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Inhibition of Copper Corrosion in H_2SO_4, NaCl and NaOH Solutions by *Citrullus colocynthis* Fruits Extract

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Abstract
The inhibitive effect of extract of *Citrullus* colocynthis fruits on copper corrosion in H_2SO_4, NaCl and NaOH solutions were studied using conventional weight loss and electrochemical polarization methods. Results obtained showed that extract functioned as effective and excellent inhibitors in the acidic, salt and alkaline media. Potentiodynamic polarization curves indicated that the plants extracts behave as mixed-type inhibitors. The fruit extract of *Citrullus* colocynthis demonstrated better inhibition efficiency in the acidic medium than in the alkaline and salt medium. The experimental data complied with the Langmuir adsorption isotherm and the value and sign of the Gibb's free energy of adsorption obtained suggested that inhibitor molecules have been spontaneously adsorbed onto the copper surface through a physical adsorption mechanism.
Keywords: Copper inhibition, kinetics, plant ex, Corrosion tract, Langmuir, weight loss, and thermodynamics.

1-Introduction

Copper is resistant toward the influence of atmosphere and many chemicals, however, it is known that in aggressive media it's susceptible to corrosion(Antonijevic M. M *et al.* 2008).The use of copper corrosion inhibitors in such conditions is necessary since no protective passive layer can be expected. Corrosion is an electrochemical process that metal surfaces interact with their environment, converting the metal atoms to ions causing the deterioration of the physical characteristics of the surface (Negm N. A et al. 2013). In general, the corrosion inhibitors are compounds known to effectively eliminate the undesirable destructive effects of aggressive media and prevent the dissolution of metals and alloys (Kumar S. H et al. 2012)**.** Plant extracts in terms of low cost and safe environment, are main advantage of using plant extracts as corrosion inhibitors because of all of the economic and environmental benefits. Until now, many plant extracts have been used as effective corrosion inhibitors for metals. The performance inhibition of plant extracts usually due to the presence in the composition of the species complex organics including tannins, alkaloids and nitrogenous bases, carbohydrates and proteins, as well as degradation products(Iloamaeke I. M.and Onuegbu T. U 2012 , Nnanna L.A. et al. 2012) Which are usually contain polar organic compounds with nitrogen, sulphur, or oxygen atoms, as well as those who have links double, triple or conjugated aromatic rings in the molecular structures, which are the main centres of adsorption(Raymond P. P. et al. 2013 , Afia L et al. 2013).

The adsorption of inhibitors on metal / solution interface is influenced by: (*i*) nature and surface charge of metal; (*ii*) type of aggressive electrolyte; and (*iii*) chemical structure of inhibitors (Ahamad I. and Quraishi M. A. 2009). The successful use of naturally occurring substances to inhibit the corrosion of metals in acidic and alkaline environments has been reported by some research groups *(*N S Patel1 et al. 2013) *(*Nnanna et al. 2013) (Al-Turkustani et al. 2010) (Okafor et al. 2010) (Iloamaeke et al. 2012) (Kumar et al. 2010) (P. Deepa Rani and S. Selvaraj 2013) .The present study on Methanol extract *of Citrullus colocynthis*is aimed to investigate the adsorption and inhibitive properties on copper in H_2SO_4 ,NaOH and NaCl media using both loss weight method and Potentiodynamic method .

2. EXPERIMENTAL

2.1 Sample collection and Preparation.

Fruits of *Citrullus colocynthis* were collected from North western desert at Nasiriyah in Iraq. Fruits were cleaned, washed by distilled water, dried at room temperature for one day, ground as powder and kept in dark glass containers for further use.

(50 g) of the powder dry fruits were placed in 500 ml round bottomed flask contain methanol (100%) and refluxed for 1h in boiling degree . Filtered in Buchner funnel by Whatman no.1 filter paper .The filtrate was also then used for chemical analysis (Tests for saponins, flavonoids, alkaloids etc.), the filtrate solution was evaporated through rotary evaporator under reduced pressure at 40°C until drying and than weighted and kept for further use.

