



Trace the determination of cadmium ions in aqueous solutions by anodic stripping cyclic voltammetry at modified graphite electrode with organic ligand 3-(4-nitrophenyl azo)-pentane-2,4-dione (L_p)

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Abstract This present paper describes the development and electrochemical application for the determination of cadmium ions in aqueous solutions using a modified graphite electrode (MGE) 3-(4-nitrophenyl azo)-pentane-2,4-dione(L_p) as the modifier ligand with analytical and technical conditions has been described by anodic stripping cyclic voltammetry (ASCV) and. The resulting brown dye 3-(4-nitrophenyl azo)-pentane-2,4-dione reached melting point 180.4 C°, yield 78%. The complex formation has been studied with Cd²⁺ ion for (L_p) dye using ¹³C NMR spectra, ¹H NMR spectra UV spectroscopy and studied Two electrolytes were studied (Britton–Robinson buffer, AcONa/AcOH). The optimal conditions for the determination of cadmium ions in aqueous solutions using modified graphite electrode (MGE) as a working electrode by anodic stripping cyclic voltammetry (ASCV) are: Electrolyte CH₃COONa/CH₃COOH, pH=5.6 Scan range –1300 to –100 mV, Accumulation potential to reach its highest value at -1100 mV Several Accumulation time t_{acc} were studied to reach the maximum value at 80 sec , These conditions were applied on a standard solution of cadmium 0.05mg/l, while standard additions method, The statistical study showed the accuracy and sensitivity for our total new working electrode in determination of Cd²⁺ using (ASCV). The highly sensitive response of Cd²⁺, The statistical study was carried out by calculating the regression factor R%= 100.5%, the standard deviation SD=0.020mg/L, the relative standard deviation RSD%= 1.97, confidence Interval the confidence(0.055±0.0497) Theoretical detection limit=0.005mg/L, in addition to the theoretical and practical detection= 0.0095mg/L, for the determination of this analyte in water

Keywords modified graphite electrode, anodic stripping cyclic voltammetry, determination of ions Cd²⁺

Introduction

One of the most important challenges facing modern analytical chemistry is the development of high-efficiency analytical methods to be able to determine the largest number of components in samples with the highest possible accuracy and sensitivity in shortest time and lowest price without the need to traditional separation and concentration, or reduce and make these operations at the minimum. The high-efficiency methods meet all or at least the quality requirements and standards set out in the international standards. These requirements include accuracy, linearity between analytical signals and concentration, sensitivity, detection limit, retroactivity and selectivity, Even the definition of analytical chemistry has been revisited, and the boundaries of the seam have been carefully drawn, and their interrelationships with other chemical specializations [1-3].

As well as the development of highly efficient analytical methods, and the most important of one which is called atomic absorption spectrometry (AAS) [4], inductively coupled plasma-atomic emission spectrometry (ICP-AES), inductively coupled plasma-mass spectrometry (ICP-MS) [5], flame atomic absorption spectroscopy (FAAS) [6], in addition to voltammetry (VA) which has been proven as one of the most efficient electroanalytical techniques for heavy metal traces determination [7] especially differential pulse anodic stripping voltammetry (DPASV) [8]. In voltammetry many working electrodes could be used like multi-mode electrode (Dropping Mercury Electrode DME, Static Mercury Drop Electrode SMDE, Hanging Mercury Drop Electrode HMDE), gold electrode AuE, silver electrode AgE, mercury film electrode MFE, graphite electrode GE, and modified graphite electrode MGE [9].

To keep up with these expectations, we have been keen to have our research in this area by developing an analytical system which combines new electrode manufactured laboratory with highly selectivity by adoption of (Hybrid Method) or (Combinative) that promote the processes of separation and simultaneous determination, and which reduces the complicated chemical procedures which govern the sample before measurement, which are often the source of many mistakes.

Materials and Reagents

797 VA Stand (Metrohm) was used in this study. Acetylacetone (Merck 97%), and p-nitro aniline (Consolidated chemical 99%) were all extra pure analytical grades and were used to prepare 3-(4-nitrophenyl azo)-pentane-2,4-dione (LP).

Solutions

Deionized water was used for all preparations and throughout all experiments. Stock solutions of cadmium nitrate (Merck 1000mg/l) was used to prepare a standard solution (Cd) 1 mg/l. Sodium acetate ($\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$ Avonchem.uk 99.0 %), acetic acid (SDFCL 99.5%), and phosphoric acid (Merck 85%), nitric acid (Merck 65%), hydrochloric acid (Scharlau 35%), sulfuric acid (ACROS 96%), boric acid (Scharlau 99.9%), sodium nitrite (Avonchem.uk 99.9%), were all extra pure analytical grades.

Preparation of 3-(4-nitrophenyl azo)-pentane-2,4-dione

First, the diazonium ion was prepared by diazotation reaction of p-nitro aniline (Figure 1). (1.3g, 10 mmol) of p-nitro aniline was dissolved in a mixture of distilled water with concentrated HCl (1: 1) ratio, while maintaining the temperature in the range 0-5 °C using an ice bath, then a solution of sodium nitrite prepared by dissolving (0.69 g, 10mmol) in 2 ml distilled water is added to the previous solution in batches and with great caution within 30 minutes to obtain a solution of diazonium salt.

