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In the Name of Allah
Most Compassionate, Mort Merciful

Edition Word

O Allah, my Lord

Cast felicity in me , facilitate my cause and unknot my tongue to perceive my speech , thanks be upon Him the Evolver of the universe and peace be upon Mohammad and his immaculate and benevolent progeny .

A fledged edition of Al-Bahr , peer reviewed scientific journal, embraces a constellation of research studies pertinent to engineering and natural sciences we do hope to overlap a scientific gap the specialists observe as an academic phenomenon worth being under the lenses of the researchers, that is why there is diversity in the studies to meet the requirements of the journal readership . For the journal, now, comes to the fore , at the efforts of the editorial and advisory boards and the researchers who strain every sinew to publish in Al-Bahr, to be global as to be published in an international publishing house in line with the global scientific journals.

On such an occasion we do pledge the promise of fealty and loyalty to those who observe our issues with love and heed in the International Al-`Ameed for Research and Studies , Department of Cultural and Intellectual Affairs in the Holy Al-`Abbas Shrine and the strenuous endeavour to cull whatever invigorates the scientific interaction and academic research in Iraq and worldwide to create a new generation keeping pace with the development of the current scientific phase and to lay the hands of the researchers, nationwide and worldwide, upon the desired missions.

Thanks be upon Him ,the Evolver ad infinitum .

Consultation and Editaril

A study of electrochemical behavior for redox peaks of Pb(II) ions in human blood samples using Nanosensor

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الخلاصة

تم استخدام تقنية الفولتامتري الحلقي في دراسة الكيمياء الكهربائية لايجاد تاثير درجات الحرارة العالية على قمتي التيار الكهرباتي للاكسدة والاختزال لاحد الملوثات الطبيعية لمحيط الدم في الانسان وهو ايون الرصاص.

الدراسة الحالية هو لمعرفة تاثير درجات الحرارة المختلفة على ايونات الرصاص في وسط الدم باستخدام التحليل بجهاز الفولتامتري الحلقي وايجاد العوامل الكيميائية الثرموداينميك.

تم استخدام متعدد الطبقات للكاربون نانوتيوب في تعديل الاقطاب العاملة الكاربون الزجاجي كمتحسسات نانوية وذلك للكشف عن تاثيرات درجات الحرارة العالية المختلفة على وسط الدم بوجود ايون الرصاص بتقنية الفولتامتري الحلقي.

اكدت نتائج قمتي الاكسدة والاختزال لايونات الرصاص عند الجهد الكهربائي(0.5-) و (0.11) فولت على التوالي عند درجة حرارة منخفضة (20) درجة مئوية ومراقبة هذه القمم بزيادة درجة الحرارة الى (60) درجة مئوية. لقد وجد بان قمة التيار الكهربائي الانودية لايون الرصاص في محيط الدم تقل بزيادة ارتفاع الحرارة، ولكن القمة الكاثودية تزداد ثلاثة اضعاف بارتفاع الحرارة الى (٦٠) درجة مئوية. لذا فان طاقة التنشيط المستخرجة من معادلة ارينيوس لقمة الاكسدة هي (15.541-) kJ.mol-1.K-1 وقيمتها لقمة الاختزال هي (35.271) kJ.mol-1.K-1 اما قيم الثرموداينمك الاخرى مثل تغير الانثالبي المنشط و تغير جبس المنشط و تغير الانتروبي المنشط تم ايجادها باستخدام معادلة ايرنج.

لقد دعمت النتائج من الاشخاص الملوثين بايونات الرصاص وتاثرها بدرجات حرارية عالية نتيجة التعرض لاسباب البيئية كما في العاملين في المصانع وذلك بتكوين المعقد بين ايون الرصاص وتركيبة الدم مما يسبب ترسب ايون الرصاص على الدماغ نتيجة اختزال ايون الرصاص الى عنصر الرصاص مما تسبب امراض مثل الزهايمر الذي يصيب الكبار او التوحد كما في الصغار.

