

Adsorptive Cathodic Stripping Voltammetry of Lead in Water Samples using 2, 2'-Bipyridine or 1,10-phenanthroline and Nitrite Ions

*Masar Hadi Jawad¹, Azizan Aziz³, Sulaiman Ab Ghani²

Abstract - A differential pulse adsorptive cathodic stripping voltammetric (DPAdCSV) method for the determination of lead levels in water sample by using pairs of ligands (complexing agents) / – nitrite and 1,10 phenanthroline - nitrite were investigated. Variables affecting the response such as pH, supporting electrolyte, deposition potential, deposition time, stirring speed, drop size, sweep rate, pulse amplitude and ligand concentration were studied. Under optimized conditions the relationship between peak current and lead concentration with 2,2'-bipyridine - nitrite and 1,10 phenanthroline - nitrite were linear in the range of 10 - 500 ng mL⁻¹ and 7-500 ng mL⁻¹ with limit of detection of 0.48 ng mL⁻¹ and 0.36 ng mL⁻¹ respectively . The relative standard deviations (RSD) for 9 determinations of 25 ng mL⁻¹ Pb (II) using 2,2'-bipyridine - nitrite and 1,10 phenanthroline - nitrite were 1.74% and 1.84%, respectively. The values obtained for the proposed technique correlated well with those of atomic absorption spectrometry (AAS) as the standard method with correlation coefficient (R²) of 0.9991 and 0.9986.

The method was applied for the determination of lead in sea, lake and tap waters. The interferences of other metals and major salts present were negligible except iron (III) and Aluminum (III).

Keywords - Adsorptive cathodic stripping voltammetry; Differential pulse; Lead; Water samples

I. INTRODUCTION

Heavy metals pollution in the environmental waters, of which one of them is lead (Pb), has been recognized as the most consequential environmental health problem in the world [1]. The lead (II) ion (Pb²⁺) enters environmental waters from mostly industrial activities such as in the production of alloys, lead smelters, anticorrosion coating, batteries and pigments [2]. Human tends to accumulate lead ions in their bodies from intake of food and water. The strong chemical toxicity of lead ions on the biological functions of the living system stems from the inhibition of a select group of enzymes [3]. Hence, monitoring of lead levels in water samples become absolutely necessary in order to maintain healthy living. The U.S. Environmental Protection Agency (EPA) and the World Health Organization (WHO) have set the maximum permissible level of Pb²⁺ in sea water and drinking water are 10 and 50 µg L⁻¹, respectively [6].

The development of anodic stripping voltammetry (ASV) and adsorptive cathodic stripping voltammetry (AdCSV) for the determination of many metal ions have introduced unlimited advantages over the

¹Iraqi Geological Survey, Ministry of Industry and Minerals, Baghdad, Iraq.

²Pusat Pengajian Sains Kimia, Universiti Sains Malaysia, 11800 USM Pulau Pinang, Malaysia.

³Pusat Pengajian Kejuruteraan Bahan dan Sumber Mineral, Kampus Kejuruteraan, Universiti Sains Malaysia, 14300 Nibong Tebal, Malaysia.

✉ Masar Hadi Jawad
*mhjm77@yahoo.com

conventional state of the arts spectroscopic methods. These include fast analysis, high selectivity and sensitivity, low instrumentation cost, good performance in saline matrices sample, capable of analyzing mixtures simultaneously and also useful for speciation studies [7].

Several complexing agents have been studied for the adsorption of lead complexes on hanging mercury drop electrode (HMDE) in AdCSV. These include xylenol Orange [8] 4, 5-dihydroxy-3-(p-sulfophenylazo) 2, 7-naphthalene disulfonic acid, trisodium Salt (SPADNS) [9], calcein-blue (CB)(8-[N,N-bis(carboxyl-methyl)aminomethyl]-4 methylumbelliferone) [10], pyrogallol red (PGR) [11], Morin [12] and 2-Acetylpyridine salicyloylhydrazone (2-APSH) [13]. The use of ligands pairing, one of which is nitrite, for the voltammetric such as 2,2'-bipyridine and nitrite determination of Co^{2+} has also been reported [14].