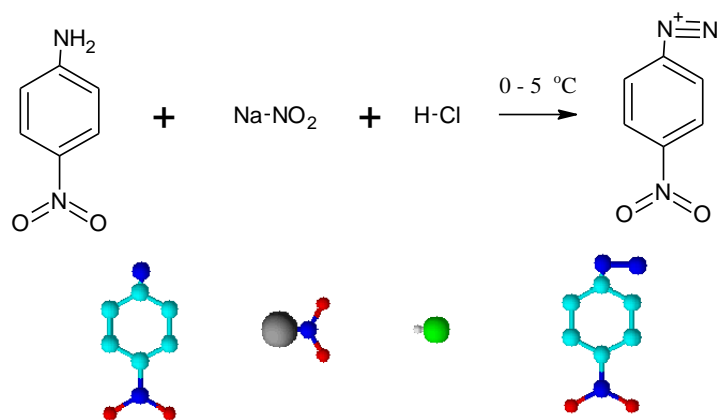


Figure 1: Diazotation reaction of p-nitro aniline

The Diazonium salt was added to acetylacetone solution (1.02 ml, 10 mmol) in 7 ml ethanol to get 3-(4-nitrophenyl azo)-pentane-2,4-dione (LP) in coupling reaction as in (Figure 2).

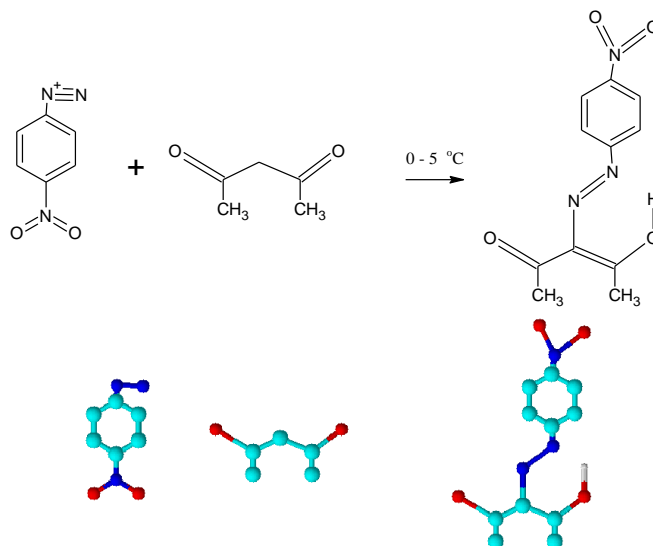


Figure 2: Coupling reaction between the diazonium salt and acetylacetone

The resulting brown dye 3-(4-nitrophenyl azo)-pentane-2,4-dione reached melting point 180.4 C°, yield 78%.

^{13}C NMR (100 MHz, CDCl_3) (Figure 3): δ 188.59 (C=O), 153.10 (ar.), 139.32 (ar.), 130.14 (ar.), 128.65 (ar.), 112.82 (=C-N/C=N-N), 33.41 (CH_3), 23.82 (CH_3).

^1H NMR (400 MHz, CDCl_3) (Figure 4): δ 13.98 (1H, OH/NH), 8.28 (2H, $J = 8.9$ Hz), 8.17 (2H, $J = 8.9$ Hz), 7.36 (2H, $J = 8.9$ Hz), 6.95 (2H, $J = 8.9$ Hz), 2.62 (3H), 2.55 (3H).

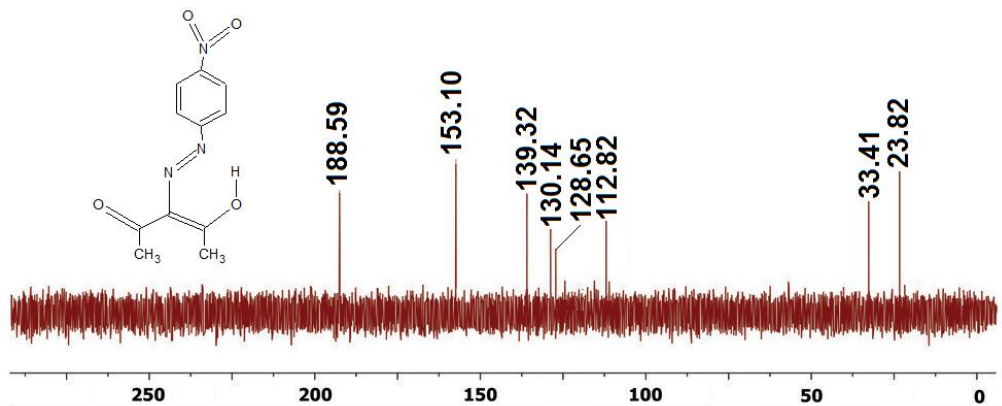


Figure 3: ^{13}C NMR spectra of 3-(4-nitrophenyl azo)-pentane-2,4-dione in CDCl_3

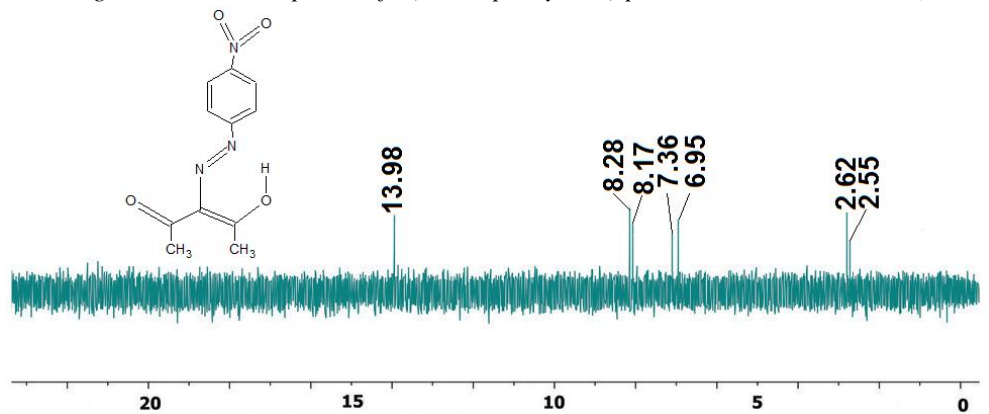


Figure 4: ^1H NMR spectra of 3-(4-nitrophenyl azo)-pentane-2,4-dione in CDCl_3



The resulting L_p dye can form complexes with copper (Cu^{2+}), nickel (Ni^{2+}) and cobalt (Co^{2+}) ions [10].

