CORROSION SCIENCE AND TECHNOLOGY, Vol.21, No.5(2022), pp.381~389 pISSN 1598-6462 / eISSN 2288-6524
[Review Paper] DOI: https://doi.org/10.14773/cst.2022.21.5.381

Anthocyanins Extracted from Grapes as Green Corrosion Inhibitors for Tin Metal in Citric Acid Solution

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(Received March 18, 2022; Revised July 30, 2022; Accepted September 17, 2022)

Cyclic Voltammetry and weight loss measurements were used to investigate corrosion prevention of tin in a 0.5M citric acid solution containing Anthocyanins extracted from grapes at various concentrations and temperatures. Results showed that the investigated chemicals, Anthocyanins extracted from grapes, performed well as tin corrosion inhibitors in 0.5M citric acid. Increasing the concentration of Anthocyanins increased their corrosion inhibition efficiencies. When the temperature dropped, their inhibition efficiencies, increased indicating that higher temperature tin dissolution predominated the adsorption of Anthocyanins at the surface of tin metal. When inhibitor concentrations were increased, their inhibition efficiencies were also increased. These results revealed that corrosion of tin metal was inhibited by a mixed type of adsorption on the metal surface. The adsorption isotherm of Langmuir governed the adsorption of Anthocyanins. Thermodynamic parameters such as the enthalpy of adsorption, the entropy of adsorption, and Gibbs free energy and kinetic parameters such as activation energy, enthalpy of activation, and entropy of activation were computed and discussed in this study.

Keywords: *Corrosion inhibitors, Tin metal, Cyclic Voltammetry, Weight loss, Adsorption models*

1. Introduction

Corrosion damage can be avoided by a variety of approaches, including material upgrades, production fluid mixing, process control, and chemical inhibition. The application of corrosion inhibitors is the most effective way for preventing metal surface deterioration in corrosive conditions [1].

The rate of metal electrochemical corrosion is greatly influenced by temperature. In the case of corrosion in a neutral solution, increasing the temperature improves the overpotential of oxygen depolarization and the rate of oxygen diffusion, but lowers the oxygen solubility. When corrosion occurs in an acid medium, the rate of corrosion increases as the temperature rises because the hydrogen evolution overpotential falls. Many studies have been conducted on the effects of temperature on acidic corrosion, most often in hydrochloric and sulphuric acids [2]. In acid corrosion, inhibitors are thought to adsorb on the metal surface, causing a structural change in the double layer and a slower pace of the electrochemical partial reaction. The electronic structure of the inhibitory molecules, as well as steric factors, aromaticity, electron density at the donor atoms, and the presence of functional groups such as C=NH, –N=N–, –CHO, R–OH, C=C, and others, impact inhibitor adsorption. Tin is commonly used in the production of soft solders, dental amalgams, bronze, and bottle cans due to its high corrosion resistance [3]. Effective can packing is primarily determined by the metal's ability to resist corrosion. The fundamental qualities of the metal and the contents stored within the container define the tinned plate's corrosive resistance [4].

As a result, the amount of corrosion generated in the tin when acidic fruits are placed within has gotten a lot of attention [5]. The majority of past research has focused on inorganic anions as a means of preventing tin corrosion

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[6]. The toxicity of several inorganic anions makes their use as corrosion inhibitors difficult. This, along with concerns about sustainability and cost, has led to a need for more research into natural resource corrosion inhibition practices. For example, anthocyanin, a pH-sensitive pigment found in red cabbage leaves, is natural, inexpensive, widely available, safe, and renewable [7,8]. Using weight loss measures, the current study aims to investigate the possible use of grape extract as a corrosion inhibitor for tin in citric acid solution.

2. Experimental

2.1. Preparation of grape peel (gp)

Although relatively harsh solvents, such as ethanol and methanol, can be used to extract anthocyanins pigments from fruits and vegetables, water is an acceptable alternative that is both safer and better for the environment [9]. Grapes were purchased from a local market, cleaned with distilled water, and then the skins were manually separated from the whole berries. Once separated, any excess water was squeezed from the peels before being dried at 60 ºC until they reached a constant weight.