الكلمات المفتاحية

ايونات الرصاص، تقنية الفولتامتري الحلقي، وسط الدم، المتحسسات النانوية.

Abstract

The electrochemical method using cyclic voltammetrictechniquewas determined the effect of high temperature on the redox current peaks of one of pollutant in an environment are lead ions in vitro for humanblood medium. The present study showed the effect of different temperatures on the lead ions in blood medium by analysis cyclic voltammetric analysis and determination the chemical thermodynamic factors. It was usedmultiwall carbon nanotube (MWCNT) / glassy carbon electrode (GCE),modified working electrode (MWCNT/GCE) as a good sensor to detection the effect of different temperatures on the blood medium in presence of Pb(II) ions.

The results was confirmed that oxidation and reduction current peak of Pb(II) ions at -(0.5) V and (0.11)V,respectively at low temperature (20)oCand monitoring the redox current peaks against increasing the temperature until (60)oC. It was found that the anodic current peak of lead ions in blood medium was decreased with increasing temperature, but cathodic current peak was enhanced about three times at high temperature (60) oC. Thus, the activation energy (E*) values were determined from Arrhenius equation for oxidative peak is (-15.541) kJ.mol-1.K-1and for anti-oxidative peak is (35.271) kJ.mol-1.K-1Other thermodynamic functions such as change in Enthalpy of activation (ΔH*), change in Gibbs of activation (ΔG*) and change in Entropy of activation (ΔS*) were determined byEyring equation. The results enhanced the blood of people pollutant with lead ions was significant affectedby environment or exposure with different source of high temperature such as workers in factories by complexation with the blood componentand causes to precipitation of heavy metal (Pb) on the brain by the reduction process of Pb(II)/Pb(0) which may be causes different disease such asAlzheimer in adults or Autism in infants.

Keywords

Lead ions, Cyclic voltammetry technique, blood medium, Nanosensor.

1. Introduction

Through previous studies was used electrochemistry techniqueby cyclic voltammetry to detection the effects of environment pollutants such as heavy metals on the composition of blood medium as an electrolyte through the emergence of oxidative and anti-oxidative stress peaks by configuring the complexes between the blood components and the contaminants [1-6].

The studies of electrochemical behavior of the red blood cell (RBC) which included the detection of hemoglobin in RBC by glassy carbon electrode modified with Nafion film at pH (3.5) [7].Different concentrations of glucose in buffer physiological solution was studied in electrochemical analysis to determine the oxidase reagent and compared with routine method [8].Cathodic sweep technique was studied of the oxidation of glucose complex at the gold electrode in different pH to determine the oxidative peak of the complex of –OH group in the process of K_2HPO_4/KH_2PO_4 [9].Cyclic voltammetry studied of the hemotoxicity of lawsone by redox current peaks which cause the hemotoxicity by metabolism of the oxidative reagent [10].Some studies were determined the effect of high temperatures on the components of human blood samples of workers in different factories exposed to the high temperatures which included the biochemical analysis results in serum of the workers [11,12].The study of the relationship between the postmortem interval and blood oxidation-reduction potential (ORP) values at different temperatures was a strong positive correlation in rabbit [13]. Also the effect of bioaccumulation of lead in water can cause health problems [14].The new study of the effect of the storage of blood samples versus the temperature under different conditions were analyzed these samples of blood components such as RBC and serum [15].Recent studies have focused on the study of metabolic and biochemical events for objectsExposed to high heat, because it is essential to understand the environmental risks posed byPollution, and reflect the damage happening in the organisms cells, tissues and organs[16,17].

In this study the electrochemical analysis of the influence of different high temperature on the blood medium in present with Pb(II) to determination the activation energy and other thermodynamic properties of both redox process.