II. MATERIALS AND METHODS

2.1 Chemicals

2,2'-bipyridine (bpy), 1, 10-phenanthroline (phen), Sodium hydroxide, Sodium nitrite, Maleic acid (99.5%), Succinic acid (99.5%), Sodium acetate were obtained from Fluka Chemicals, Switzerland. Formic acid (95%), Potassium hydrogen phthalate (KHP) was obtained from Sigma Chemicals, USA. The 3, 3-Dimethylglutaric acid was purchased from Aldrich Chemicals, Switzerland. Acetic acid (99.5%) was obtained from R & M England.

2.2 Apparatus

Voltammetric measurements were performed by using a 797 VA-Trace Analyzer from Metrohm, Switzerland. The three electrodes system electrochemical cell was used comprising a HMDE working electrode, a double junction Ag/AgCl (3 M KCl) and Pt wire auxiliary electrode. The mercury was

triple-distilled quality. Drop size of the HMDE for bpy and phen were 9 a.u. and 6 a.u., respectively. All the potentials were measured against reference electrode. A Teflon stirrer bar was immersed in solutions in the voltammetric cell for stirring. All experiments were carried out at room temperature with solutions initially deoxygenated with oxygen free nitrogen (OFN) for 5 min prior to each experiment. The pH measurements were carried out with pH/ion meter model DUAL STAR (Orion, USA). Verification of the proposed method was done with an AAS model A Analyst 200 (Perkin Elmer, USA). Variable micropipette (10–100 μL) model Reference (Gilson, France) was used to pipette micro liter volume of solutions. All glassware and storage bottles were soaked overnight in 10% Nitric acid and thoroughly rinsed with water before used.

2.3 Reagent Preparation

A mixture of either 0.4 mM bpy and 1 mM sodium nitrite or 0.5 mM phen and 1mM sodium nitrite and 1000 mg L^{-1} lead (II) was diluted accordingly using ultra-pure water ($18.2 \text{ M}\Omega \text{ cm}^{-1}$) from Direct-Q (Millipore, USA). Ammonium buffer solutions (pH 7.0 - 8.6) were prepared using various concoction of 0.2 M NH_3 , 0.2 M NH_4Cl . Acetate buffer solutions (pH 2.6 – 7.0) were prepared using various concoctions.[15] while pH 4.6 were prepared using various chemicals viz. (i) 0.1 M Formic acid and 0.2 M NaOH diluted to 100 mL, (ii) 0.1 M 3, 3-Dimethylglutaric acid and 0.2 M NaOH diluted to 100 mL, (iii) 0.2 M Maleic acid and 0.2 M NaOH diluted to 100 mL and (iiii) 0.2 M Succinic acid and 0.2 M NaOH diluted to 100 mL (bpy system). The pH 5.6 was prepared using combination of 0.1 M KHP and 0.1 M NaOH diluted to 100 mL (phen system).

2.4 Measurement Procedure

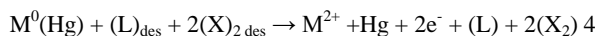
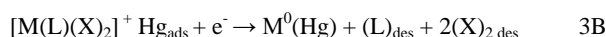
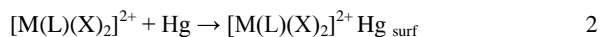
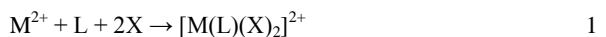
The 25 mL of buffer and ligand were pipetted into the voltammetric cell. The solution was saturated with OFN gas for 5 min purging prior to analysis. The OFN flow was stopped just before the mercury drop was introduced. Parameters used were deposition potential for the analysis -0.58 V, deposition time 180 s (bpy system) and 150 s (phen system) and angular velocity of stirrer 2000 rpm (bpy system) and 3000 rpm (phen system). Then the stirrer was switched off and a quiescence time was allowed at the potential scan started at -0.9998 V and ended at $+0.0499$ V. Voltammogram was recorded with differential pulse mode at a sweep rate of 60 mVs $^{-1}$ (bpy system) and 50 mVs $^{-1}$ (phen system).