2.2. Extraction of anthocyanins

The anthocyanins were extracted from 20 g sample of Grape Peel (GP) using a solute and methanol as solvent ratio of 1:10 w/w in a 200 mL beaker that was magnetically stirred for 12 hours. The acidified water used in the extraction process was (0.1% HCl, with pH was 3) and fed at a rate of 30 mL/min at constant pressure of 40 bar.Then the sample was exposed under two temperatures ranging between 110 ºC and 160 ºC at 40 bar of stable pressure [10]. Filter paper was used to separate the extracted liquid, and the resulted material was then freeze dried for five hours [11] Finally, these materials were milled by using a mortar to produce anthocyanins powder which were then stored in light-proof containers until they used for this research work.

2.3. Cyclic voltammetry measurements

The working electrode was a tin rod (A = 0.785 cm^2), with platinum (Pt) serving as the counter electrode and a silver chloride electrode (Ag/AgCl) serving as the reference electrode. The tin electrode was polished with various grades of emery paper before being immersed in deionized water for the rinse stage. To execute the cyclic voltammetry investigations at room temperature, an X-Y recorder programmer, series 2000 Ominographic, was linked to an EG & G Princeton Applied Research Potentiostat Galvanostat Model 263A. (297 ºK). 1000 CE pH, mV, and temperature meters were used to record the pH of the solution.

2.4 Weight loss measurements

Weight loss experiments are the most basic yet most informative corrosion testing. Weight loss measurements at various inhibitor concentrations aid in finding the optimum inhibitor concentration and understanding the manner of adsorption of the inhibitor molecules via the appropriate adsorption isotherm. Based on this, studies are carried out at various immersion temperatures to extract the various parameters. As previously stated, the coupons (A=14.4 cm^2) were abraded with emery sheets, cleaned, rinsed with water followed by acetone, dried, and precisely weighed. Tin coupons were submerged in 0.5 M citric acid in the absence and presence of increasing amounts of anthocyanins and held at the proper temperature using a thermostat. After an hour of immersion, the Tin specimens were removed, washed with distilled water, followed by an acetone wash, dried, and weighed. equation (1) was used to calculate the corrosion rate (CR) of Tin specimens in acid solution. [12]:

$$CR = 10^4 \frac{ML}{\rho A T} \quad (1)$$

where ML = sheet weight loss, A = sheet area, ρ = tin metal density, and T = corrosion time.

Equation (2) was used to compute the inhibitory efficiency (IE %) [13]:

$$IE(\%) = \frac{W_1 - W_0}{W_1} \times 100 \quad (2)$$

where W_0 and W_1 are the tin corrosion rates in citric acid solutions in the presence and absence of inhibitor, respectively. equation (3) was used to determine surface coverage (θ) values [14]:

$$\theta = \frac{W_1 - W_0}{W_1} \quad (3)$$

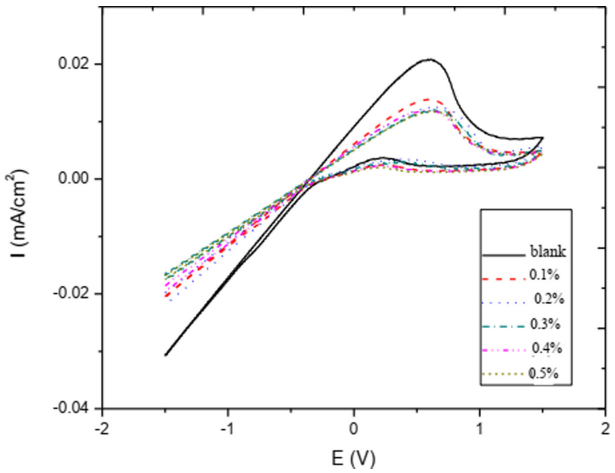


Fig. 1. Cyclic voltammetry curves for tin electrode at different concentration of inhibitor in 0.5 M citric acid at 297 °K

3. Results and Discussion

3.1. Cyclic voltammetry studies

Fig. 1 shows the effect of adding anthocyanins to 0.5 M citric acid at 297 °K with a potential range of -1.5 to 1.5 V on tin corrosion. These data imply that an increase in anthocyanins is linked to a drop in I_p and a change in E_p toward the negative. This has a strong inhibitory effect on anthocyanins. The absorption inhibitor, which prevents the adsorption of citrate anions, inhibited the tin surface.

3.2. Weight loss studies

The weight loss test is performed to assess the loss due to corrosion. The weight of a tin coupon with known composition and dimensions is recorded before and after immersion in the corrosive test medium (0.5 M citric in this example), and the difference is referred to as the weight loss.