The possibility of complex formation with Cd^{2+} ion has been studied [11], cadmium nitrate (1 mmol) was added in 10 ml ethanol to L_p dye (2 mmol) in 20 ml (1:1) ethanol – chloroform mixture.

UV spectroscopy for (L_p) dye (Figure 5) illustrated clear shifting (from 380 nm to 450 nm) of absorption peak when a complex was formed with cadmium ions Cd^{2+} .

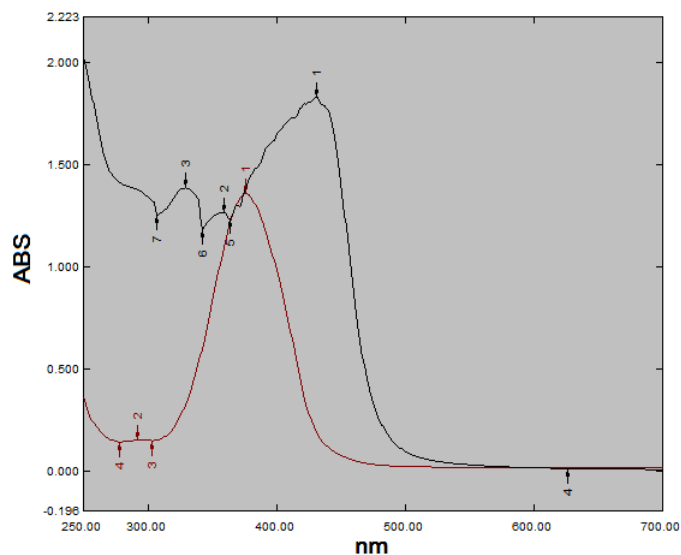


Figure 5: UV Spectrum for L_p (red) and the complex of L_p with Cd^{2+} (black)

IR spectrum shows the vibration of bonds for L_p dye (Table 1), and L_p complex with Cd^{2+} (Table 2).

Table 1: Bonds vibrations in IR spectra for (L_p)

Bond type	C-O	N=N	C=O	C-H Ar	O-H
ν_{max} (cm^{-1})	1265- 1273	1509-1526	1650 - 1680	3038-3071	3432- 3454
ν_{max} (Reference cm^{-1}) [10]	1271	1521	1676	3060	3443

Table 2: Bonds vibrations in IR spectra for(L_p) complex with Cd^{2+}

Bond type	N=N	C=O	O-H
ν_{max} (cm^{-1})	1528	1675 - 1685	3450- 3460
ν_{max} (Reference cm^{-1}) [10]	1523	1675	3447