2. Experimental part:

2.1. Reagents and chemicals

Lead(II) sulphate (purity 99%) and carbon nanotubes (purity 99%) supplied fromFlukacompany (Germany), potassium chloride (KCl) powder with purity (99%) from SCRC (china). The human blood samples were taken from center medicine of Baghdad City as well the other chemicals and solvents which used received from the manufacturer. Deionizewater was used for the preparation of aqueous solutions. All solutions were oxygen free by nitrogen gasfor (10-15) minutes prior to making the measurement.

2.2. Apparatus and procedures

The instrument EZstat series (Potentiostat/Glvanostat) NuVant Systems Inc. (made in USA). The Electrochemical Bio-analytical cell connect with potetiostatedevice and monitoring through the special program that have been installed on the personal computer to perform Cyclic Voltammetry (CV). the silver-silver chloride reference electrode(Ag/AgCl in 3M NaCl) and Platinum wire (1 mm diameter) was used as a reference and counter electrodes respectively. The glassy carbon working electrode (GCE) modified with (CNT) was used in this study after cleaning with alumina solution.

2.3. Preparing the modification of GCE with CNT (CNT/GCE):

The mechanical technical method to prepare the (CNT/GCE) working electrodewas employed that mentioned elsewhere [18,19]. The technique included abrasive application of (MWCNT) nanoparticles at the clean surface of (GCE), forming an array of (MWCNT) nanoparticles as (MWCNT/GCE) which immerse in (10) ml of electrolyte or blood sample in the cyclic voltammetric cell.

2.4. Measurements of different temperatures

It has been using a cell measuring of cyclic voltammogram size(10) ml and replaces the solution which required for studying at different temperatures, and then submerged in it three electrodes (working, reference and counter electrodes) as well as the thermometer to measure the degree of the temperature of study solution, then connect the three electrodes with thepotentiostat. The cell placed in a water bath to install the required temperature and can be used regular hot plate to increasing the temperatures.

3. Results and discussions

3.1. Enhancement of redox current peaks using CNT/GCE

It was used a modification working electrode GCE with CNT as a good sensor to determination of redox current peaks of Pb(II) in blood medium at different high temperature(35–60)^{o}C to evaluation the electrochemical properties of the contamination blood by lead ions. It was found that the CNT has a good catalyst with pb(II) in blood medium as shown in Fig.(1)at normal temperature(37) ^{o}Cof human blood medium with high resolution of redox current peaks.It was appeared one of oxidation current peak at (-387) mV and one of reduction current peak at (-1147) mV at CNT/GCE which referred to oxidation and reduction current peaks for lead ions at (CNT/GCE) electrode.

3.2. Effect of temperaturesin range (37-60)^{o}C on the redox of Pb(II) in blood medium

Cyclic voltammetric technique used to determine the effect of temperature on blood composition in the presence of lead ions by tracking the values of redox current peaks using electrochemical analysis which has shown that the results of the analysis is complicated blood with the lead ions has been affected by rising cell device prone to heat.It has been monitoring the redox current peaks during different high temperature from the cyclic voltommagram as shown in Fig.(2). Thus results showed that the decline of the oxidation current peak of the lead ions in blood medium from (52) mA at (37)°C (temperature of human body) to (42) mA at (60)°C. But, the reduction current peak was observed at high temperature which calculated (90) mA at (37) °Cto (122) mA at (60)°C.

3.3. The activation energy (E^*) value:

The effect of different temperature on the redox reaction of Pb(II)in blood medium was studied. The reduction current peak of the lead ions was changing in properties at two steps first one increasesgradually at the temperature of (35-44)°Cand the second one decreases gradually at the temperature of(46-62) °C. The plotting of log (Ip_c) (reduction current) of Pb(II)versus reciprocal of temperature which is found to be fairly linear in agreement with thermodynamicexpectation of Arrhenius equations (1) and (2) [20,21], as shown in Figs.(1), (2) and (3).

$\sigma = \sigma^o \text{Exp} (- E^*/ RT)$............(1)

$D = D^o \text{Exp} (-E^*/ RT)$ ....(2)

Where σ / D are conductivity / diffusibility and σ^o /D^o are standard conductivity / the initialdiffusibility.