Table 1. Relation between anthocyanins concentration and dissolution current densities for Tin in 0.5 M citric acid at 297 °K

Inhibitor concentration (%)	I_p ($\mu A/cm^2$)	E_p (mV)	Corrosion rate (mpy)
Blank	20.59	642.4	21.63
0.1	12.52	642.4	13.23
0.2	12.14	624.5	12.82
0.3	11.94	618.6	12.60
0.4	11.80	612.6	12.45
0.5	13.91	606.7	14.68

The weight loss test is carried out to assess the loss due to corrosion. The weight of a tin coupon with known composition and dimensions is recorded before and after immersion in the corrosive test medium (in this example, 0.5 M citric), and the difference is referred to as the weight loss. The weight loss investigations were conducted to assess the influence of acid concentration, immersion period, and temperature on tin sheet corrosion in citric acid. The results of this investigation demonstrated that as the concentration of acid increases, so does the rate of corrosion. Both the time of immersion and the temperature CR rise as the period of immersion and the temperature rise. Tables 2 and 3 incorporate all of the findings [15].

The corrosion phenomena is greatly influenced by temperature. In general, when the temperature rises, the rate of corrosion rises with it. We investigated the effect of temperature on anthocyanin efficiency. We measured weight loss in the absence and presence of anthocyanins at various doses of this inhibitor throughout 1 hour of immersion for this aim. Table 4 shows the corresponding information.

Table 2. Influence of citric acid concentration on weight loss of tin in absence inhibitor at different temperatures

Acid concentration (mol/l)	297 °K		307 °K		317 °K	
	Corrosion rate (mpy)	Weight loss (mg)	Corrosion rate (mpy)	Weight loss (mg)	Corrosion rate (mpy)	Weight loss (mg)
0.1	149.96	7	782.69	24	619.63	19
0.2	278.49	13	978.36	30	978.36	30
0.3	299.91	14	684.85	21	1369.69	42
0.4	310.63	14.5	1141.42	35	978.36	30
0.5	321.34	15	1565.37	48	1597.98	49

Table 3. Influence of time of immersion for tin coupons in citric acid without inhibitor on weight loss at different temperatures

Time (h)	297 °K		307 °K		317 °K	
	Corrosion rate (mpy)	Weight loss (mg)	Corrosion rate (mpy)	Weight loss (mg)	Corrosion rate (mpy)	Weight loss (mg)
0.5	456.57	7	2152.38	33	3195.96	49
1	321.34	15	1858.88	57	3424.25	105
1.5	369.60	17	2261.09	104	3739.49	172
2	391.34	24	2184.99	134	3587.31	220
2.5	286.98	22	2295.88	176	3522.08	270

Table 4. Effect of anthocyanins addition in 0.5 M citric acid for tin coupons at different temperatures for 1hr

T °K	Concentration of inhibitor by percentage	Weight loss (g)	Corrosion rate (mpy)	IE%	Surface coverage (θ)
297	blank	0.015	321.34	---	---
	0.1	0.02	652.24	33.33	0.3333
	0.2	0.01	326.12	58.33	0.5833
	0.3	0.009	293.51	62.5	0.625
	0.4	0.009	293.51	62.5	0.625
	0.5	0.008	260.89	66.66	0.6666
307	blank	0.057	1858.88	--	--
	0.1	0.041	1337.09	14.58	0.14583
	0.2	0.04	1304.48	16.66	0.1666
	0.3	0.039	1271.86	18.75	0.1875
	0.4	0.039	1271.86	18.75	0.1875
	0.5	0.038	1239.25	20.83	0.20833
317	blank	0.105	3424.25	--	--
	0.1	0.047	1532.76	4.08	0.0408
	0.2	0.045	1467.53	8.16	0.08163
	0.3	0.043	1402.31	13.95	0.13953
	0.4	0.039	1271.86	20.41	0.20401
	0.5	0.038	1239.25	22.45	0.22449

Table 4 displays the development of corrosion rate (CR) with anthocyanin content (C) at various temperatures. It shows that as the concentration of anthocyanins grows, the corrosion rate of Tin decreases. Table 4 shows the inhibition effectiveness values derived from weight loss for various inhibitor doses and temperatures in 0.5 M citric acid. The data show that the inhibition efficiencies of the studied purines increase as the concentration of the respective anthocyanins increases, implying that the inhibition efficiency is a function of the amount of the inhibiting species present in the system and that the area of the tin surface covered by the adsorbed inhibitors grows. Furthermore, the results demonstrate that the inhibitory efficacy diminishes with rising temperature, indicating that higher temperature tin dissolution predominates on anthocyanin adsorption at the surface. It is apparent that when inhibitor concentration rose, inhibition efficiency improved.