III. RESULTS AND DISCUSSION

3.1 The Adsorptive Stripping Mechanism of The Lead (II)-Complex

Two complexes are expected to form during the analysis. They are Pb–bpy (NO₂)₂ for bpy system and Pb–phen (NO₂) (O₂CCH₃) for phen system. The structure consists of lead (II), 2,2'-bipyridine ligand acts as chelating agent to form monomeric compound. Where the six coordinated Pb (II) cation was bonded to four nitrogen atoms, two from bpy and two from nitrite ions, and the rest to water molecules. In this regard, Jovanovski et al., (1999) suggested a structure of (2,2'-bipyridine) lead (II) saccharinate monohydrate by Jovanovski et al., [16] while the proposed structure of the second complex of Pb – phen (NO₂) (O₂CCH₃) was suggested by Morsali and Mahjoub [17]. The coordination number in this complex is six (two of “phen”, four of nitrite and acetate ligands) the Pb cation is six coordinated to two nitrogen atoms from phen and four oxygen, two from acetate and two from nitrite ions). The arrangement of the

(phen) ligand, acetate and nitrite anions suggest a gap in the coordination around the Pb (II) occupied probably by a stereo active lone pair of electrons on Pb (II) where the coordination around the lead atoms is hemidirected. There is a π - π stacking interaction between the parallel aromatic rings of an adjacent chain in the compound which could help for increasing the “gap” in the coordination around the Pb (II). This model suggests that face-to-face π -stacked interactions will be disfavored because of the dominance of π - π repulsion [18]. Thus, it be able to be postulated that within the molecule discussed here the electron poor pyridyl rings will interact with less electron-poor rings such as phenyl groups [17]. In this study, the nitrite seems to have synergistic effect on the complex formation of Pb-(bpy) and to improve the sensitively for Pb⁺² using catalytic reaction [19]. The complete mechanism of lead (II) complexes in the AdCSV that gives rise to the signal measured are the same to both of bpy and phen systems can be summarized as in the following Equations 1- 4 [20].



where M is Pb; L is ligands bpy and phen ; X is nitrite and acetate; ads is adsorbed; des is desorbed and surf is surface.

3.2 The Effects of pH and The Supporting Electrolyte

The AdCSV peak intensities for Pb (II) were measured as a function of the pH in the presence of 0.1 mM bpy and phen ligands . The pH values were changed in the range

from 2.6 to 8.6 for both ligands. The stripping peak current intensity is obtained at pH 4.6 and 5.6 for Pb-bpy complex and Pb-phen complex respectively. The highest stability of these complexes in sodium formate and sodium acetate solution for Pb-bpy complex and Pb-phen complex respectively. Thus can be attributed to the reduction of the azomethine group (C=N) drawn in a four electron transfer [21]. After determining the optimum pH values for complex formation. The effect of different buffer solutions as supporting electrolytes was also tested. This experiment was developed to investigate if the presence of concentrations of organic or inorganic anions in the electrolyte could deteriorate the stripping voltammetry signal because of the formation of sparingly soluble compounds in the solution during the electrochemical analysis. Thus, Figs. 1 and 2 show the differential pulse voltammograms of the supporting electrolytes on the stripping peak current intensities with bpy and phen ligands respectively, by using different buffer solutions.

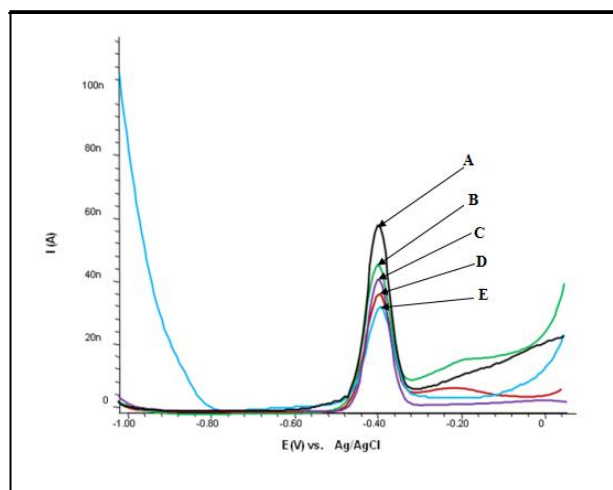


Fig. 1 Differential pulse voltammograms of the supporting electrolyte on the stripping peak current of Pb (II) with bpy using different buffer solutions: (A) Sodium formate, (B) Sodium acetate, (C) 3, 3-Dimethylglutaric acid and sodium hydroxide,

(D) Succinic acid and sodium hydroxide (E) Maleic acid and sodium hydroxide at pH= 4.6.

