Polarographic Reduction And Electrode Kinetic For The Interaction Of Chrysin And Hesperetin With Pb^{+2} Ion

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الخلاصة

تعد مرتبطات الفلافونيد من المركبات متعددة الفينولات ذات المنشأ الغذائي ، وهي موجودة بكثرة في النباتات ، ولها أستخدامات طبية واسعة بسبب فعاليتها كمواد مضادة للاكسدة ، ولقدرتها على الارتباط مع أيونات الفلزات ، في هذا العمل تم أجراء دراسة كهروكيميائية لارتباط أيون الرصاص الثنائي مع مرتبطات الفلافونيد، الكريسين والهسبرتين في الوسط الحامضي حيث أستخدمت تقنية البولاروغراف النبضي المشتق لغرض تعيين المتغيرات الحركية كذلك حساب الدوال الثرموداينميكية ، الانثالبي، طاقة جبس الحرة، والانتروبي لعملية التعقيد في مدى من درجات الحرارة (كلفن 293-313) ، ومن حساب ثوابت لحركيات القطب تبين أن عمليات القطب غير عكسية ومسيطر عليها بالانتشار.

Abstract

Dietary flavonoids (poly phenols) are important phytonutrient widely distributed in plant foods, flavonoids have beneficial biological activities, such as antioxidant activity, flavonoids can chelate with metal ions, the interaction of lead (II) ion with a poly hydroxylated flavonoids, the chrysin and hesperetin molecules, were investigated electrochemically in acidic media. The Differential puls polarographic Technique was used to determine the kinetic parameters (K_f, h, α_n) using meites-israel method, also thermodynamic parameters such as enthalpy change (ΔH), free energy change (ΔG), entropy change (ΔS) of Pb^{+2} – complexes with chrysin and hesperetin at (293, 313) ^0K. The (K_f, h, α_n) values for the kinetics of the electrode processes show that the electrode processes were irreversible and diffusion controlled.

Key words: Flavonoids, chrysin, hesperetin, Pb(II) – chrysin complex, Pb(II) – hesperetin complex, Polarographic, kinetic parameters, thermodynamic parameters.

Introduction:

Flavonoids are a class of polyphenolic compound which were present in most plants , synthesized by the phenyl propanoid pathway , more than 6000 different flavonoids have been identified making them the largest group of plant chemicals , classified as flavones, flavonols, flavanons, flavanols and isoflavonoes[1,2].

In recent years, flavonoids were found to have particular biological activities and therefore have gained increasing attention previous studies showed that flavonoids have antibacterial, antioxidizing[3,4], and anti-inflammatory activities[5], as well as functions for prophylaxis of cancer and cardiovascular diseases[6-10].

The pharmacological effects are related to the antioxidant activity of flavonoids, arising through their ability to scavenge free radicals, when generated in excess, free radicals can damage biomolecules, and are therefore implicated in the etiology of several disease and ageing[11].

Lead is naturally occurring bullish – gray metal found in earth's crust. Lead can combine with other chemicals to form what are known as Lead salts. These compounds are water –soluble, while elemental lead is not [12]. The propensity for lead to catalyze oxidation reactions and generate reactive oxygen species has been demonstrated in multiple studies [13-15].

In this work, the interaction of chrysin, hesperetin, and Pb (II) ions was studied using and electrochemically by differential pulse polarographic technique, the stability constant for the formation of the complexes were determined at different temperature

Experimental:

Chemicals and solutions: chrysin and hesperetin was obtained from Aldrich chemical company, Methanol from scharlau, Lead nitrate from Himedia Labortatories, Hydrochloric acid from BDH, Sodium hydroxide, and Potassium chloride from GCC-England.

chrysin and hesperetin**:** The stock solution of rutin (10^{-3}M) was prepared by dissolving 61 mg 0f rutin in 100ml volumetric flask using 50% methanol/water mixture as a solvent. All other chemicals were prepared using double distilled water.

Pb (II) solution: A stock solution of Pb (II) (10^{-3}M) was prepared by dissolving (33.1mg) of Pb $(NO_3)_2$ in 100ml volumetric flask using double distilled water.

Polarographic measurements: Electrochemical experiments, differential pulse polarography were carried out using a par model 797Va poarographic analyzer equipped version 1. 2. The current voltage curves were measured manually and performed with three electrode system consisting of a medium size hanging mercuric drop electrode (HMDE) as the working electrode, a platinum wire counter electrode and an Ag/AgCl (saturated KCl) reference electrode.

Electrochemical measurements were performed in (15ml) accurately measured solution placed in a polarographic cell and deoxygenated with pre-purified nitrogen for at least 5 minutes prior to each experiment and the nitrogen atmosphere was maintained thereafter.

The operating parameters were; pulse amplitude 50mv, pulse time 0.04 sec, scan rate 15 mv/s, initial potential (-1.0V), end potential (+1.0V), drop size 9 mm^3, voltage step 0.006V, voltage step time 0.4 sec, deposition time 60sec, equilibrium time 5 sec.

Results and Discussion:

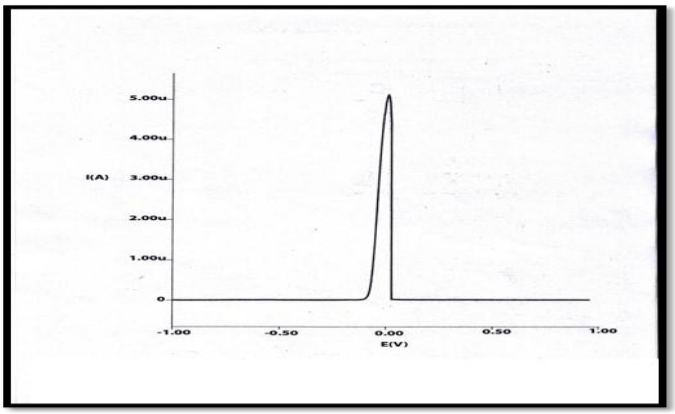
Polarographic study: A variety of supporting electrolyte can be used in determination of organic compounds. There are usually buffers or solutions of strong acids or strong bases ,the concentrations of them is kept at least 20 times higher than concentration of the electroactive species.

The polarographic measurements for Chrysin (Chr), were performed, Table (I), using NaOH as a solvent and supporting electrolyte. The addition of NaOH solutions is due to the low solubility of this compound in ethanol. Differential pulse polarograms of $1.2*10^{-4}$M of chrysin were recorded and illustrated in figure (1). Differential pulse polarograms of chrysin in a various concentrations of NaOH solutions showed a one polarographic wave in all cases.

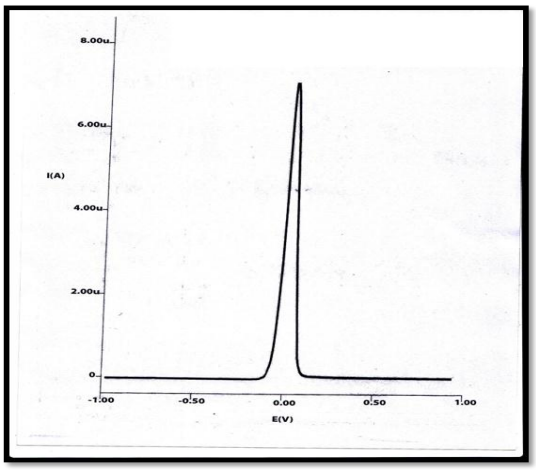
The maximum peak current (Ip) was found in 0.01 M of NaOH, and the peak potential shifts to more negative potential with increase in NaOH concentration that means its reduction become more difficult.

Table (I): Peak potential and peak current of $1.2*10^{-4}$M Chrysin in NaOH

Concentration of supporting electrolyte	E_p (V)	I_d (µA)
1M	- 0.0359	5.18
0.1M	0.0357	7.10
0.01M	0.0595	13.5



(A)



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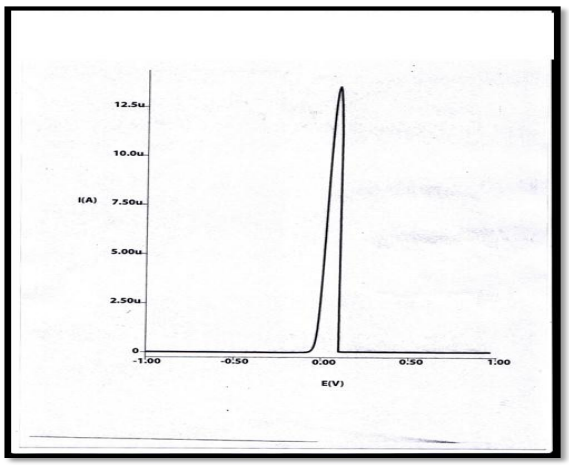


(C)