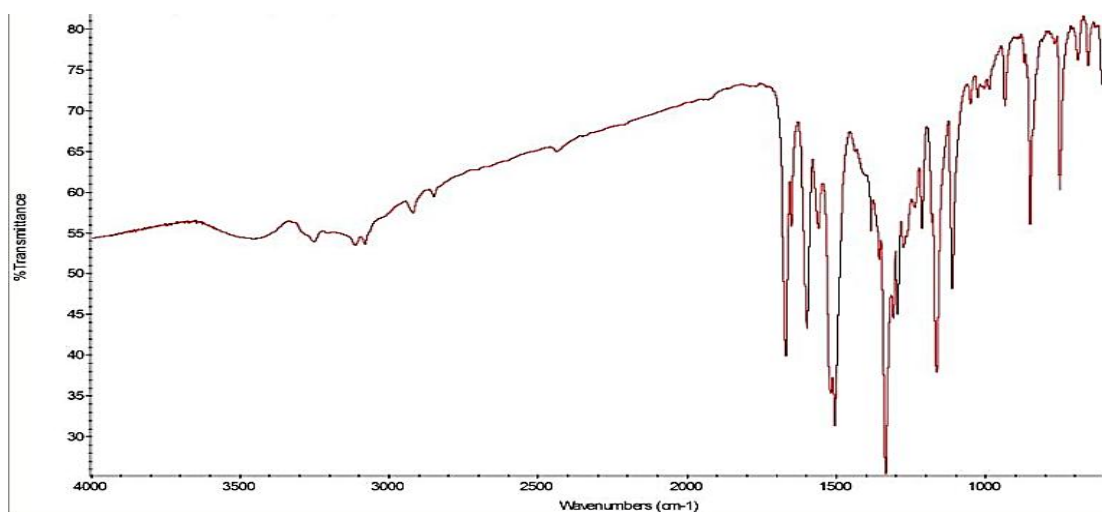


Figure 6: IR Spectrum for L_p



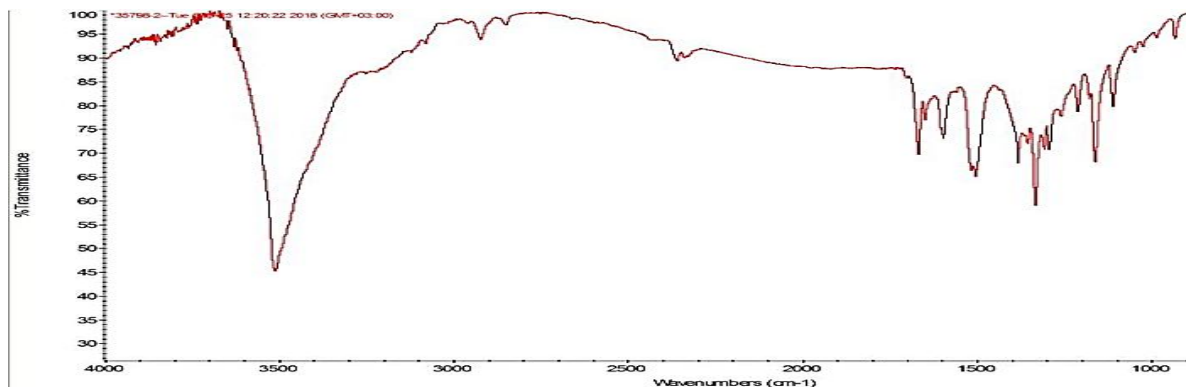
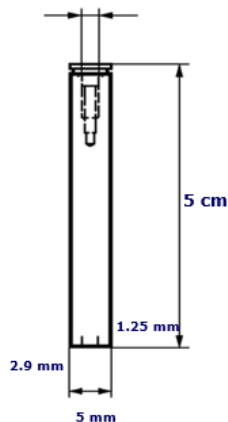


Figure 7: IR Spectrum for the complex of L_p with Cd^{2+}

Preparation of the modified carbon paste electrode

Teflon cylindrical tube (5 cm length) with a hole at one end (2.9 mm inner diameter and 1.25 mm of deep cavity) for the carbon paste filling served as the electrode body.

Unmodified electrode was prepared by thoroughly hand-mixing 0.1 g of high purity graphite powder with 0.042 g of paraffin oil in a mortar and pestle until a homogeneous carbon paste was obtained [12]. The MGE was prepared in a similar way except that the graphite powder (0.07 g) was first mixed with the desired weight of 3-(4-nitrophenyl azo)-pentane-2,4-dione (L_p) (0.03 g) in a mortar followed by the addition of 0.042 g of paraffin oil to the carbon paste mixture and mixed until obtaining a uniform paste. Subsequently, the paste was packed firmly into the electrode cavity and smooth surfaces were obtained by applying manual pressure to the tip while polishing on a sandpaper.



Analytical Conditions

• Electrolyte and pH

Two electrolytes were studied (Britton–Robinson buffer, AcONa/AcOH) (Table 3).

The effects of prepared electrolytes on of the voltammetric curves of cadmium were studied in terms of their effect on the anodic peak current I_{pa} (peak height) beside the anodic and cathodic peak voltage E_{pa} , E_{pc} , in a wide range of PH values.

When Britton–Robinson buffer was used as supporting electrolyte (Figure 8), the anodic peaks at pH = 1.3 were distorted and had bad repeatability, whereas at pH values from 2 to 7 they were sharp, and had good repeatability. while there was a shift of the anodic peaks potential E_{pa} towards the negative potential increased with pH to reach an optimum limit -640 mV at pH = 4, then it started to shift in the opposite direction to reach -615 mV, on the other