3.3 Adsorption isotherm

The adsorption of natural inhibitor molecules from aqueous solution depends on pH and the process consider

a substitution process [16]. The protection of the Tin surface based on the way that the inhibitor adsorbed on the surface of the metal and ionization and polarization of molecule [17]. The adsorption isotherms were studied by the degree of coverage of the inhibitor molecules on the surface of the Tin and it has plotted against the concentration which is shown in Fig. 2 using Langmuir equation which is the appropriate adsorption model. The adsorption isotherm q , equilibrium constant K_{ads}, and the concentration of inhibitor Cinh, can be expressed by the following equation (4) [18].

$$\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh} \quad (4)$$

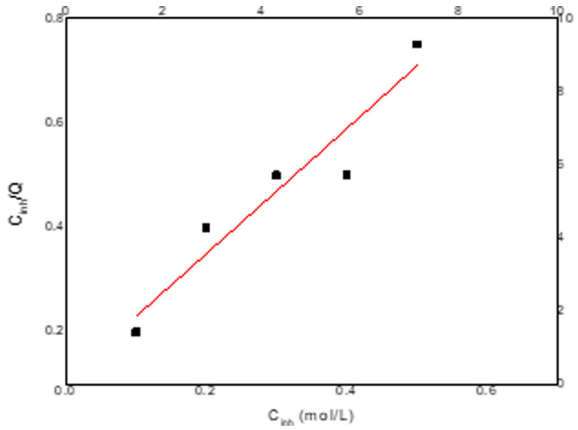
where K_{ads} is the equilibrium constant of the inhibitor adsorption process, C_{inh} is the inhibitor concentration and (C_{inh} denotes the concentration of anthocyanins in mM) Θ is the surface coverage and it was found by equation (3). the equation is for Langmuir's model of adsorption isotherm and it was used widely in the literatures for different metal/inhibitor/acid solution systems [19-21].

The slope obtained from plot C_{inh}/θ versus C_{inh} was a straight line with value nearly of unity and it was shown in Figs. 2a, b, c at three different temperatures (297,307,317 in kelvin). The values of (R) can be calculated from the intercept lines on the C_{inh}/θ for different three temperatures were recorded on table 5. The results show that the adsorption was of monolayer type or the occupation of molecules only on one site and there are no interactions with other adsorbed species [22]. The K_{ads} values obtained from the intercept lines on the C_{inh}/ Θ-axis in this is regarding to the standard free energy of adsorption (ΔGads) with the equation (5):

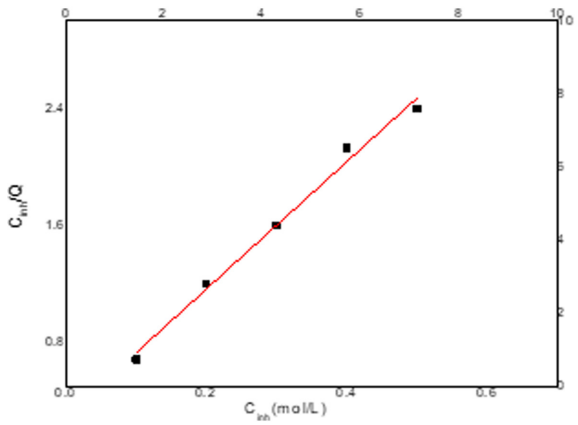
$$\Delta G^{o} = -RTLn(55.5K_{ads}) \quad (5)$$

where R is the gas constant and T is the absolute temperature. The constant value of 55.5 is the concentration of water in solution in mol/L [23].

The effect of temperature on adsorption of Grapes extracted from anthocyanins on Tin was studied at three different temperatures 297, 307 and 317 K. The calculation of thermodynamic parameters such as enthalpy of activation and entropy of activation using the following relation:



(a)



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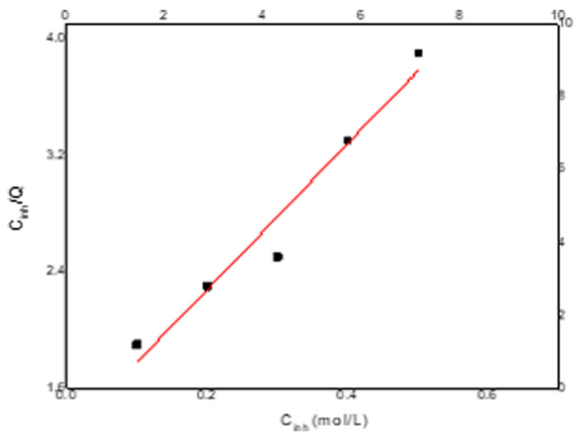