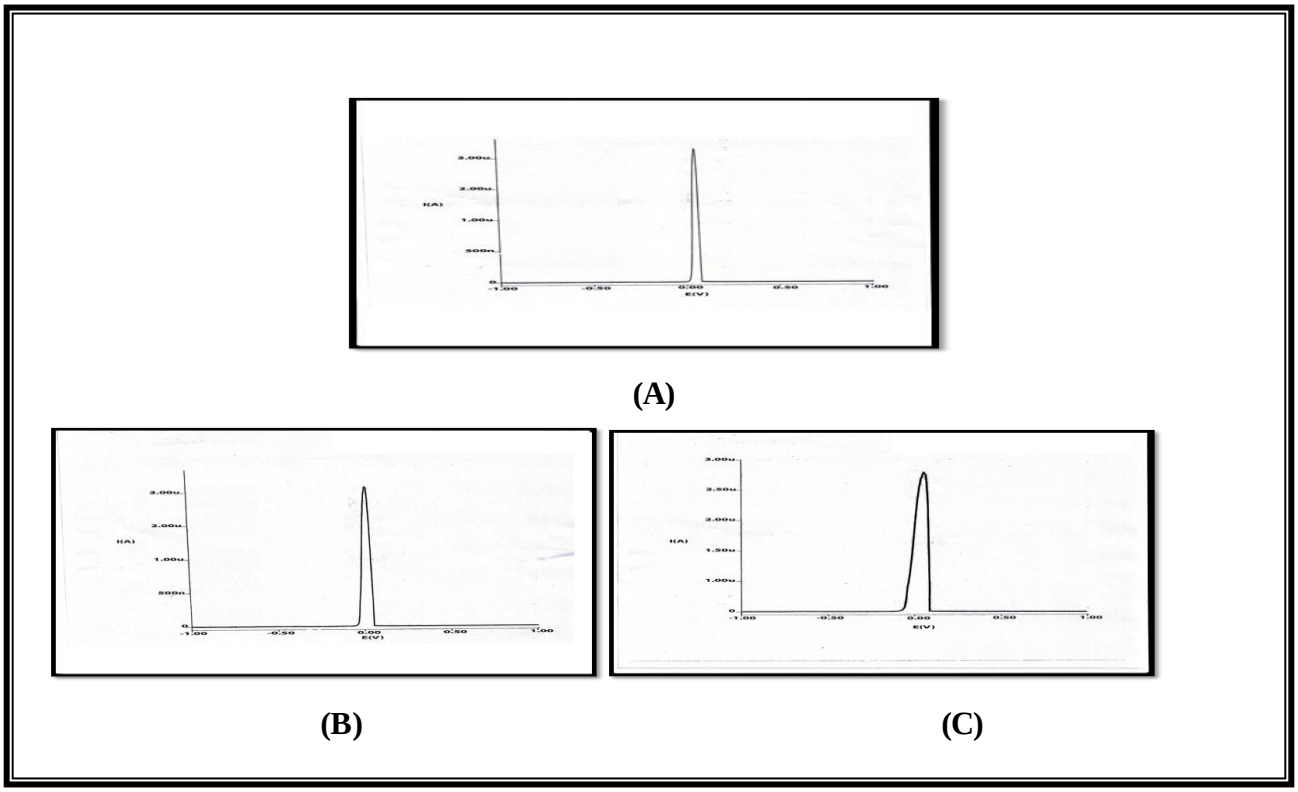
Figure (1): Differential pulse polarogram of $1.2*10^{-4}$M of Chrysin in (A) 1M NaOH, (B) 0.1M NaOH, (C) 0.01M NaOH.

Table (II) display the influence of different supporting electrolyte on a polarographic wave and diffusion current of Hesperetin at a hanging mercury drop electrode (HMDE).

Under initial conditions, differential pulse polarograms of $1.2*10^{-4}$M of Hesperetin were recorded and illustrated in figures (2-4). The polarogram shows a one polarographic wave in acidic media, while in a basic medium a new peak at E_p = 0.416V appears.

Table (II): Peak potential and Peak current of $1.2*10^{-4}$M Hesperetin in different supporting electrolyte

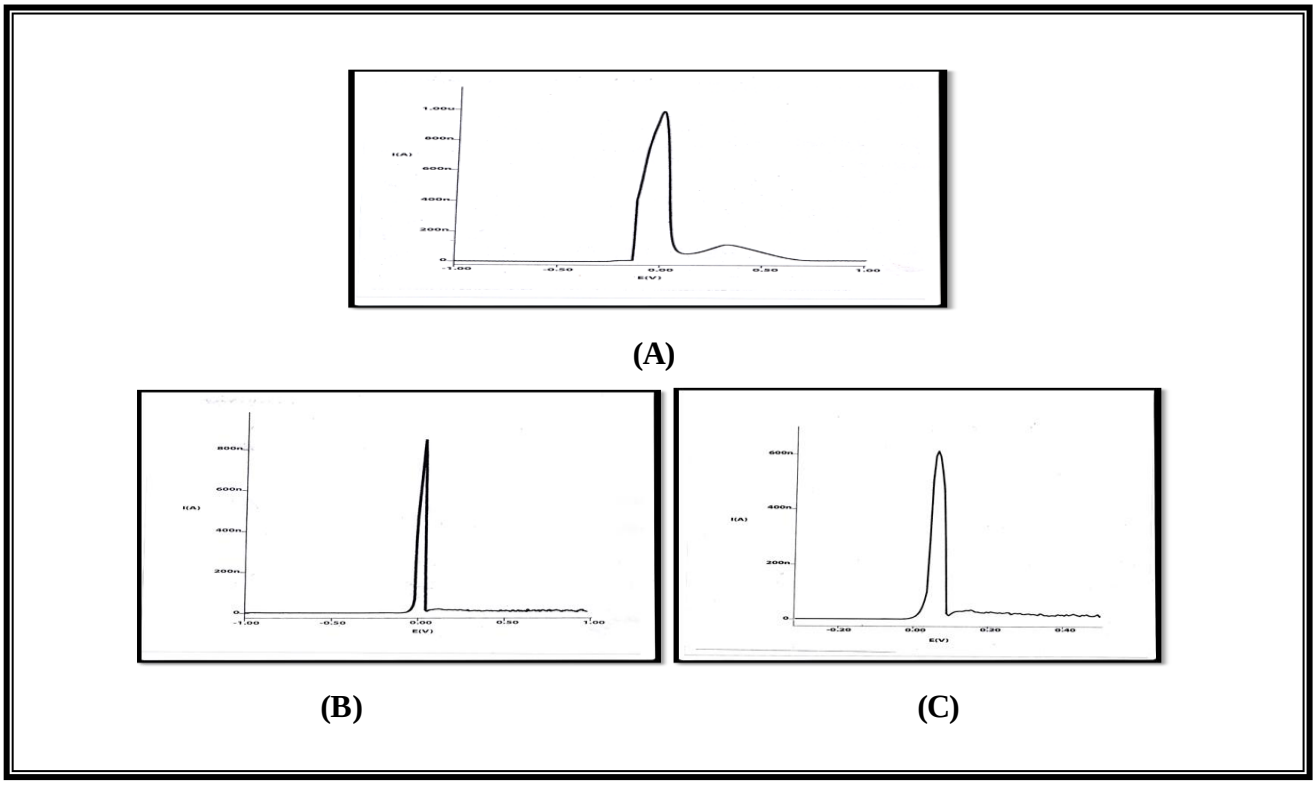
Concentration of supporting electrolyte	**Potassium chloride**		**Sodium hydroxide**		**Hydrochloric acid**	
	E_p (V)	I_d (µA)	E_p (V)	I_d (µA)	E_p (V)	I_d (µA)
1M	0.0470	0.790	– 0.0418 0.416	0.918 0.140	0.0712	3.40
0.1M	0.0534	0.839	0.0238	0.820	0.0655	3.28
0.01M	0.0592	1.21	0.0891	0.615	0.0653	2.71



(A)

(B) **(C)**

Figure (2): Differential pulse polarogram of $1.2*10^{-4}$M of Hesperetin in (A) 1M HCl, (B) 0.1M HCl, (C) 0.01M HCl.



(A)

(B) **(C)**

Figure (3): Differential pulse polarogram of $1.2*10^{-4}$M of Hesperetin in (A) 1M NaOH, (B) 0.1M NaOH, (C) 0.01M NaOH.