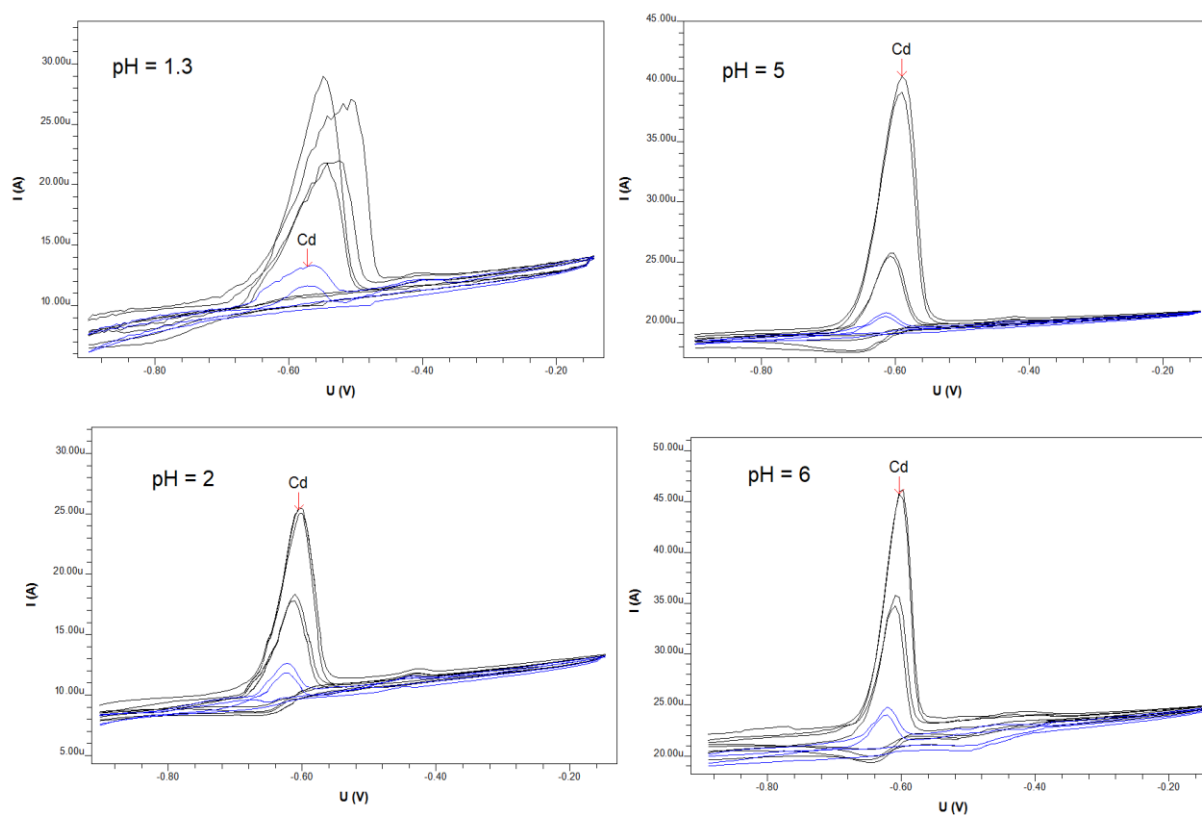


hand the cathodic peaks potential ranged between -682 mV and -633 mV. The anodic peak current increased with pH, and the highest value was $I_p = 26.78 \mu\text{A}$ at pH = 7.

Table 3: E_{pa} , E_{pc} and I_{pa} in terms of pH for Britton-Robinson buffer and AcONa/AcOH as electrolytes

Electrolyte	I_{pa} (μA)	E_{pc} (mV)	E_{pa} (mV)	pH
Britton-Robinson buffer	11.32	-682	-567	1.3
	12.26	-633	-596	2
	14.73	-649	-602	3
	17.80	-652	-640	4
	20.49	-645	-638	5
	24.17	-640	-634	6
	26.78	-642	-615	7
AcONa/AcOH	18.59	-594	-571	3.6
	18.67	-583	-558	4
	18.71	-680	-617	4.4
	21.96	-626	-562	4.8
	24.01	-639	-614	5.2
	28.12	-645	-622	5.6

The anodic peaks that resulted when AcONa/AcOH was used as electrolyte, were ideal, sharp, and had good repeatability. E_{pa} values ranged between -558 mV and -622 mV, whereas E_{pc} values between -583 mV and -680 mV. The anodic peak current increased with pH, and the highest value was $I_p = 28.12 \mu\text{A}$ at pH = 5.6. Between the two studied electrolytes AcONa/AcOH gave the highest value of I_p .



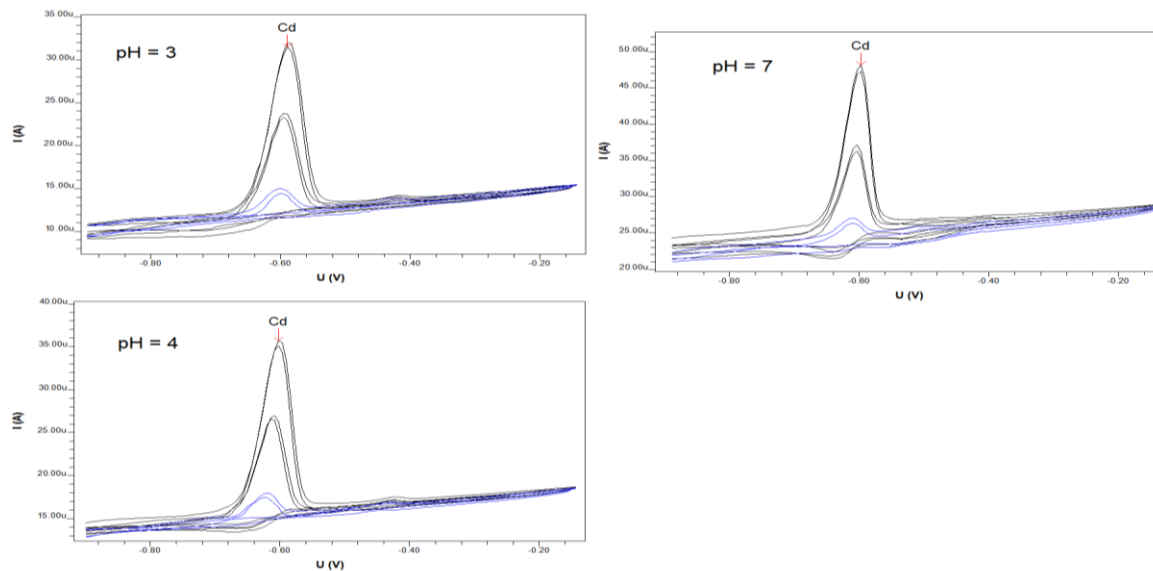


Figure 8: Voltammetric curves when Britton–Robinson buffer was used as supporting electrolyte