(c)

Fig. 2. (a) Langmiur adsorption isotherm for anthocyanin onto tin sheets at 297 °K; (b) Langmiur adsorption isotherm for anthocyanin onto tin sheets at 307 °K; (c) Langmiur adsorption isotherm for anthocyanin onto tin sheets at 317 °K

The free energies (ΔG_{ads}) of adsorption were calculated and listed in Table 5, the values of ΔG_{ads} were negative, it indicates that the adsorption of Anthocyanins onto Tin

Table 5. Thermodynamic parameters for adsorption of Anthocyanins onto Tin surface at different temperatures

Temp (K)	K_{ads} (mM^{-1})	ΔG^{o}_{ads} (J/mol)	ΔH^{o}_{ads} (J/mol)	ΔS^{o}_{ads} (J/mol.K)	E_a kJ/mol.K
297	1.28	-54.59	-151.67	-32.68	0.127
303	0.29	- 42.31	-152.12	-36.24	
317	0.11	-34.17	-150.59	-36.79	

sheet surface was spontaneous [24], and the interactions between inhibitor molecules and Tin surface was strong [25]. The free energies (ΔG_{ads}) of adsorption were calculated and listed in Table 5; the values of ΔG_{ads} were negative, it indicates that the adsorption of Anthocyanins onto Tin sheet surface was spontaneous, and the interactions between inhibitor molecules and Tin surface was strong. The obtained free energies (ΔG_{ads}) values for adsorption were ranging between (-54.53, -42.31, and -34.17 kJmol^{-1}) at temperatures 297 K, and 307 K and 317 K respectively the type of adsorption is physisorption, the free energy values of adsorption were associated with chemisorption as a result as transfer of electrons from adsorbate of Anthocyanins molecules onto Tin surface to form a coordination .In our work the adsorption of anthocyanins on Tin surface was mixed and the type of adsorption were physisorption and chemisorption. Thermodynamically, ΔG^{o}_{ads} is related to the standard enthalpy and entropy of adsorption, ΔH^{o}_{ads} and ΔS^{o}_{ads}, respectively, and they can be calculated by the following equation (6):

$$\Delta G = \Delta H - T\Delta S \quad (6)$$

According to the van't Hoff equation [26]: the standard enthalpy of adsorption (ΔH^{o}_{ads}) can be calculated

$$LnK_{adS} = -\frac{\Delta H_{ads}}{RT} + constant \quad (7)$$

The plot of ln K_{ads} versus 1/T gives a straight line, ΔH^{o}_{ads} /R were obtained from the slope, the value of ΔH^{o}_{ads} listed in Table 5, and shown in Fig. 3 the value of ΔH^{o}_{ads} obtained from the slope were negative that means the adsorption of inhibitor molecules onto the Tin sheet surface is an exothermic process, the value of ΔH^{o}_{ads} for chemisorption; is about 100 kJ/mol, while the value of ΔH^{o}_{ads} in physisorption process is less than 40 kJ /mol. In this work

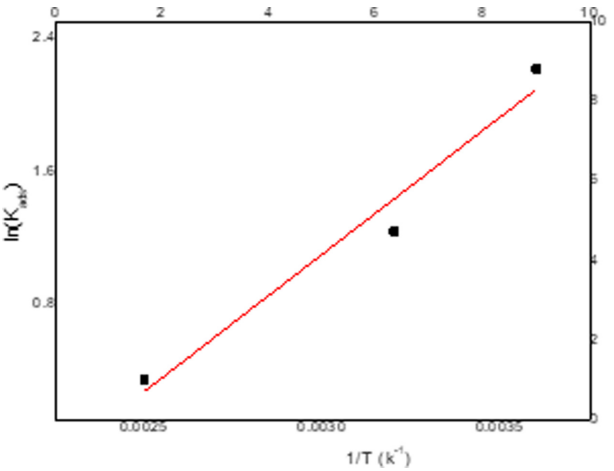

Fig. 3. ln K_{ads} against 1/T plots of anthocyanin onto tin surface

the result of standard ΔH^{o}_{ads} indicating the physical adsorption. , the negative values of ΔS* indicates that the formation of active complex and the rate determining step is the dissociation step of the complex [27-29].In the present case; the standard adsorption heat -39.299 kJ mol-1 shows that a comprehensive adsorption (physical adsorption) might occur [30]. ΔHads = -39.299 kJ mol^{-1} found by the Van't Hoff equation, may be also evaluated by the Gibbs–Helmholtz equation, which is defined as follows:

3.4 Effect of activation energy and temperature on the corrosion rate

The effect of temperature on the Tin sheet during inhibition process is a complicated process due to different changes occurs on the surface of Tin such as rapid etching and desorption of inhibitor, and the decomposition of the inhibitor [31]. The effect of temperature on the corrosion parameter of Tin in in 0.5 M citric acid was studied at 297, 307, and 317 K. The mechanism of inhibition can be investigated by comparing the activation energy of the inhibitor. Arrhenius equation used to evaluate activation

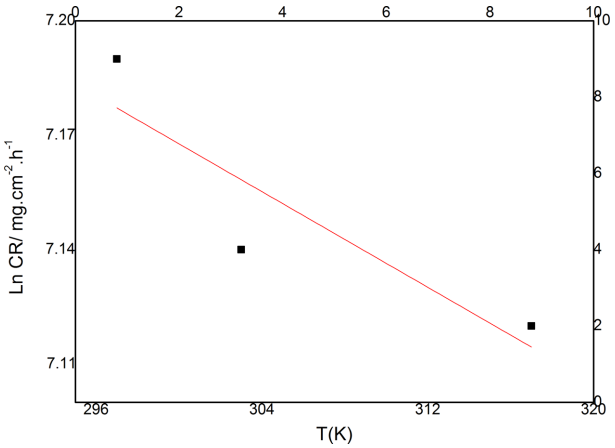

Fig. 4. Activation parameters for anthocyanin adsorption onto tin surface

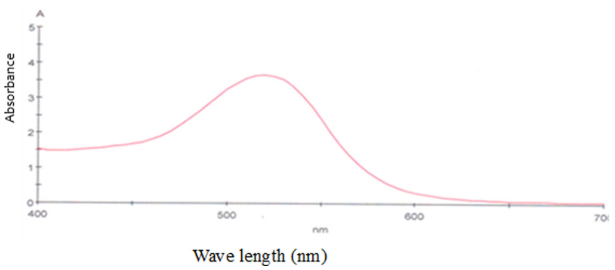

Fig. 5. Absorbance spectrum in UV-Vis region of grapes

energy by plotting $\ln K_{ads}$ against 1/T the activation energy (E_a) can be evaluated.

$$C_R = A_{exp}(-Ea/RT) \quad (8)$$

$$LnC_R = -E/RT + Ln\ A \quad (9)$$

Where, R the gas constant, T the absolute temperature, A the preexponential factor, C_R is the corrosion rate to plot it should be used the logarithm.

As the result of plot ln (C_R) against T applying Arrhenius equation for tin in 0.5 M citric acid with the inhibitor gives a straight line with a slope of ($-E_a/R$) observed in Fig. 4 and calculated and recorded in Table 5.

3.5 UV-Visible spectra

The UV-Vis are yet useful to describe anthocyanin structure [32-34]. the absorption of light by anthocyanins is selective and thus they show colors [35]. also anthocyanins the depends on the pH. The positive charge on the interior ring of anthocyanins and at low pH which is 1.0 the absorption of light is between 460 and 550 nm and have a maximum absorption at 520 nm [36] so it is colored at pH1.0 in high acidic pH. Fig. 5 show (λmax) which is the absorption maximum in the visible region was found to be at around 510–520 nm.

4. Conclusion

Cyclic voltammetry and weight loss techniques under optimal circumstances were used to investigate the corrosion behavior of tin in citric solution in the absence and presence of inhibitors. In 0.5 M citric acid solutions, anthocyanins are a good tin corrosion inhibitor. An increase in anthocyanin concentration makes it more effective, as evidenced by an increase in inhibition efficiency. Because tin dissolves more readily at higher temperatures, the inhibitory efficiency decreased with rising temperature. The activation energy of the corrosion process is increased when anthocyanins are added. With rising temperature, the adsorption equilibrium constant (K_{ads}) dropped. G^{o}_{ads} with a negative value indicates spontaneous adsorption on the metal surface.

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