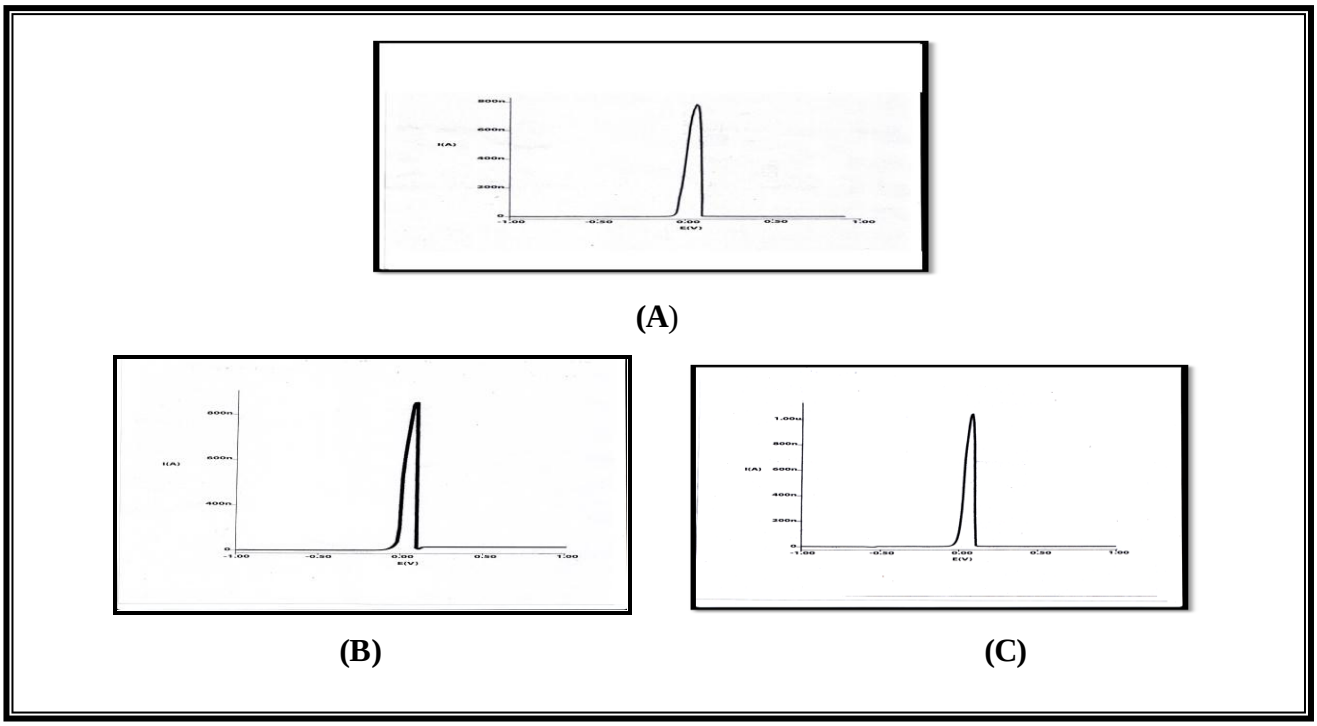


Figure (4): Differential pulse polarogram of $1.2*10^{-4}$M of Hesperetin in (A) 1M KCl, (B) 0.1M KCl, (C) 0.01M KCl.

The effect of drop size on the peak current of flavonoids was studied in range between (1 to 9 mm^3). As surface area of mercury drop (HMDE) increases the peak current increases, due to an increase in a reduction process on the surface of the mercury drop.

Table (III) shows the correlation between drop size and peak current in 1M HCl solution for hesperetin and in 0.01M NaOH for chrysin.

Table (III): Dependence of peak height and peak potential on the drop size in D.P.P

Species	Drop size(mm^3)	E_p (V)	I_d (µA)
Chrysin	1	0.0592	1.70
	3	0.0592	3.18
	5	0.0595	4.15
	7	0.0595	4.31
	9	0.0595	5.07
Hesperetin	1	0.0702	0.920

	3	0.0710	1.79
	5	0.0710	2.15
	7	0.0708	2.61
	9	0.0712	2.82

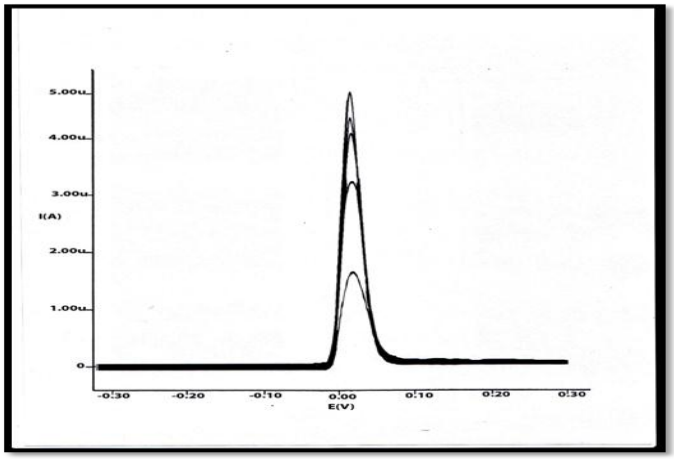


Figure (5): Polarogram of (1.2*10^{-4}M) Chrysin in 1M NaOH recorded on different drop size.

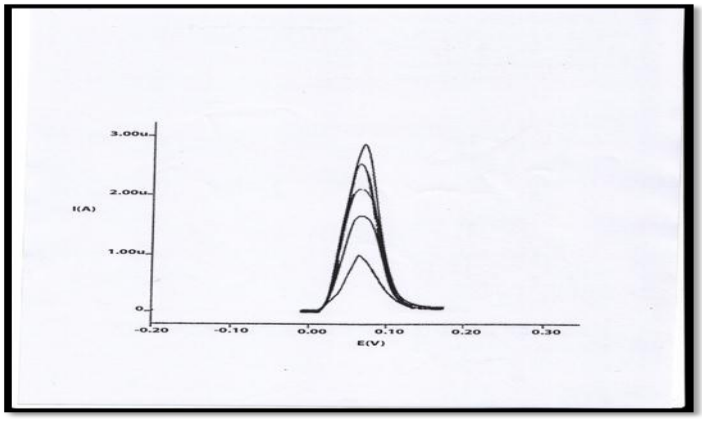


Figure (6): Polarogram of (1.2*10^{-4}M) Hesperetin in 1M HCl recorded on differen drop size.

The effect of deposition time of 5 to 70 sec. was examined for the polarographic measurements of 1.2*10^{-4}M flavonoids in 1M HCl solution for Hesperetin and in 0.01M NaOH for Chrysin. Table (IV) presents the relation between deposition time with peak potential and peak current, which shows that the peak potential does not exhibit any significant changes while the peak current increase gradually with the increase in deposition

time also the peak shape deteriorated over (60sec.), so the optimum deposition time of 60 sec. was selected for our optimization for all of them.

Table (IV): Correlation between peak height and peak potential with the Deposition time in D.P.P

Flavonoid	Chrysin		Hesperetin	
Deposition time (sec)	E_p (V)	I_d (µA)	E_p (V)	I_d (µA)
5	0.0595	3.45	0.0710	1.24
10	0.0595	3.97	0.0710	1.33
15	0.0595	4.06	0.0713	1.39
20	0.0594	4.08	0.0712	1.46
25	0.0594	4.17	0.0711	1.61
30	0.0593	4.23	0.0712	1.67
35	0.0592	5.15	0.0712	1.83
40	0.0592	5.20	0.0712	1.92
45	0.0590	5.30	0.0712	1.98
50	0.0592	5.98	0.0712	2.07
55	0.0591	6.23	0.0712	2.15
60	0.0590	6.25	0.0712	2.37
65	0.0590	7.05	0.0712	2.10
70	0.0590	8.42	0.0712	1.95

The polarographic measurements were carried out for two flavonoids ($1.2*10^{-4}$M) to determine the optimum equilibrium time. The effect of this operating parameter was studied over the range of (1-10 sec.) at constant temperature 298K, drop size 9 mm^3, and deposition time 60 sec. The results in table (V) showed that the peak current had a higher value at equilibrium time (5 sec.), while the peak potential approximately constant, and figure (4).

Table (V): Effect of equilibrium time on peak potential and peak current in D.P.P

Flavonoid	Chrysin		Hesperetin	
Equilibrium time (sec)	E_p (V)	I_d (µA)	E_p (V)	I_d (µA)
1.0	0.0595	4.30	0.0713	1.51
2.0	0.0595	5.87	0.0713	1.78
3.0	0.0597	6.51	0.0715	2.06
4.0	0.0592	8.37	0.0712	1.95
5.0	0.0592	9.67	0.0712	2.41
6.0	0.0590	9.15	0.0712	2.15
7.0	0.0592	7.34	0.0710	1.58
8.0	0.0592	7.06	0.0715	1.44
9.0	0.0591	6.90	0.0715	2.13
10.0	0.0592	6.81	0.0713	1.41

The polarographic measurements of $1.2*10^{-4}$M flavonoids were performed to determine the optimum pulse amplitude at constant temperature 298K, drop size 9 mm^3, deposition time 60 sec., and equilibrium time 5 sec. The effect of this operating variable was studied over the range of (10 – 100mv), Tables (VI). It was found that the peak current increased with the increase in pulse amplitude, figures (5), (6), also it was observed that the best shape of peak was obtained at 50 mV pulse amplitude, over this the shape of the peak became deformed. So, 50 mV pulse amplitude was the preferred choice for this work.

