 2: Comparison of Result on Pb^{+2} Analysis from Proposed Method in Water Samples and a Standard ICP-AES.

Sample no.	Spiked Pb^{+2} [M]	Measured values [M]	Recovery (%)	Measured values from ICP-AES[M]
1	1×10^{-6}	1.03×10^{-6}	102.8	1.10×10^{-6}
2	3×10^{-6}	2.96×10^{-6}	98.67	2.75×10^{-6}
3	5×10^{-6}	5.19×10^{-6}	103.8	5.02×10^{-6}
4	7×10^{-6}	7.19×10^{-6}	102.74	7.24×10^{-6}
5	9×10^{-6}	9.55×10^{-6}	106.11	9.06×10^{-6}
6	1×10^{-5}	1.06×10^{-5}	105.8	1.014×10^{-5}
7	5×10^{-5}	5.22×10^{-5}	104.4	5.024×10^{-5}

4. Conclusion

The electrooxidation of Pb^{+2} was studied using bare and modified CP electrodes. Carbon paste electrodes, modified with SBA-15, MC and MWCNT was constructed and used as electro analytical sensors for Pb^{+2} determinations. Optimization the experimental conditions for the determination of Pb^{+2} were obtained using linear-sweep and square wave voltammetry at the surface of the constructed MWCNT/CP electrode. Limit of detection of 3×10^{-8} M Pb^{+2} was achieved using SW-AdASV at MWCNT/CP electrode. This method was applied for the electrochemical determination of Pb^{+2} in different water samples and compared favorably with a standard ICP-AES.

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