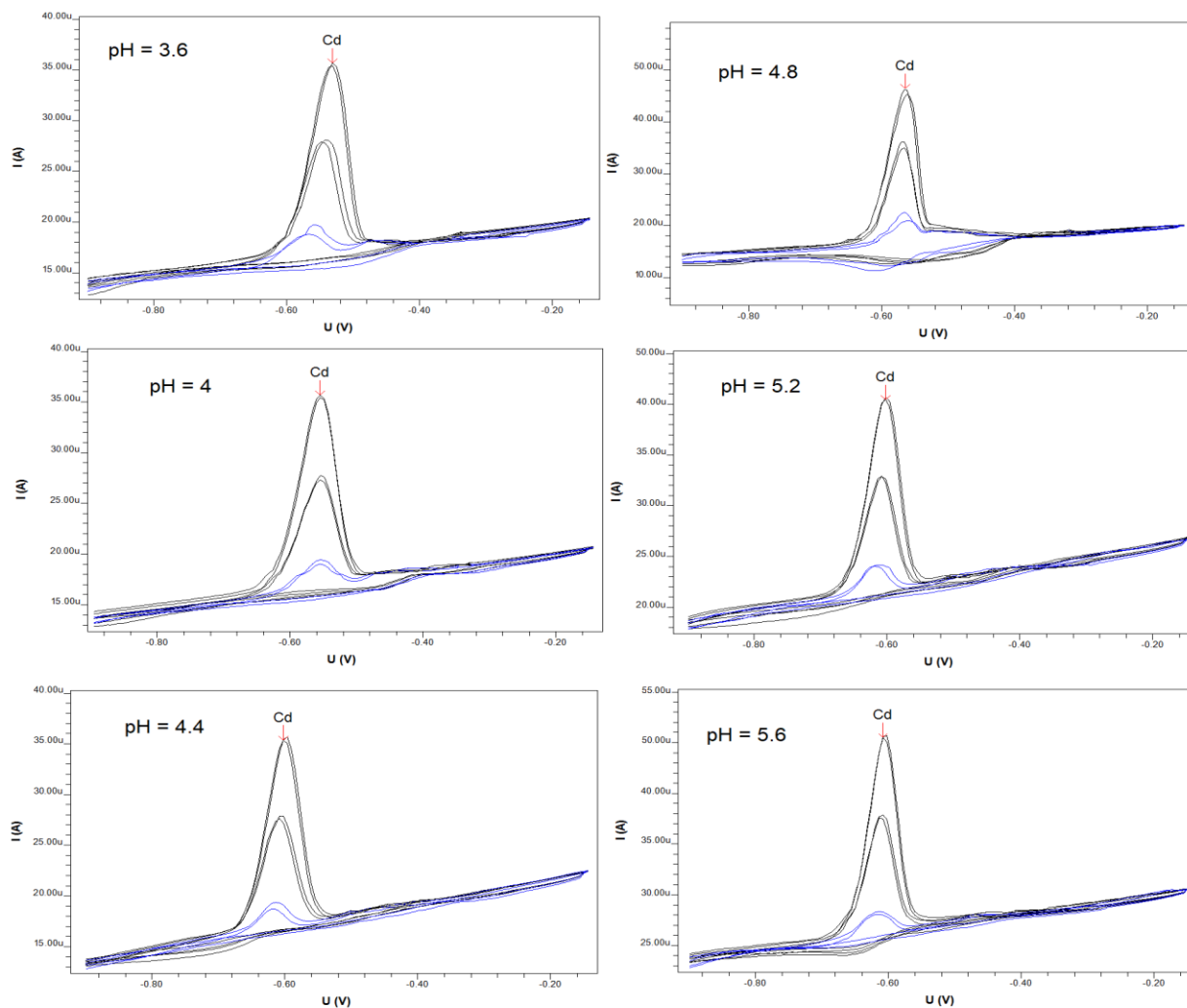


Figure 9: Voltammetric curves when AcONa/AcOH was used as supporting electrolyte

Technical Conditions**Accumulation Potential**

A range of potential between -900mV and -1300mV was applied (Table 4), as we can see from (Figure 10), I_{pa} increases with the decrease in the applied potential to reach its highest value at -1100 mV with ideal peaks shape, then the voltammetric curves starts to distort at low applied potentials.

Table 4: E_{pa} , E_{pc} and I_{pa} in terms of accumulation potential

E_{acc} (mV)	E_{pa} (mV)	E_{pc} (mV)	I_{pa} (μ A)
-900	-634	-650	17.21
-1000	-636	-643	18.08
-1100	-629	-641	23.96
-1200	-622	-646	18.83
-1300	-635	-654	14.67