Table (VI): Correlation between peak height, peak potential with the pulse amplitude in D.P.P

Flavonoid	Chrysin		Hesperetin	
Pulse amplitude (V)	E_p (V)	I_d (µA)	E_p (V)	I_d (µA)
0.010	0.0651	4.56	0.0774	1.75
0.020	0.0633	5.23	0.0772	2.23
0.030	0.0595	6.16	0.0712	2.68
0.040	0.0595	7.19	0.0710	3.22
0.050	0.0595	8.24	0.0710	3.59
0.060	0.0595	9.48	0.0702	4.81
0.070	0.0595	10.6	0.0702	5.08
0.080	0.0590	11.9	0.0700	5.64
0.090	0.0590	12.5	0.0702	6.04
0.100	0.0592	11.8	0.0702	5.09

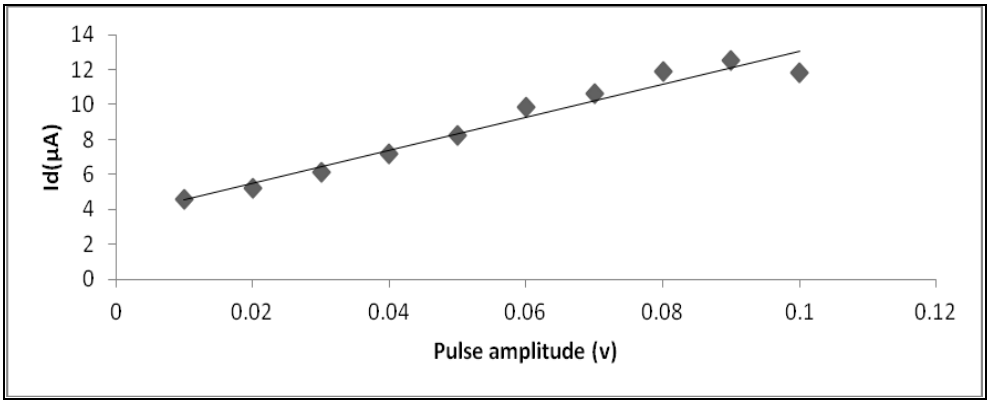


Figure (5): The effect of Pulse amplitude on a peak current of Chrysin using D.P.P

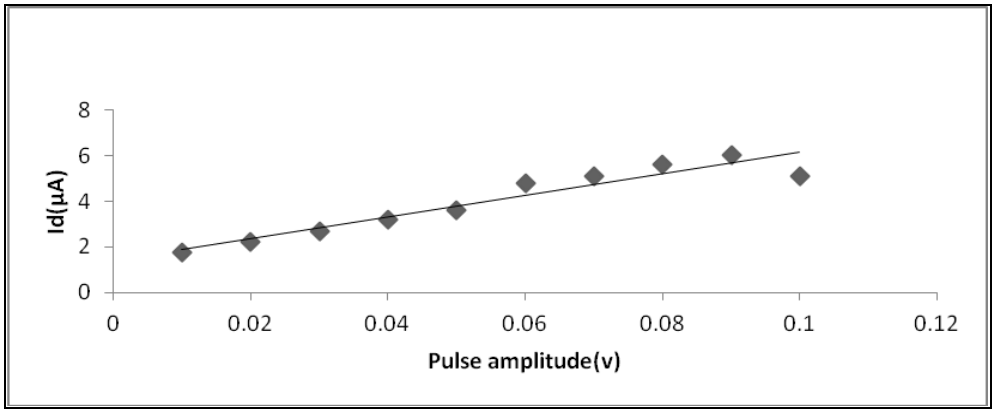


Figure (6): The effect of Pulse amplitude on a peak current of Hesperetin using D.P.P

The polarographic measurements of $1.2*10^{-4}$M flavonoids were performed to determine the optimum pulse time at constant temperature 298K, drop size 9 mm^3, deposition time 60 sec., equilibrium time 5 sec., pulse amplitude 50 mV. The effect of this operating variable was studied over the range (10 - 50 m.sec.). Tables (VII, VIII) show the relation between pulse time in second and the peak potential and peak current, which implies that 400 m.sec was the best choice for, Chrysin, and Hesperetin also in figure (7, 8).

Table (VII): Dependence of the Chrysin reduction peak height on the pulse time in D.P.P

Pulse time (sec)	E_p (V)	I_d (µA)
0.010	0.0598	6.46
0.020	0.0598	7.28
0.030	0.0603	8.25
0.040	**0.0601**	**11.2**
0.050	0.0594	9.51

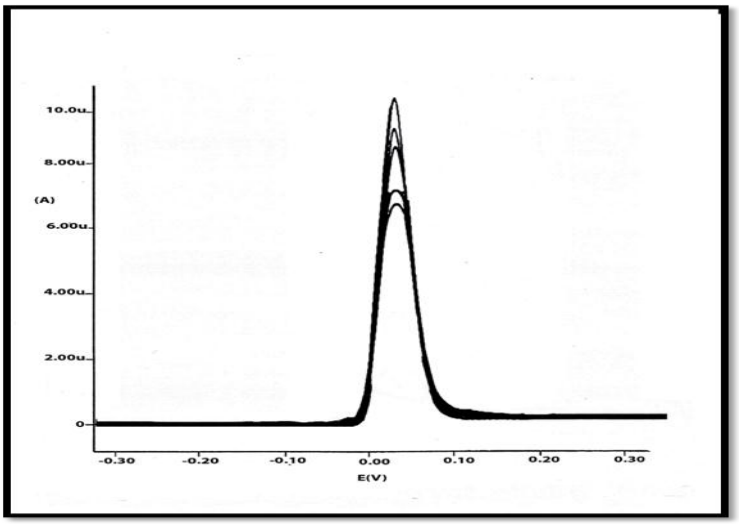


Figure (7): The effect of Pulse time on a peak current of ($1.2*10^{-4}$M) Chrysin using D.P.P

Table (VIII): Dependence of the Hesperetin reduction peak height on the pulse time in D.P.P

Pulse time (sec.)	E_p (v)	I_d (µA)
0.010	0.0702	0.844
0.020	0.0710	1.27
0.030	0.0710	1.65
0.040	**0.0715**	**3.07**
0.050	0.0712	2.13

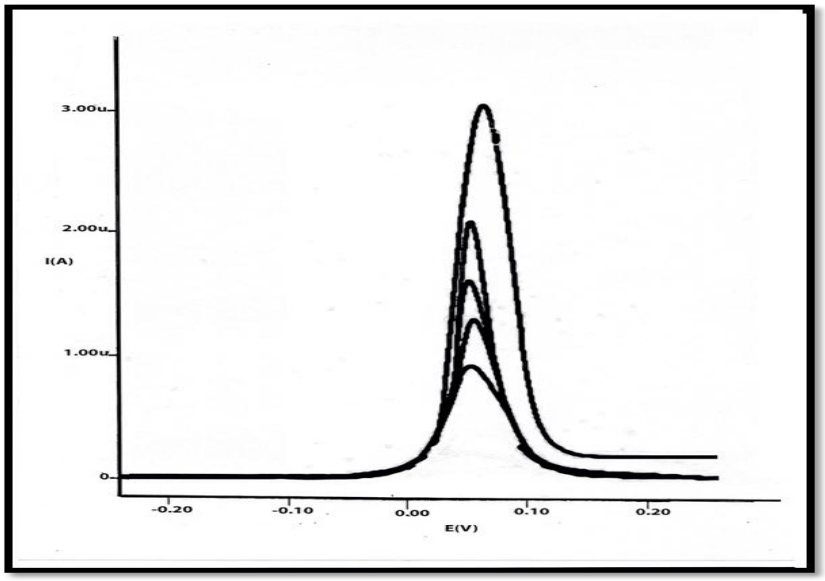


Figure (8): The effect of Pulse time on a peak current of ($1.2*10^{-4}$M) Chrysin using D.P.P

Table (IX) shows the experimentally optimum conditions used in this work.

Table (IX): The optimal conditions for Flavonoids, using (D.P.P.) at Hanging Drop Electrode (HMDE).

Instrumental conditions and its units	Chrysin	Hesperetin
Initial potential (V)	- 1.00	- 1.00
Final potential (V)	+ 1.00	+ 1.00
Drop size (mm^3)	($9mm^3$)	($9mm^3$)
Deposition time (sec)	60 sec	60 sec
Equilibrium time (sec)	5 sec	5 sec
Pulse amplitude (V)	0.050	0.050
Pulse time (sec)	0.040	0.040
Voltage step (V)	0.006	0.006
Voltage step time (sec)	0.40	0.40
Scan rate (V/s)	0.015	0.015
Initial purge time (Min)	5	5
Supporting electrolyte	1M NaOH	1M HCl

The direct proportionality between the limiting diffusion current and depolarizer concentration is expressed in an equation derived by Ilkovic [16, 17], equation (1.1). The diffusion current is directly proportional to the analytical concentration of depolarizer in the solution:

$$i_d = KC$$

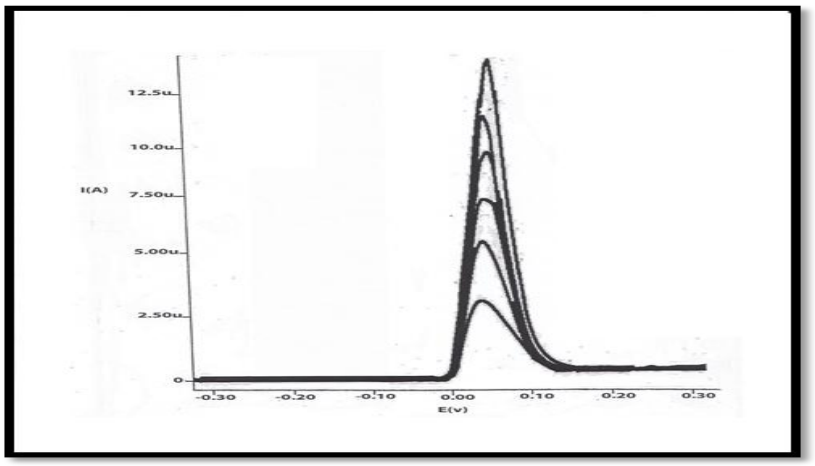


Figure (9): Polarograms of different concentrations of Chrysin in 0.01M NaOH supporting electrolyte by (D.P.P.)