Also, Arrhenius' equation gives the dependence of the rate constant k of a chemical reaction on the absolute temperature T (in kelvins), where A is the pre-exponential factor (or simply the pre-factor), E* is the activation energy, and R is the universal gas constant:[22,23,24]

$k = A \text{ EXP}(-E^*/RT)$ ....(3)

$\text{Log}(I_p)=\text{Log}A - E^*/2.303RT$ ....(4)

From plotting $\text{Log}(I_p)$ against 1/T, the slope of the linear line of the relation is

(-E*/2.303R).

Where: k is rate constant which replaced with (I_p) the current peak of the oxidation or reduction process of electrochemical reaction.

3.4. The values thermodynamic functions(ΔH*, ΔG*, ΔS*)

The relationship between the change in Enthalpy of activation, Gibbs of activation and Entropy of activation is in equation (5): [25,26,27]

$\Delta H^* = \Delta G^* + T \Delta S^*$ .... (5)

The different units are accounted for in using either the gas constant R (8.314 $J.mol^{-1}k^{-1}$), the Boltzmann constant k_B($1.381x10^{-23}$ $m^2kg.sec^{-2}k^{-1}$), and Plank constant h (6.66 x 10-34 J.sec.) as the multiplier of temperature T (K).

Where: Change in Enthalpy of Activation (ΔH*),change in Gibbs of activation(ΔG*) and Entropy of Activation (ΔS*).

The relationship between activation energy and change of enthalpy was found from the following equation:

$\Delta H^* = E^* - RT$ .... (6)

So, activation enthalpy change was calculated from the value of activation energy as shown in equation (6).

From Eyring equation can be determined the activation Gibbs change (ΔG^*) as in the following equation: [28,29,30]

$\Delta G^* = -RT \, Ln \, (k \, h / T \, k_B)$ .... (7)

It is possible to replace the (Ip) current peak of oxidation or reduction process of species in the electrolyte alternatively to the rate constant (k) in equation (7).

Finally, the activation entropy change (ΔS^*) can be calculated from the equation 5 by compensation values of each of the ΔG^* from equation (7) and ΔH^* from equation (6) at different temperature.

3.5. Effect of different high temperatures on the E*

Through previous studies about the effect of high temperatures on the contaminated blood composition, there was significantly felt when electrically studied by finding activation energies that expressed over the effect of heat on blood components [11,12].

It was found that the study of Pb(II) ions in blood medium at different temperature causes to affect the rate constant (k) asoxidation current peak (Ipa) in the cyclic voltammogram was decreased against to the increasing of temperature and reduction current peak was increased versus increasing temperatureas shown in Fig. (1)and(2) at (37)°C and (60)°C, respectively.

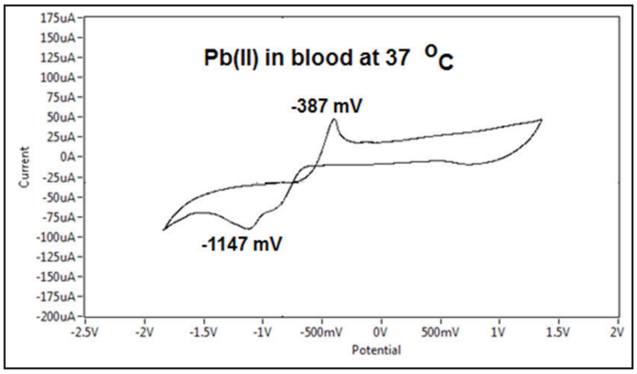

Fig.(1): cyclic voltammogram of(1)mMPb(II) in blood medium, using CNT/GCE versus Ag/AgCl at (37)°C, (100) mV s^{-1}.