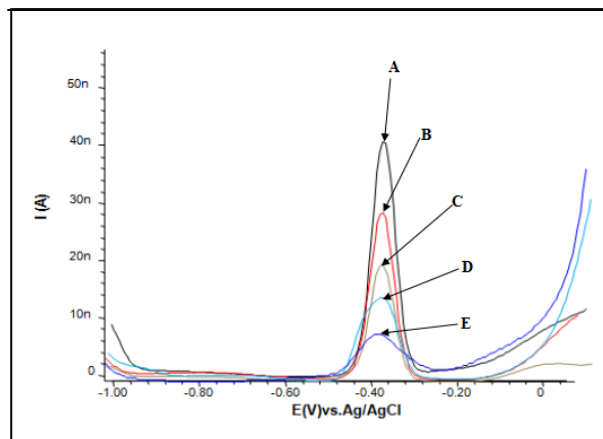


Fig. 2 Differential pulse voltammograms of the supporting electrolyte on the stripping peak current of lead with *phen* using different buffer solutions: (A) Sodium acetate, (B) 3, 3-Dimethylglutaric acid and sodium hydroxide, (C) Succinic acid and sodium hydroxide, (D) Maleic acid and sodium hydroxide, (E) KH Phthalate and sodium hydroxide at pH= 5.6.

As can be seen from Figs. 1 and 2, the highest intensity of the stripping peak current can be observed with the sodium formate and sodium acetate buffer solutions respectively. Therefore, sodium formate and sodium acetate buffer solutions are chosen as the supporting electrolytes for further studies.

3.3 Effects of Deposition Potential and Deposition Time

The effects of deposition potential were examined at various potentials ranging from -0.144 to -1.15 V. The peak current increased with decreasing the deposition potential toward more negative potentials up to maximum value of -0.58 V due to the characteristic peak potential for Pb-bpy and Pb-phen complexes. This indicates that the studied Pb (II) was reduced and amalgamated on the HMDE. Therefore, a deposition potential of -0.58 V was utilized for the optimization of deposition time. The

deposition time was applied in the range of 5 to 210 s after fixing all the optimum conditions obtained previously. The peak currents of the Pb-bpy and Pb-phen complexes increased linearly with increasing the deposition time to reach the optimum deposition time at 180 s and 150 s for Pb-bpy and Pb-phen complexes respectively. The peak currents tend to level off beyond these optimum deposition times indicating that the adsorptive equilibrium was achieved. In fact, longer period of deposition time leads to more adsorption of Pb-bpy and Pb-phen complexes on the electrode surface, as a result, the peak currents become larger. In this respect, Collado-Sanchez et al., [22] recorded 180 s as optimal for determining Pb (II) by using AdCSV in sea water.

3.4 Effect of Drop Size and Stirring Speed

Various drop sizes between 2 - 9 a.u were applied in order to optimum the drop size of HMDE for the adsorption of Pb-bpy and Pb-phen complexes. It was found that the peak currents increases directly with increasing of drop size until the largest drop size of 9 a.u. and 6 a.u for Pb-bpy and Pb-phen complexes respectively. It has been reported that the bigger drops give rise to higher back ground and border peaks [23]. The effect of stirring rates was studied at stirring speed of 1200 - 3000 rpm with stepwise increment at 400 rpm with all other parameters were kept constant. The results indicate that the peak currents constantly increases with increasing of the stirring speed up to 2000 rpm and 3000 rpm for Pb-bpy and Pb-phen complexes respectively. No further increases of the peaks current can be detected beyond these stirring speeds. Therefore, these stirring speeds are used as the optimum values for the respective complexes in the next studies.