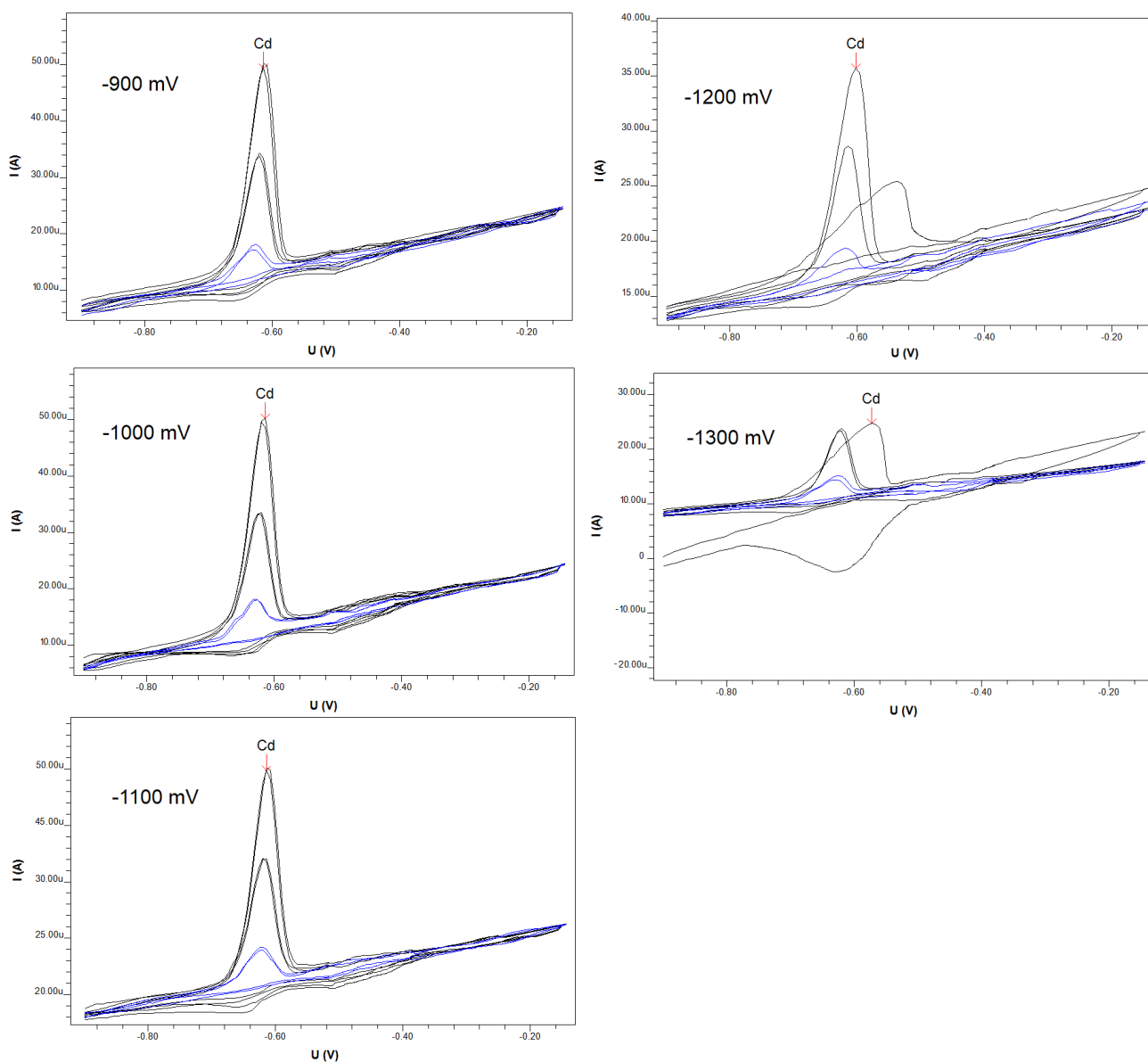


Figure 10: Voltammetric curves at different values of accumulation potential



Accumulation time

Several t_{acc} were studied (Table 5), as we can see from Figure 11, Anodic peak current rise steadily to reach the maximum value at 80 sec then fell down slightly at 100 sec.

Table 5: E_{pa} , E_{pc} and I_{pa} in terms of accumulation time

t_{acc} (sec)	E_{pa} (mV)	E_{pc} (mV)	I_{pa} (μ A)
20	-627	-644	17.98
40	-543	-587	20.21
60	-616	-658	21.01
80	-598	-665	22.83
100	-611	-650	18.60