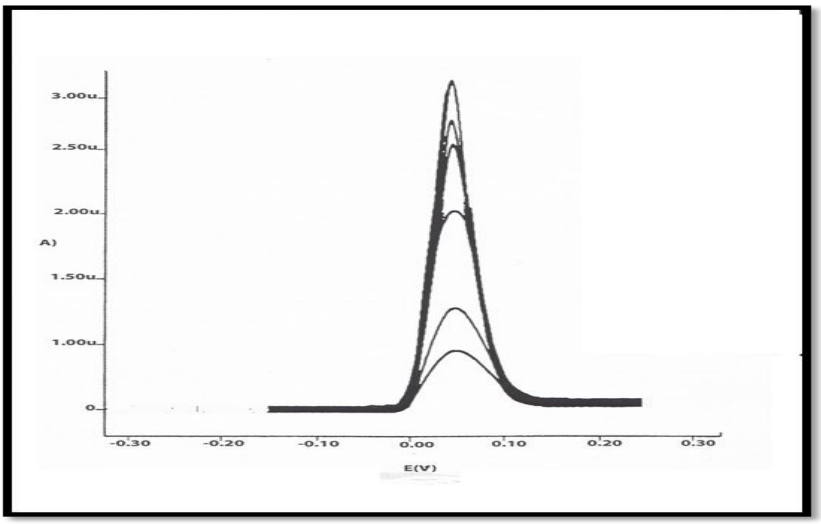


Figure (10): Polarograms of different concentrations of Hesperetin in 1M HCl supporting electrolyte by (D.P.P.)

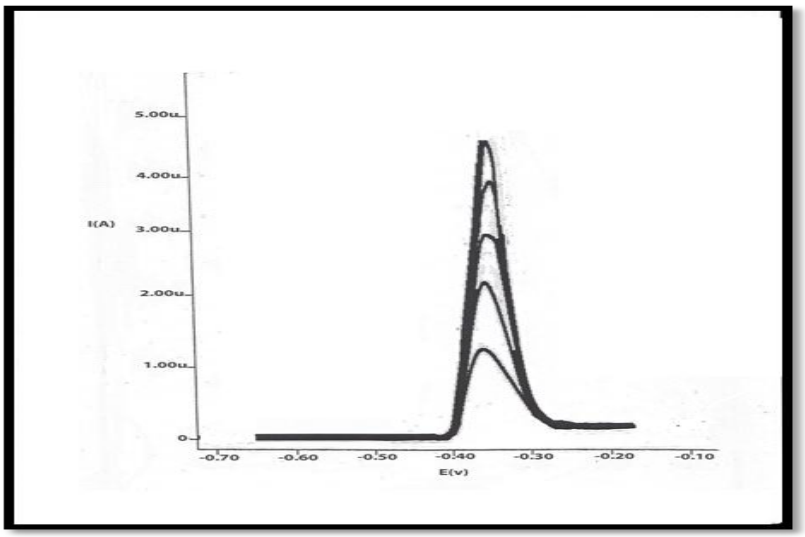


Figure (11): Polarograms of different concentrations of Lead (II) in 1M HCl supporting electrolyte by (D.P.P.)

The peak height was plotted against the concentration of these species, figure (12-14), and the treated value for the calibration graphs are summarized in Table (XI).

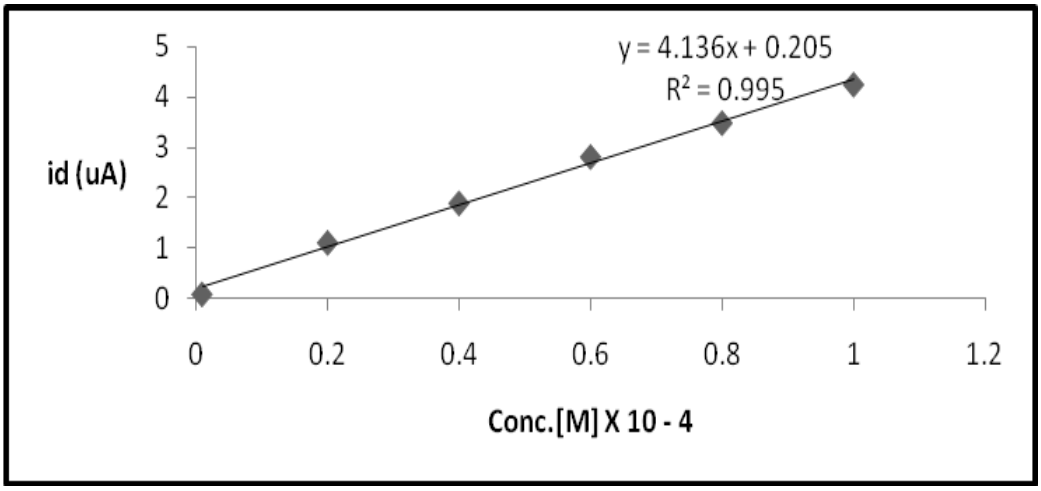


Figure (12): Relation between concentration and Peak current of Lead (II).

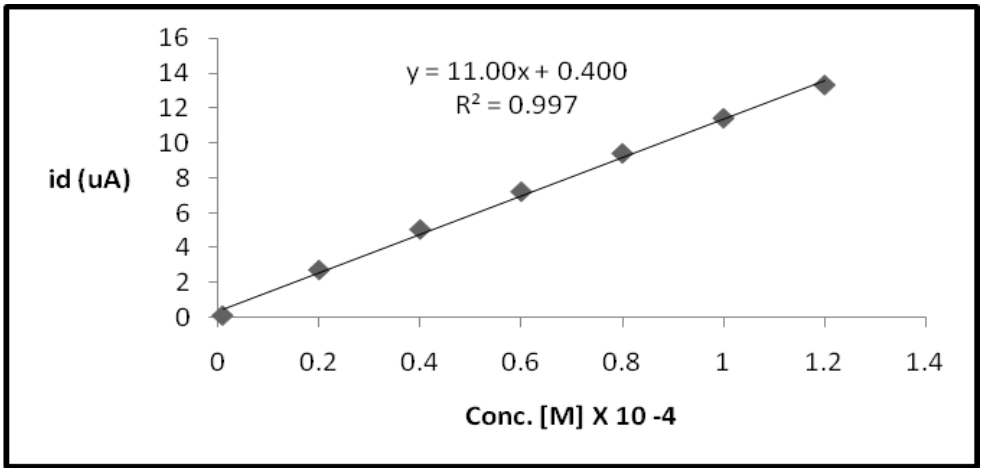


Figure (13): Relation between concentration and Peak current of Chrysin.

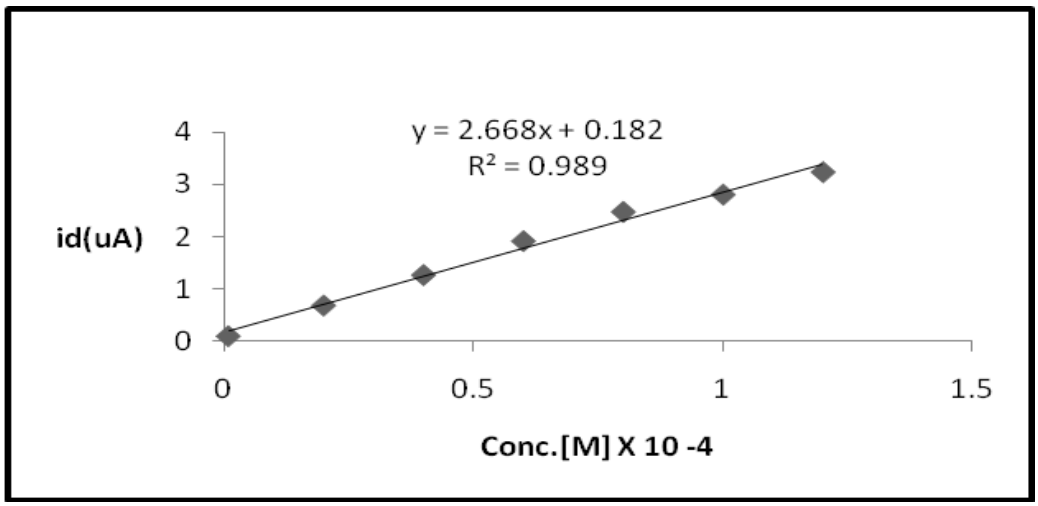


Figure (14): Relation between concentration and Peak current of Hesperetin.