3.5 Effects of Pulse Amplitude and Sweep Rate

The effects of pulse amplitude on AdCSV peak currents was studied in the range of 0.01 - 0.06 V. The linear increment of peak current reaches maximum at 0.05 V and 0.06 V for Pb-bpy and Pb-phen complexes respectively. Additionally, the sweep rate on peak currents of the Pb-bpy and Pb-phen complexes were studied over the range of 5-70 mVs^{-1} . The stripping peak height for the reduction of adsorbed species is expected to increase linearly with v in the absence of a contribution of diffusion currents, while diffusion-controlled currents are known to increase linearly $v^{1/2}$ [24]. The highest peak currents of the Pb-bpy and Pb-phen complexes are obtained at sweep rates of 60 mV s^{-1} and 50 mV s^{-1} respectively. The respective sweep rates and pulse amplitudes values are used for the following studies.

3.6 Effect of Ligand Concentrations

The effect of ligand concentration on the peak current of Pb-bpy complex was studied by mixing of 0.1 - 2 mM bpy 1 mM NaNO_2 . Fig. 3 shows that the peak current of the Pb-bpy complex increases with increasing of bpy concentration up to 0.1 mM, and then gradually decreases at higher bpy concentrations. This phenomenon can be attributed to the high competition of the uncomplexed ligand with Pb-bpy complex on the electrode surface [25]. This optimum concentration of 0.4 mM of bpy was used for further studies.

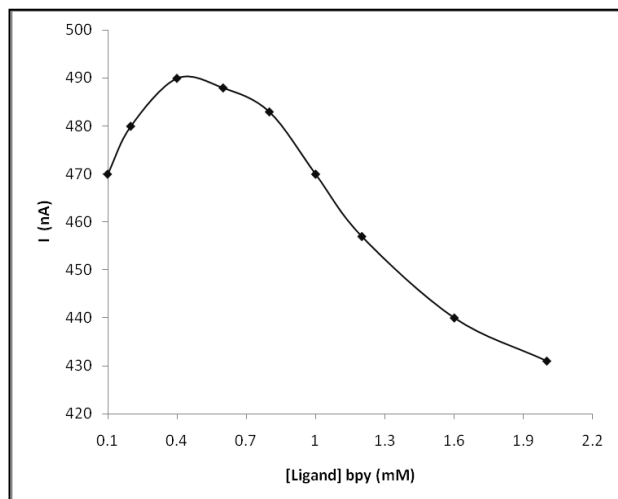


Fig. 3 Effect of bpy concentration on the peak currents of Pb (II). Other conditions are fixed as: pH 4.6, sodium formate as a buffer solution and supporting electrolyte, stirring speed up to 2000 rpm, drop size 9, deposition potential -0.58 V, initial purge time 300 s, sweep rate of 60 mV s^{-1} , pulse amplitude 0.05 V, deposition time 180 s.

Moreover, the effect of the different concentrations (0.1 - 0.9 mM) of phen mixed with 1mM sodium nitrite on the peak current of Pb (II) was also studied. Fig. 4 shows that the peak current of the Pb-phen complex increases with increasing phen concentration up to 0.1 mM, and then remains constant at higher concentrations. This observation can be attributed to the competition of Pb-phen complex with phen for adsorption on the surface of HMDE [26]. This optimum concentration of 0.5 mM phen was used for further studies.

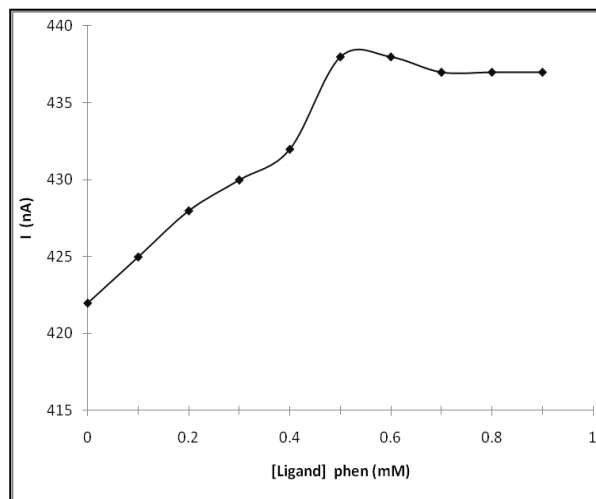


Fig. 4 Effect of phen concentration on the peak currents of Pb (II). Other conditions are fixed as: pH 5.6, buffer solution of sodium acetate as a supporting electrolyte, stirring speed up to 3000 rpm, drop size 6, deposition potential -0.58 V, sweep rate of 50 mV s^{-1} , pulse amplitude 0.06V, deposition time 150 s.