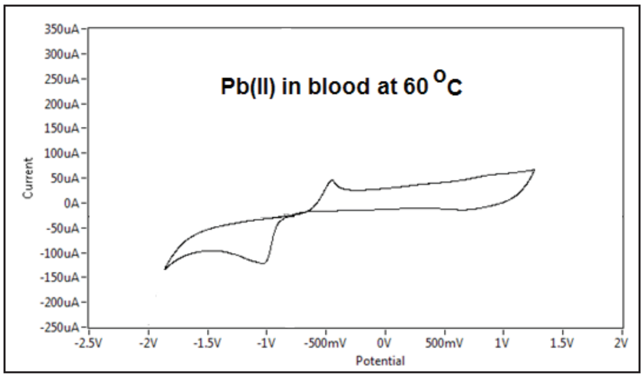

Fig.(2): cyclic voltammogram for the (1)mMPb(II) in blood medium, using CNT/GCE versus Ag/AgCl at (60)°C, (100) mV s^{-1}.

Fig.(3) and (4) show the relationship between Log(I_{pc}) of cathodic current peak of Pb(II) in blood medium against (1/T), to calculation the value of activation energy (E*) from the Arrhenius equation(4), the results of the study has two values of the E* in temperature for the reduction process Pb(II)/Pb(0)as in the following determination:

E* = -slope.(2.303).R from equation (4) to determine E*.

(Cathodic) $E^*,_1$ = -(-1.842 x 2.303 x 8.3144) = (35.271 KJ.mol^{-1}.K^{-1}) at(35-44)°C

(Cathodic) $E^*_{,2}$ = -0.1743 x 2.303 x 8.3144 = (-3.338) $KJ.mol^{-1}.K^{-1}$ at (46-62)°C

In addition to finding the activation energy of oxidation current peak of Pb(II) in blood medium as shown in Fig.(5)which decreased against to increasing of temperature in range from(35) to (58)°C.

(Anodic) E* = -0.8116 x 2.303 x 8.3144 = (-15.541) $KJ.mol^{-1}.K^{-1}$at (35-58)°C

A new phenomenon was studied of the effect of high temperatures on the composition of the blood medium in present with Pb(II) ions by cyclic voltammogramthroughthe thermodynamic functionsE*,ΔH*,ΔS* and ΔG*. Table (1) illustrated thermodynamic functions at different temperatures for oxidative current peak of lead ions in blood medium which determined from Arrhenius equation and Eyring equations. It was determined E* of decreasing of anodic current peak against increasing of the temperature from (35)°C to (60)°C with E* = (-15.541) $kJ.mol^{-1}.K^{-1}$, it means that the oxidation process of lead ions in blood medium need a low activation energy through higher temperature to converted Pb(II) to Pb(IV) as in the oxidation process in the following equation (8)[31]:

$Pb^{2+} + 2e = Pb^{4+}$ ……..E_{oxd} = 387 mV …..(8)

In the other thermodynamic functions was determined as shown in Table (1) different properties of an increasing in the values of ΔH*,ΔS* and ΔG* against to increasing of temperature [32].

Table (2) explain two phenomenon of the lead ions in blood medium for the reduction current peaks at different temperature, there are increasing of the current against to increasing of temperature from (35)°C to (44) °C with activation energy value of (35.271) $kJ.mol^{-1}.K^{-1}$, it means that the included limit of body temperature (35-40)°C the reduction of lead ions was increased against to increasing the temperature at low range as shown in the relationship at Fig.(3). The reduction process of lead ions at this range of temperature as Pb(II)/Pb(0) which causes precipitation of lead ions to lead metal as in the following equation(9) [31]:

$Pb^{2+} + 2e = Pb^0$ ………….. E_{red} = 1147 mV at35-40°C …….. (9)

The other phenomenon was noticed at high temperature through the range(46-62)°C the reduction current peak of lead ions started to decrease against to increasing the temperature as shown in the relationship at Fig.(4). The reduction process of lead ion at high temperature causes to converted Pb(IV) to Pb(II) as in the following equation(10) [31]:

$Pb^{4+} + e = Pb^{2+}$ ……… E_{red}= 1061 mV at 46-62°C ……….(10)

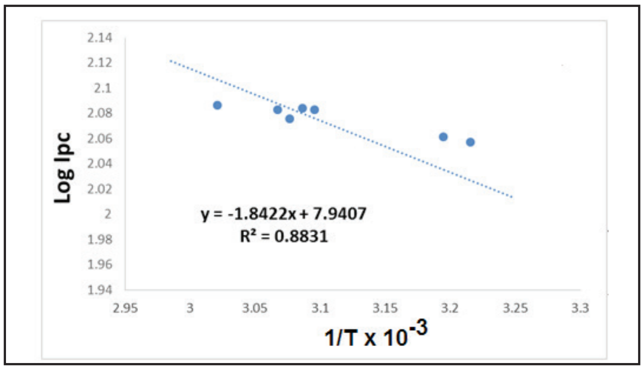

Fig.(3): Dependence of reduction current peak of (1)mMPb(II) in blood medium as a function of temperature range (35-44)°C using CNT/GCE versus Ag/AgCl at (100)mVsec^{-1}scan rate.

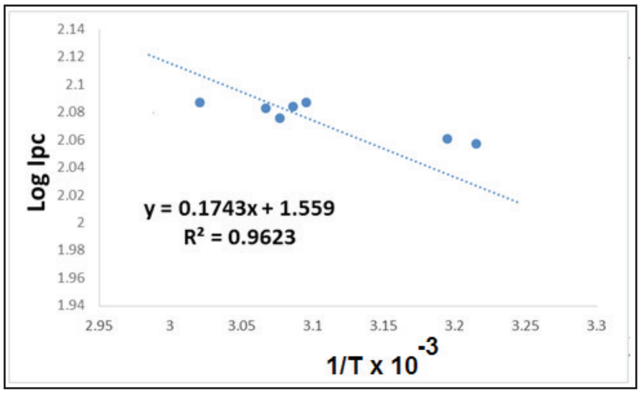

Fig.(4): Dependence of reduction current peak of (1)mMPb(II) in blood medium as a function of temperature range (46-62)°C using CNT/GCE versus Ag/AgCl at (100) $mVsec^{-1}$scan rate.

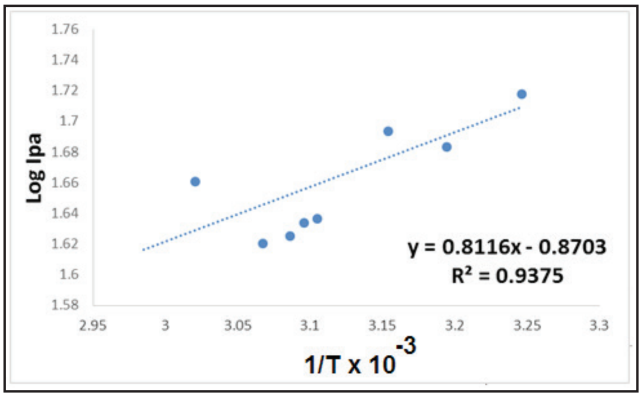

Fig.(5): Dependence of oxidative current peak of (1)mMPb(II) in blood medium as a function of temperature range (35-58)°C using CNT/GCE versus Ag/AgCl at (100) $mVsec^{-1}$scan rate.

Table (1): Kinetic and thermodynamic parameters (E*,ΔH*,ΔS* and ΔG*) of the anodic current peak of (1)mMPb(II) in blood medium at different temperatures and scan rate (100) mV sec^{-1}using CNT/GCE versus Ag/AgCl.