Table (X): Relation between concentration and peak current

Species	Conc. (M)	E_p (V)	I_d (µA)
Chrysin	$0.2*10^{-4}$	0.0590	2.71
	$0.4*10^{-4}$	0.0595	5.03
	$0.6*10^{-4}$	0.0595	7.19
	$0.8*10^{-4}$	0.0598	9.39
	$1.0*10^{-4}$	0.0590	11.40

	$1.2*10^{-4}$	0.0595	13.30
Hesperetin	$0.2*10^{-4}$	0.0712	0.688
	$0.4*10^{-4}$	0.0712	1.27
	$0.6*10^{-4}$	0.0712	1.92
	$0.8*10^{-4}$	0.0712	2.48
	$1.0*10^{-4}$	0.0712	2.81
	$1.2*10^{-4}$	0.0712	3.24
Lead (II)	$0.2*10^{-4}$	– 0.387	1.12
	$0.4*10^{-4}$	– 0.387	1.90
	$0.6*10^{-4}$	– 0.387	2.82
	$0.8*10^{-4}$	– 0.387	3.49
	$1.0*10^{-4}$	– 0.387	4.25

Table (XI): Analytical value of treatment of calibration graphs

Parameters	**Value**		
	Chrysin	**Hesperetin**	**Pb (II)ion**
Correlation coefficient (r^2)	0.9995	0.9928	0.9978
Regression equation (y = ax + b)	Y=10.79-0.665	Y=2.677+0.2207	Y=3.925+0.361
Slope (a) (µA. µM)	10.79	2.677	3.925
Intercept (b)	- 0.665	+ 0.2207	+ 0.361
Linear range (M)	$(0.2\text{-}1.2)*10^{-4}$	$(0.2\text{-}1.2)*10^{-4}$	$(0.2\text{-}1.0)*10^{-4}$
Peak potential E_p (V)	0.0595	0.0712	- 0.387

The actual number of transferred electrons in a reversible electrode process, and the actual value of $E_{½}$, can be determined by the Heyrovsky – Ilkovic equation which describes the cathode reduction wave [18].

$$E_{.d.c.} = E_{1/2} - \frac{0.0591}{n} \log \frac{i}{id - i} \qquad \text{…….. (3.1)}$$

Where:

E: applied potential (V),

n: number of electrons transferred,

i: diffusion current at applied potential (E) in (µA),

id: limiting diffusion current in (µA).

Table (XII): Potential and current calculated from polarograms of ($1.2*10^{-4}$M) Chrysin in 0.01M NaOH.

E (V)	i (µA)	i/id – i	Log i/id – i
0.0551	6.2	0.849	– 0.0711
0.0563	6.4	0.901	– 0.0453
0.0570	6.48	0.923	– 0.034
0.0590	6.7	0.985	– 0.007
0.0612	6.9	1.045	0.019
0.0632	7.2	1.143	0.058
0.0651	7.5	1.250	0.097

Table (XIII): Potential and current calculated from polarograms of ($1.2*10^{-4}$M) Hesperetin in 1M HCl.

E (V)	i (µA)	i/id – i	log i/id – i
0.062	1.10	0.477	– 0.321
0.064	1.30	0.619	– 0.208

0.067	1.50	0.789	– 0.103
0.0712	1.65	0.942	– 0.026
0.0718	1.90	1.267	0.103
0.0765	2.10	1.614	0.208
0.0778	2.30	2.089	0.320

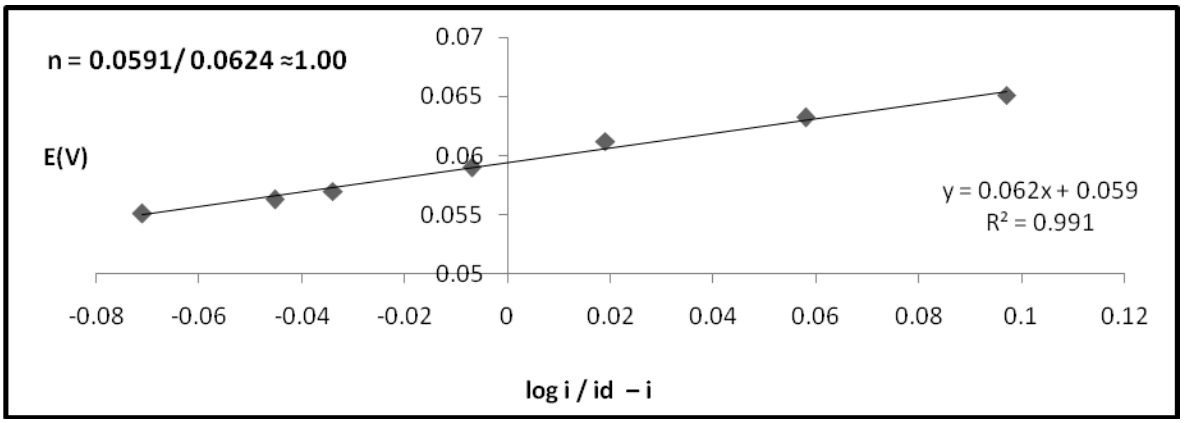


Figure (15): Relation between log (i/id – i) vs. E applied for ($1.2*10^{-4}$M) Chrysin in 1M NaOH.

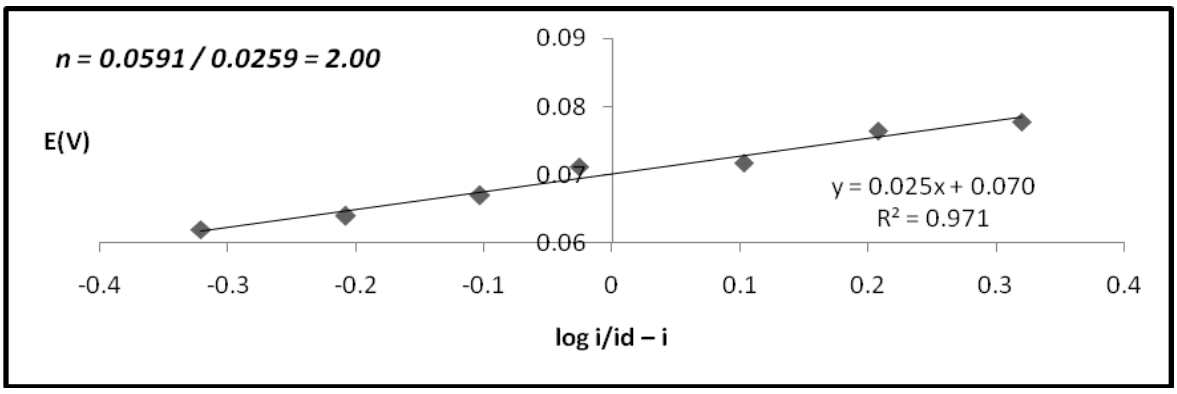


Figure (16): Relation between log (i/id – i) vs. E applied for ($1.2*10^{-4}$M) Hesperetin in 1M HCl.

Table (XIV): Number of electrons from a plot of Heyrovsky – Ilkovic equation

Parameter	Chrysin	Hesperetin

Correlation coefficient (R^2)	0.9916	0.9715
Slope	0.0624	0.0259
Number of electrons	1.0	2.2
$E_{1/2}$ (V)	0.0594	0.0701

Addition of different concentration of Flavonoids (Chrysin, Hesperetin) in a range of ($2*10^{-5}$ – $1*10^{-4}$M) to a solution of a constant concentration ($1*10^{-4}$M) of Pb (II) ion, show the appearance of a new peak in a more negative potential than the Pb (II) peak, with a gradual decrease in a peak current of Pb (II) ions which suggests the complex formation between them, figure (17, 18).

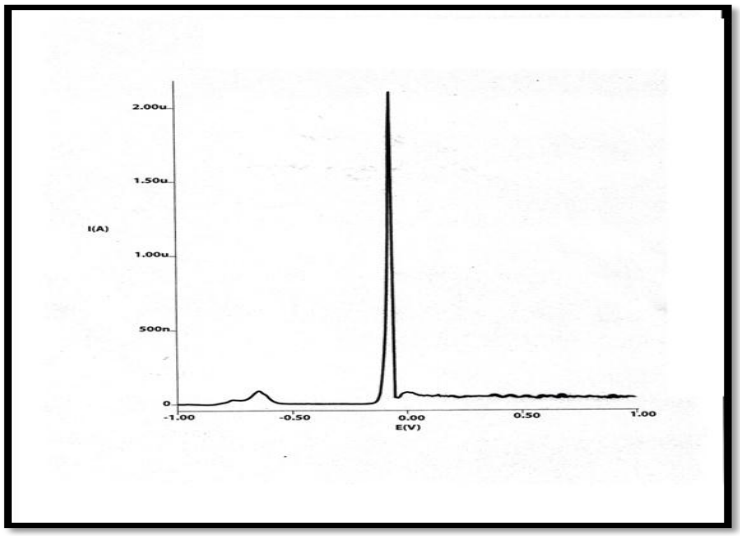


Figure (17): Differential pulse polarogram of Chrysin – Pb (II) complex in 0.0 1M NaOH, at 298K.