3.7 Calibration Graph

Fig. 5 verifies the linear relationship between peak currents and Pb (II) at optimum conditions, i.e. 0.4 mM bpy buffer pH 4.6, deposition potential - 0.58 V, deposition time 180 s, pulse amplitude 0.05 V, sweep rate 60 mV s^{-1} , drop size 9 a.u. and stirring speed 2000 rpm. The calibration equation obtained by least-squares method is $y = 4.6786x - 1.2613$ with linear regression (R^2) 0.9991. In the same manner (Fig. 5) under optimum conditions, 0.5 mM phen, pH 5.6, deposition potential - 0.58V, deposition time 150 s, pulse amplitude 0.06V, sweep rate 50 mVs^{-1} , drop size 6 a.u. and stirring speed 3000 rpm the calibration equation is obtained by least-squares method as $y = 4.0647x - 1.2428$ ($R^2 = 0.9986$) where x is the concentration of Pb (II) in ng mL^{-1} and y is the peak current (nA). From this study the stripping peak current of Pb-bpy and Pb-phen complex were found to be directly proportional to the lead concentration in the range of 10 - 500 ng mL^{-1} and 7 - 500 ng mL^{-1} , respectively. The

concentration limit of detection (C_{LOD}) of Pb (II) at 0.48 ng mL^{-1} and 0.36 ng mL^{-1} were always obtained for the respective Pb-bpy and Pb-phen continually were obtained under the optimal experimental conditions by measuring nine blanks and using criterion $C_{LOD} = 3sb/S$, where sb is standard deviation of the blank measured and S is the slope of the calibration plot [27]. The relative standard deviation (RSD) for nine replicate measurements of 25 ng mL^{-1} Pb(II) for Pb-bpy and Pb-phen complexes are 1.74% and 1.84%, respectively.

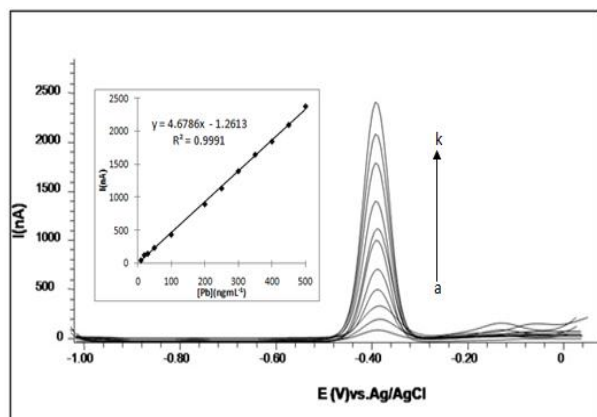


Fig 5: Differential pulse cathodic stripping voltammograms and calibration graphs of different Pb (II) concentrations (a)10, (b) 20, (c) 30, (d) 50, (e) 100, (f) 200, (g) 250, (h) 350, (i) 400, (j) 450, and (k) 500 ng mL^{-1} .

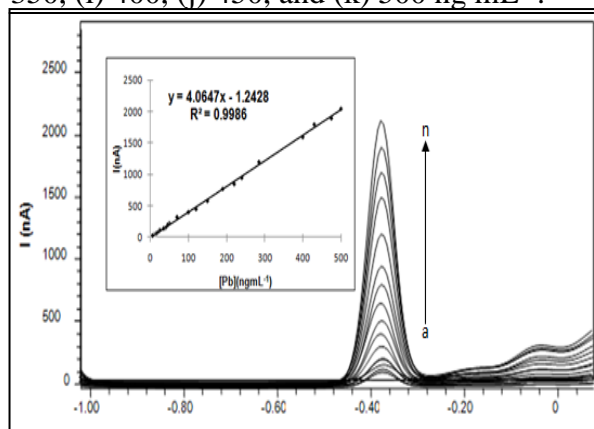


Fig. 6: Differential pulse cathodic stripping voltammograms and calibration graphs of different Pb(II) concentrations (a)7, (b)10, (c)15, (d) 40, (e) 50, (f)100, (g) 120, (h)150,

(i)180, (j) 250, (k) 300, (l) 400, (m) 425 and (n) 500 ng mL^{-1} at optimum conditions.