Temp., K	Ipa, mA	Epa, mV	ΔH*, $kjmol^{-1}$	ΔG*, $kjmol^{-1}$	ΔS*, $kjmol^{-1}$	E*, $kjmol^{-1}$
308	52.19	387.6	-2.576	-65.287	0.22	-15.541
309	48	396.8	-2.585	-65.713	0.221	-15.541
311	56.35	379	-2.601	-65.757	0.22	-15.541
313	48.23	396.8	-2.618	-66.597	0.221	-15.541
317	49.35	400.8	-2.668	-67.406	0.221	-15.541
319	50.14	406.9	-2.668	-67.816	0.221	-15.541
322	43.28	429.5	-2.693	-68.863	0.222	-15.541
323	43.03	425.8	-2.701	-69.104	0.222	-15.541
324	42.18	435	-2.709	-69.389	0.223	-15.541
325	39.72	444.8	-2.718	-69.743	0.223	-15.541
326	41.73	443.3	-2.726	-69.834	0.223	-15.541
331	45.8	450.9	-2.767	-70.697	0.222	-15.541
335	45.56	461	-2.801	-71.609	0.222	-15.541

Table (2): Kinetic and thermodynamic parameters (E*,ΔH*,ΔS* and ΔG*) of the cathodic current peak of (1)mMPb(II) in blood medium at different temperature and scan rate (100) mV sec^{-1}using CNT/GCE versus Ag/AgCl.

Temp.,K	Epc, mV	Ipc, mA	ΔH*, Kjmol-1	ΔG*, Kjmol-1	ΔS*, Kjmol-1	E*, Kjmol-1
308	1147	89.08	-2.525	-63.913	0.216	35.271
309	1119	90.55	-2.534	-64.083	0.216	35.271
311	1125	114	-2.55	-63.921	0.214	35.271
313	1093	115	-2.567	-64.327	0.214	35.271
317	1074	130.2	-2.6	-64.859	0.213	35.271
319	1061	128.3	-2.656	-65.327	0.213	-3.338
322	1061	124.3	-2.68	-66.051	0.213	-3.338
323	1057	122.2	-2.689	-66.308	0.214	-3.338
324	1052	121.4	-2.697	-66.535	0.214	-3.338
325	1045	119.1	-2.705	-66.802	0.214	-3.338
326	1045	121	-2.714	-66.971	0.214	-3.338
331	1030	122.1	-2.755	-68.017	0.214	-3.338
335	1036	119.9	-2.789	-68.919	0.214	-3.338

In previous study showed thatthe effect of high temperatures in a number of biochemical variables inSerum groups studied. As heat-exposed showed a significant decrease in the amount ofProtein and total cholesterol, while the amount of urea showed a significant increase with increasing duration exposure, and the results showed a significant increase in the effectiveness of the some enzymes such as Amin Alasparti carrier Alanine aminotransferase [12].

The current study showed that the effect of high temperatures on the human body by elecrtochemical analysis on the blood as antioxidant oxidizing agents such as lead and impressive reduction in the deposition of lead metal on the some organ of the body, causing the destruction of brain cells or damage of red blood cells (RBC).

It was observed from the experimental results that the rate constants for electron transfer reactions of thePb(II)in blood medium-increase with the increase in temperature. It is suggested that an increase in temperature increases the kinetic energy of theradical cations, which in turn increases the mass controlled diffusion rate of the reactive species.

4. Conclusion

Electrochemical study of lead ions in blood medium using cyclic voltammetric method to determination the effecting of different temperatures (37–60)^{o}Con the redox current peaks of Pb(II) in blood samples. It was found the values of activation energy (E^*) for the oxidation-reduction current peaks of Pb(II) depend on the reaction between the lead ions as toxic pollutants and blood component by the decomposition. The redox current peaks showed a rise in the effectiveness of enzymatic Serum, and it can be explained these rises because of the effect of high temperatures in the different blood cells. So, does the installation cellular permeability change leading to increased cellular permeability chemical blood cell membranes, which in turn leads to the liberation of liquid enzymes inside the blood cell Damage any of harm. Extracellular fluid is extracted from Entercellular to the body of tissue due to exposure to high temperature.

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