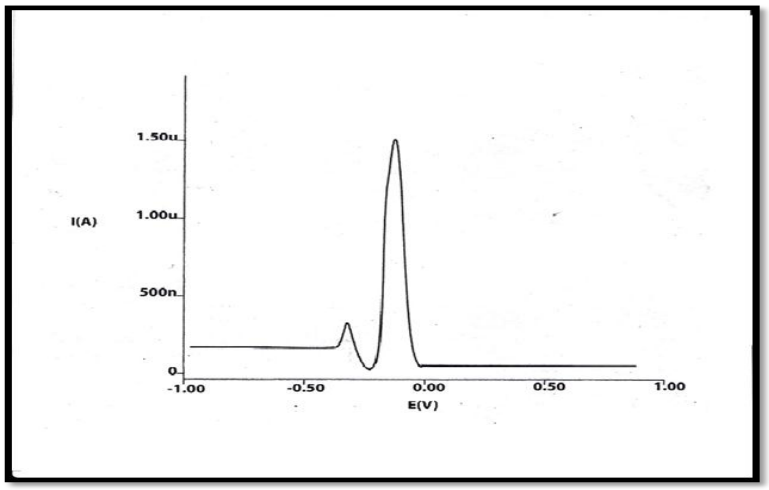


Figure (18): Differential pulse polarogram of Hesperetin – Pb (II) complex in 1M HCl, at 298K.

Table (XV): Electrochemical reduction of Pb (II) – flavonoids systems at (HMDE) by differential pulse polarography

Flavonoid (L), and medium	Conc. of (L) (M)	I_p Pb (II) (µA)	E_p Pb (II) (V)	I_p complex (µA)	E_p complex (V)
Hesperetin in1M HCl	**$2*10^{-5}$**	**0.155**	**- 0.387**	**0.126**	**- 0.393**
	$4*10^{-5}$	0.141	- 0.387	0.133	- 0.401
	$6*10^{-5}$	0.119	- 0.387	0.185	- 0.409
	$8*10^{-5}$	0.116	- 0.387	0.191	- 0.416
	$10*10^{-5}$	0.112	- 0.387	0.211	- 0.421
Chrysin in 0.01M NaOH	**$2*10^{-5}$**	**0.269**	**- 0.702**	**0.069**	**- 0.706**
	$4*10^{-5}$	0.257	- 0.702	0.073	- 0.720
	$6*10^{-5}$	0.233	- 0.703	0.102	- 0.737
	$8*10^{-5}$	0.226	- 0.703	0.105	- 0.742
	$10*10^{-5}$	0.138	- 0.705	0.117	-0.744

The stoichiomtery and the stability constant of lead (II) complex with flavonoids using a polarographic method were calculated by lingane equation [19].

$$\Delta E = E_M - E_C = \frac{0.0591}{n} \log K_{ML_P} + P \frac{0.0591}{n} \log[L]$$

……. (3.2)

Table (XVI): Application of lingane equation in pb - Chrysin complex at 298K, and $1*10^{-4}$M Pb (II) ion.

No.	Conc. of (L), M	Log (L)	$\Delta E_{½}$, (V)
1	$2*10^{-5}$	- 4.69	- 0.004
2	$4*10^{-5}$	- 4.39	- 0.018
3	$6*10^{-5}$	- 4.22	- 0.035
4	$8*10^{-5}$	- 4.09	- 0.040
5	$10*10^{-5}$	- 4.00	- 0.042

Table (XVII): Application of lingane equation in Pb - Hesperetin complex at 298K, and $1*10^{-4}$M Pb (II) ion.

No.	*Conc. of (L), M*	*Log (L)*	$\Delta E_{1/2}$, (V)
1	$2*10^{-5}$	- 4.69	- 0.006
2	$4*10^{-5}$	- 4. 39	- 0.014
3	$6*10^{-5}$	- 4.22	- 0.022
4	$8*10^{-5}$	- 4.09	- 0.029
5	$1*10^{-4}$	- 4.00	- 0.034

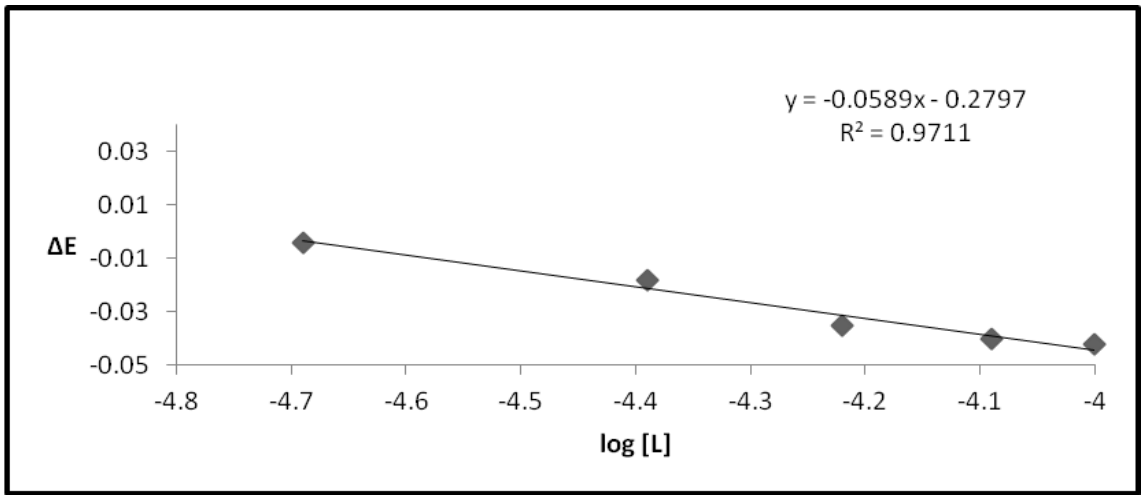


Figure (19): Lingane plot of $\Delta E_{½}$ of Pb – Chrysin vs. log (L).

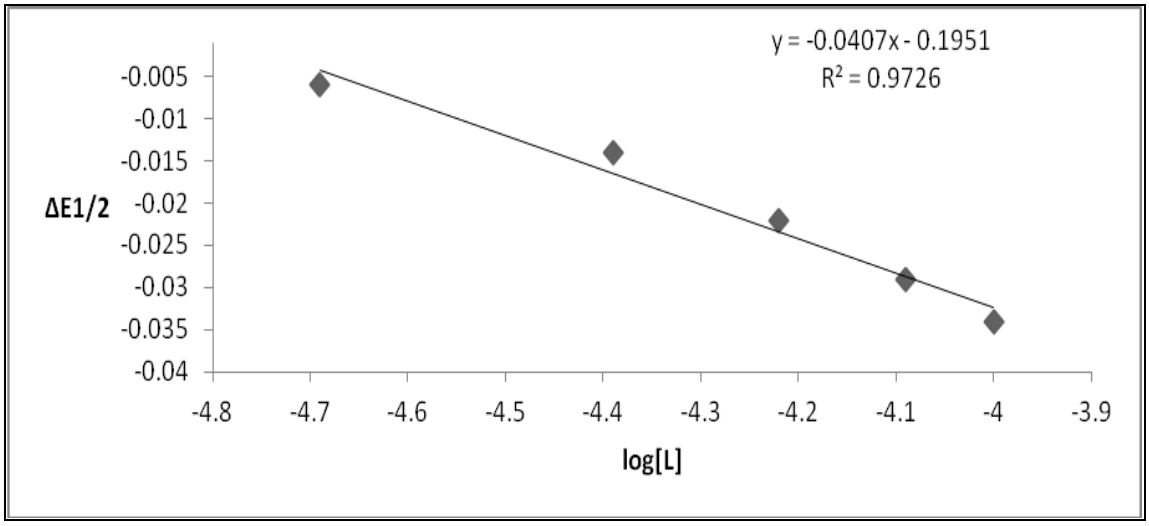


Figure (20): Lingane plot of $\Delta E_{1/2}$ of Pb – Hesperetin vs. log (L).

Table (XVIII): Stability constants of metal – flavonoid.