3.8 Interference Study

The influence of several anions and cations on determination of Pb (II) was studied. The readings was taken at a fixed 50 ng mL^{-1} Pb (II), the maximum tolerance levels which do not affect the peak current of Pb-bpy and Pb-phen beyond the limits of $I_p \pm 3s$ of those obtained in the absence of interference. Table 1 shows that most of the examined ions are tolerated at high levels, almost $1000 W_{ion}/W_{Pb}$. and Fe^{3+} at $200 W_{ion}/W_{Pb}$. Thus, Iron (III) in reduced form and also dissolved Aluminium (III) (in case of phen) must not be presence in the sample for the analysis. These ligands are known reagents for the determination of iron (II) [28].

Table 1: Interferences study for the determination of Pb²⁺ as lead (II) complexes with two ligands under optimum conditions.

Ligand	Species	Tolerance limit (W_{ion}/W_{Pb})
bpy	Mg(II), Na(I), Al(III), Zn(II), Ca(II), K(I), Ni(II), Co(II), Cu(II), SO_4^{-2} , NO_3^- , Cl^-	1000
	Cr(III), Cd(II), HCO_3^- , CO_3^{-2}	600
	HPO_4^{-2}	400
	Fe(III), Fe(II)	200
phen	Mg(II), Na(I), Zn(II), Ca(II), K(I), Ni(II), Co(II), Cu(II), Cr(III), Cd(II), SO_4^{-2} , NO_3^- , Cl^-	1000
	HCO_3^- , HPO_4^{-2}	800
	CO_3^{-2}	600
	Fe(III), Fe(II), Al(III)	200

3.9 Application of The Proposed Methods to Real Samples Analysis

Three real water samples were chosen for corroboration this method, First sample was seawater collected from the coast of Penang island, second sample lake water collected from USM main campus and the third sample was tap water. All of these samples were analyzed by stripping voltammetry after filtration process filtered with Whatman paper no. 1, then acidified with HNO_3 and also added with 0.02 M hydrogen peroxide. The samples were subjected to the UV irradiation for two hours in order to digest and degrade any organic matters presented in the samples. After that, the lake water was spiked with $50 \text{ ng mL}^{-1} \text{ Pb}^{2+}$ and tap water was spiked with $100 \text{ ng mL}^{-1} \text{ Pb}^{2+}$. The results of standard addition method of proposed and recommended procedures (AAS) are summarized in Table 2.

Table 2: Determination of Pb^{2+} in real samples as lead (II) complexes with two ligands

Ligand	Water Samples	Pb(II) spacing (ng mL^{-1})	Pb(II) found AdCSV (ng mL^{-1})	Pb(II) found AAS (ng mL^{-1})	Recovery (%)
bpy	Sea water	-	104 ± 0.15	102 ± 0.5	-
	Lake water	100	108 ± 0.2	110 ± 0.8	101.85
	Tap water	200	198 ± 0.3	196 ± 0.25	98.98
phen	Sea water	-	102 ± 0.15	101 ± 0.4	-
	Lake water	100	105 ± 0.22	108 ± 0.3	102.85
	Tap water	200	202 ± 0.3	198.6 ± 0.4	96.56

IV. CONCLUSION

This work presents a new application of two novel ligands namely 2,2'-bipyridine and nitrite or 1,10-phenanthroline, acetate and nitrite for determining Pb (II) in different water samples by using adsorptive cathodic stripping voltammetry (AdCSV). These ligands offer a practical potential for the analysis of traces Pb (II) in the environment water with high sensitivity, simplicity and speed analysis. By comparing the obtained results of two applied ligands, it can be concluded that the Pb-phen complex has a lower detection limit, wider liner range and higher RSD compare to the Pb-bpy complex.

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