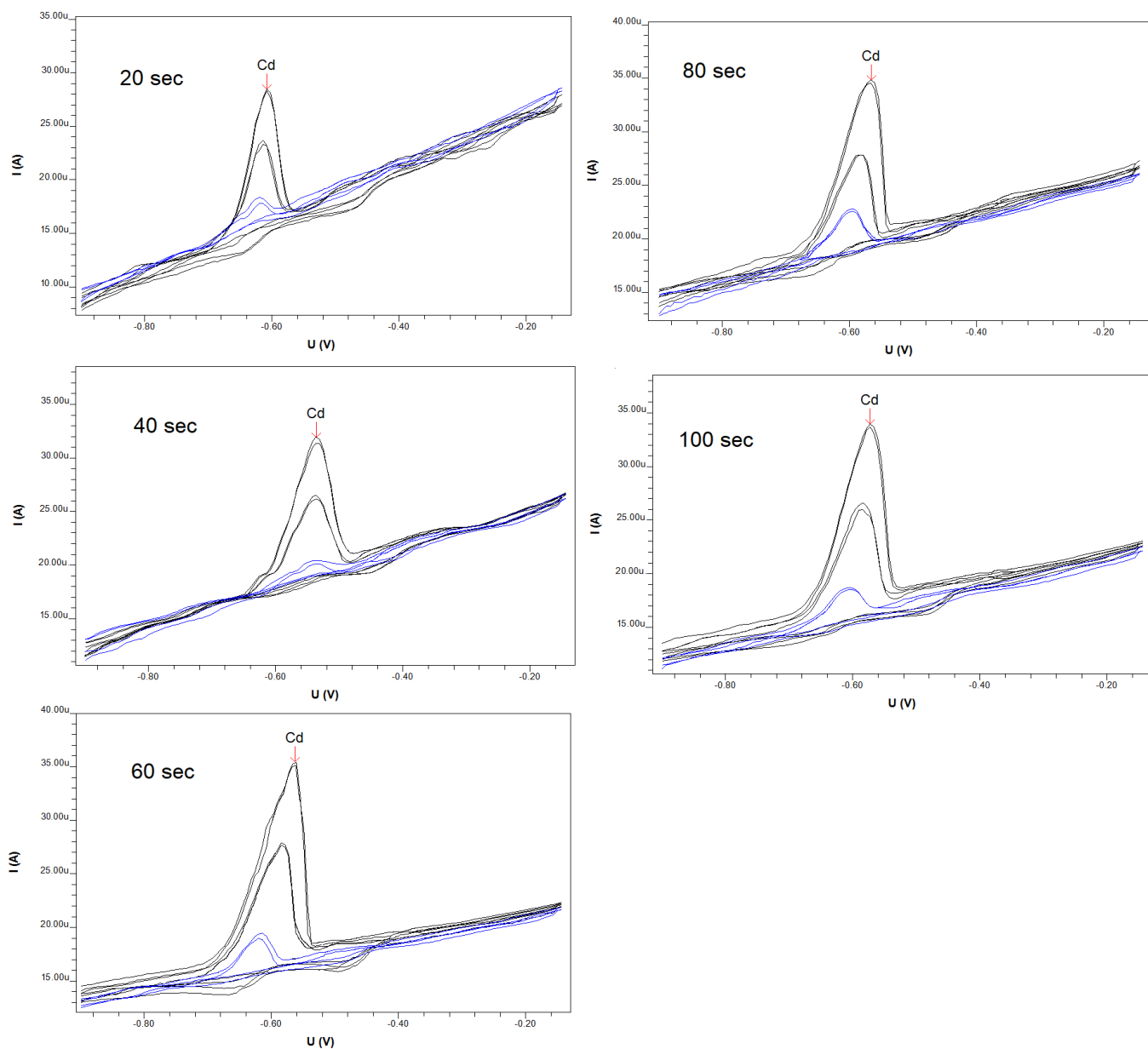


Figure 11: Voltammetric curves at different values of accumulation time

Optimal Conditions

The optimal conditions of the determination of cadmium ions in aqueous solutions using modified graphite electrode (MGE) as a working electrode by anodic stripping cyclic voltammetry (ASCV) are shown in (Table 6)

Table 6: Optimal conditions of the determination of cadmium ions using MGE by CV

Condition	Value/Type
Method	ASCV
Electrolyte	CH ₃ COONa/CH ₃ COOH
pH	5.6
Scan range	-1300 → -100 mV
Accumulation potential	-1100 mV
Accumulation time	80 sec

These conditions were applied on a standard solution of cadmium and lead 0.05mg/l, while standard additions method was used and an optimal curves were obtained $I_{pa} = 28.92 \mu\text{A}$ (figure 12).

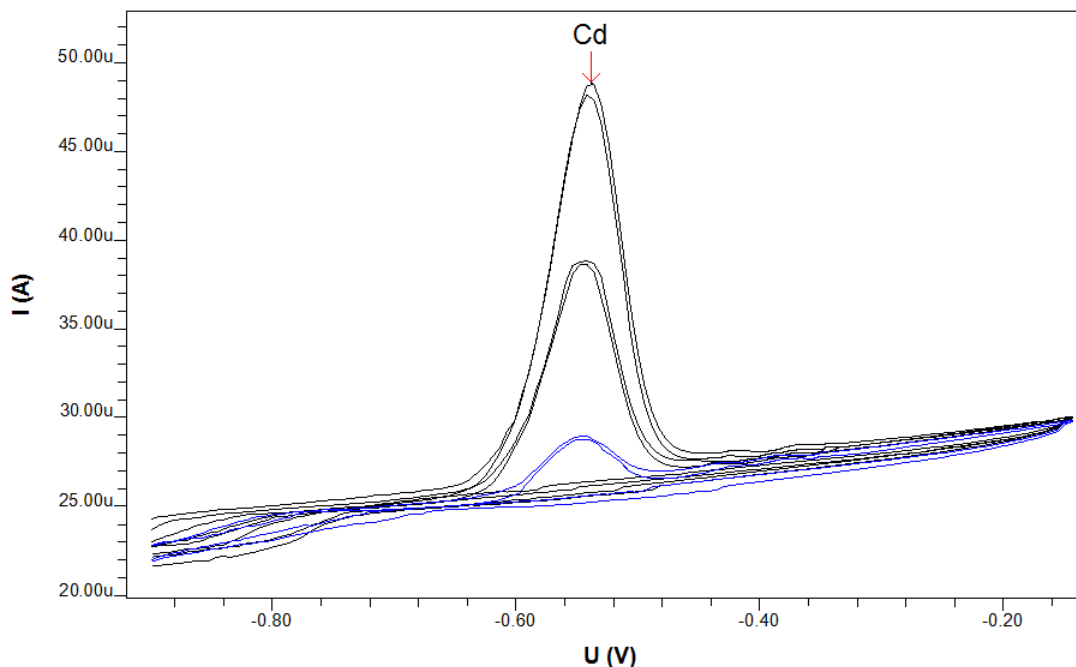


Figure 12: ASCV curves for Cd^{2+} standard solution 0.05mg/l ($n=2$)

The statistical study was carried out by calculating the regression factor R%, the standard deviation SD, the relative standard deviation RSD%, the confidence interval within the field (95%), in addition to the theoretical and practical detection limit (Table 7).

Table 7: Regression factor R%, the standard deviation SD, the relative standard deviation RSD%, the confidence interval, theoretical and practical detection limit

Conc. mg/L	Measured Conc. mg/L	SD mg/L	RSD %	R %	confidence Interval	Theoretical detection limit mg/L	Practical detection limit mg/L
0.05	0.055	0.020	1.97	100.5	0.055 ± 0.0497	0.005	0.0095

Conclusion

A selective and easy new procedure for the determination of cadmium ions in aqueous solutions using a modified graphite electrode (MGE) by anodic stripping cyclic voltammetry (ASCV) and 3-(4-nitrophenyl azo)-pentane-2,4-dione(L_p) as the modifier ligand with analytical and technical conditions has been described. The statistical study showed the accuracy and sensitivity for our total new working electrode that determined of Cd^{2+} using (ASCV). The highly sensitive response of Cd^{2+} , simplicity and rapid response show that it is an adequate cadmium -free alternative for the determination of this analyte in water.

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