Pb (II) - flavonoid complex	Pb (II) - flavonoid	Stability constant
Pb (II) - Chrysin	(1:1)	$5.40*10^4$
Pb (II) - Hesperetin	(1:1)	$4.00*10^6$

Temperature has an effect upon several of the variables that govern the diffusion current for a given species, the most temperature – sensitive of the factors in the Ilkovic equation is the diffusion coefficient, and as a consequence, temperature control is necessary for accurate polarographic measurements. So all measurements were performed at different temperature (293 - 313K), Table (XIX) - (XX) shows the calculated electrode parameters for the Pb – flavonoid systems

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Table (XIX): Electrochemical reduction of (1:1) Pb (II) - Chrysin complex at HMDE in 0.01M NaOH at various temperatures

T (K)	$E_{1/2}$ (V)	I_d (µA)	An	$D^{1/2}$ (cm^2/s)	K^o_{fh} (cm/s)
293	- 0.725	0.122	0.9945	0.7291	$1.507*10^{-13}$
298	- 0.744	0.129	1.003	0.7709	$5.976*10^{-14}$
303	- 0.751	0.181	1.024	1.0817	$3.473*10^{-14}$
308	- 0.763	0.211	1.036	1.2610	$1.717*10^{-14}$
313	- 0.763	0.215	1.050	1.2840	$8.200*10^{-15}$

Table (XX): Electrochemical reduction of (1:1) Pb (II) - Hesperetin complex at HMDE in 1M HCl at various temperatures

T (K)	$E_{1/2}$ (V)	I_d (µA)	αn	$D^{1/2}$ (cm^2/s)	K^o_{fh} (cm/s)
293	- 0.393	0.107	2.030	0.3242	$3.069*10^{-15}$
298	- 0.421	0.118	1.914	0.3572	$1.866*10^{-15}$
303	- 0.432	0.130	1.931	0.3942	$9.954*10^{-16}$
308	- 0.441	0.143	1.925	0.4333	$6.209*10^{-16}$
313	- 0.446	0.157	1.939	0.4757	$3.708*10^{-16}$

The enthalpy of activation at constant pressure ΔH^*_p, has been calculated by substituting the value of slope of the plot (log K^o_{fh} vs. 1/T) in the van't Hoff equation, figure (21, 22).

Slope = ─ ΔH / 2.303 R

ΔH^*_p = 2.303R * Slope ….. (3.5)

R = Gas constant

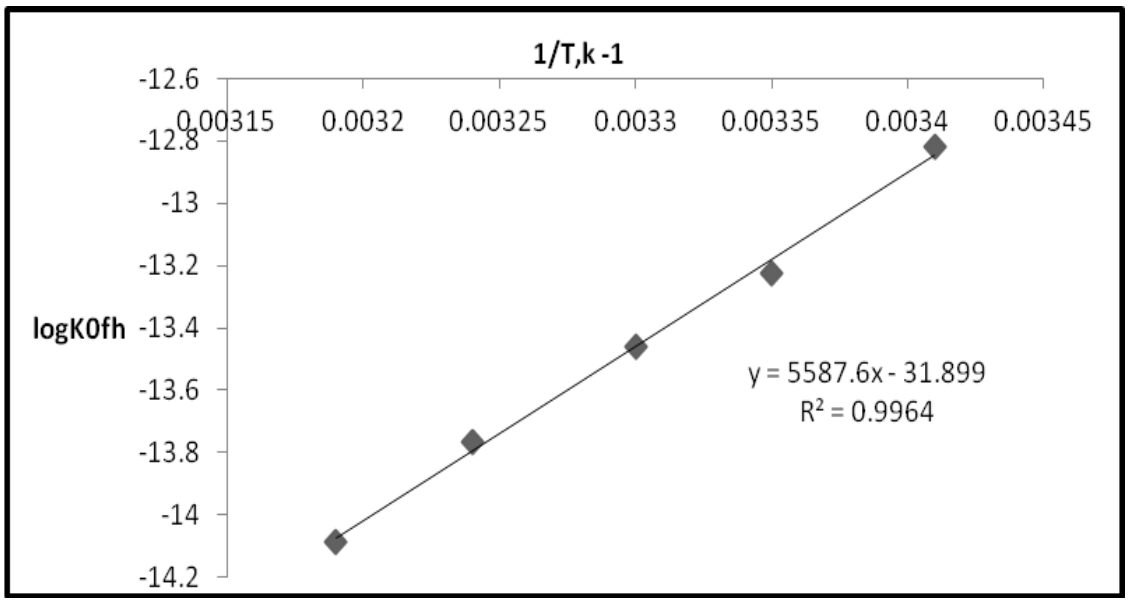

Figure (21): log K^o_{fh} vs. 1/T of Pb (II) - Chrysin interaction.

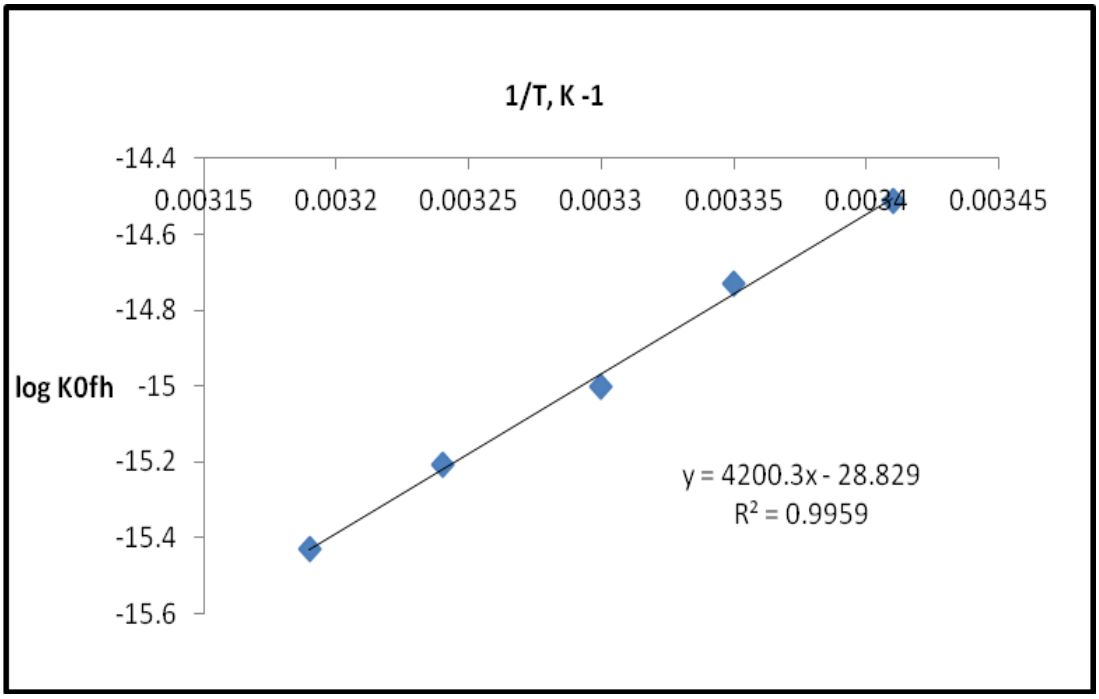

Figure (22): log K^{o}_{fh} vs. 1/T of Pb (II) - Hesperetin interaction.

The enthalpy of activation at constant volume (ΔH^*_v) was evaluated from equation (3.6).

$$\Delta H^*_p = \Delta H^*_V + RT \qquad \ldots\ldots\ldots (3.6)$$

The activation free energy change (ΔG^*) were determined by the equation (3.7) [20]

$$K^{o}_{fh} = (K\ T/h)\ .\ ro\ .\ \exp^{(-\Delta G^*/R\ T)} \qquad \ldots\ldots\ldots (3.7)$$

Where

K: Bolzman constant = $1.38*10^{-23}$ $J.K^{-1}$

h: Plank s constant = $6.62*10^{-34}$ J.s

ro: mean distance between depolarized ions in the bulk solution, ro is taken as $2*10^{-8}$ cm [21].

And the entropy of activation (ΔS^*) was calculated using following equation:

$$\Delta G^* = \Delta H^*_V - T\ \Delta S^* \qquad \ldots\ldots (3.8)$$

$$\Delta S^* = (\Delta H^*_V - \Delta G^*)\ /\ T \qquad \ldots\ldots (3.9)$$

Table (XXI): Thermodynamics parameters at different temperature for the interaction of Chrysin with lead (II) ion

T (K)	ΔH^*_P (J/mole)	ΔH^*_V (J/mole)	ΔG^* (J/mole)	ΔS^* (J/k)
293	- 106987	- 109423	71929	- 619
298	- 106 987	- 109465	75449	- 620
303	- 106987	- 109506	78082	- 619.1
308	- 106987	- 109548	81172	- 619.2
313	- 106987	- 109584	84415	- 621

Table (XXII): Thermodynamics parameters at different temperature for the interaction of hesperetin with lead (II) ion

T (K)	ΔH^*_P (J/mole)	ΔH^*_V (J/mole)	ΔG^* (J/mole)	ΔS^* (J/k)
293	- 80424	- 82860	109936	- 658
298	- 80424	- 82902	113087	- 657.6
303	- 80424	- 82943	116609	- 658.6
308	- 80424	- 82985	119784	- 658.3
313	- 80424	- 83026	123113	- 658.6

Conclusion

The result obtained prove that hydrochloric acid was the most suitable supporting electrolyte for the reduction of Chrysin and hesperetin by a differential puls polarography, the presence of a new peak in the more negative potential and a decrease in the current peak confirms the complex formation between lead (II) and Chrysin and hesperetin with a parameters (ΔH*p, ΔH*v, ΔG*, ΔS*) were determined at different temperature, which suggests the non-spontaneous of the electrode reduction.

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