2.2 Quantification of Total Alkaloids, flavonoids and saponins Content in *Citrullus colocynthis* extract.

Quantification of total Alkaloids, flavonoids and saponins content was made according to References (Djilani A. et al. 2006, Bohm A.B and Kocipai A.C 1994, Harbome J.B 1972)

Specimens of (D 6.8 ,T 3.4) mm copper of the following composition (wt%): Ag(0.037), Al (0.049),pi(0.018), Cr(0.031) , Fe (0.0139), Mn (0.051), Si (0.0111) ,Sn(0.0214),Zn(0.0208) and Cu(99.1). They were polished mechanically using SiC emery papers of grade 220, 400 and 600, washed thoroughly with distilled water and degreased with ethanol and acetone and stored in moisture free desiccators before their use in corrosion studies (Anozie1 I. U.et al. 2011, Niamien P.M.et al. 2011) **.** The experiments were performed for various parameters such as Concentration of the inhibitor (0.025, 0.05, 0.075 g/l), temperature variation (303, 323, 333 °K), Different corrosive media (H_2SO_4, NaOH, NaCl),) and different immersion time (2, 4, 8, 24 hours).

2.4 Corrosion Rate

From the change in weight of specimens the corrosion rate was calculated using the following relationship (Nnanna L. A.et al. 2011)

$$Rc_{corr}.(mpy) = \frac{534.W}{D.T.A} \quad \ldots\ldots\ldots (1)$$

$R_{corr.}$Corrosion rate was the used in calculation of Ea,ΔS, ΔH,*W:*weight loss in milligram, *D:* density of specimen g/cm^3, *A:* area of specimen in square inch (noting that 1 in^2 = 6.5416 cm^2.),*Ex*posure time in hours, mpy = mils per year (1 mill= 1inch /1000)

2.5 Electrochemical Measurements

The polarization measurements were made according to references (Al-Sahlanee H.H et al. 2013, Shyamala M. and Arulanantham A 2008, Ehteram A.N. 2008, Abd E-Lateef H. M et al. 2012) to evaluate the corrosion current, corrosion potential and Tafel parameters

3. RESULTS AND DISCUSSION

3-1.Quantification of Total Alkaloid, flavonoids and saponins Content in *Citrullus colocynthis* extract.

Results of quantitative total flavonoids, saponins and alkaloid contents of extract of Citrullus colocynthis are shown in Table 1.

Table 1: Total flavonoids, alkaloid and saponins content (mg/gm) of extract of *Citrullus colocynthis*.

Name of Extract	Alkaloids(mg/g)	Saponins(mg/g)	Flavonoids (mg/g)
Citrullus colocynthis.	4.23	2.14	4.66

3-2. Effect of concentration and temperature

The variation of the inhibition efficiencies obtained from the weight loss in different inhibitor concentrations in 1M H_2SO_4, NaOH and NaCl at variable temperatures (303, 323, and 333 ^{0}K) are shown in Figs 1 to 3. The results show that inhibition efficiency increases as the concentration of inhibitor increases from 0.025 to 0.075 g/L at 303, 323 and 333 ^{0}K. The maximum inhibition efficiency for the inhibitor was found to be about 90% in 1M H_2SO_4 solution. The inhibition was estimated to be 66.66% at 303 0K even at very low concentrations (0.025 g/L) in NaCl solution, and at 0.075g/L its protection was more than 70% (303 ^{0}K- 333 ^{0}K) in all media. This trend may result from the fact that the adsorption amount and the coverage of surfactant on copper increase with the inhibitor concentration, thus copper surface is efficiently separated from the medium (Olasehinde E.F.et al. 2012, Irshedat M. K.et al. 2013).Decrease in inhibition efficiency with increase in temperature is suggestive of physical adsorption mechanism. A similar conclusion has been reached by (Nnanna et al. 2011, Patel et al. 2013, Abdul Nassera et al. 2012) . Figs.1to 3 show that the inhibition efficiency decreased with an increase in corrosion temperature at the same inhibitor concentration.

3-3.Effect of exposure time

Figs.4 to 6 show the effect of changing immersion time at 303, 323, and 333 ^{0}K on the inhibition efficiency of *Citrullus colocynthis* extract at 0.075 g/L optimum dose in presence of 1M H_2SO_4,NaOH and NaCl. Figs. 4-6 show that *Citrullus colocynthis* extract inhibits the corrosion of copper for all immersion time at all concentrations of *Citrullus colocynthis* extract. Generally increasing immersion time resulted in increasing inhibition efficiency (IE). The inhibitor shows efficiencies in the range from 75.29% to a maximum 90.58% in 1M H_2SO_4, 78.84% to a maximum 84.61% in 1M NaOH and 66.66% to 77.08% in 1M NaCl. The enhanced (IE) may be explained due to increase of adsorbed of inhibitor molecules on metal surface with time(Singh A. et al 2010 , Leelavathi S.and Rajalakshmi R. 2013) This result is consistent with the findings of (El Maghraby and SororT.Y. 2010, Nnanna et al. 2011, Senthooran R. and Priyantha N. 2012 , Singh A. et al. 2013)

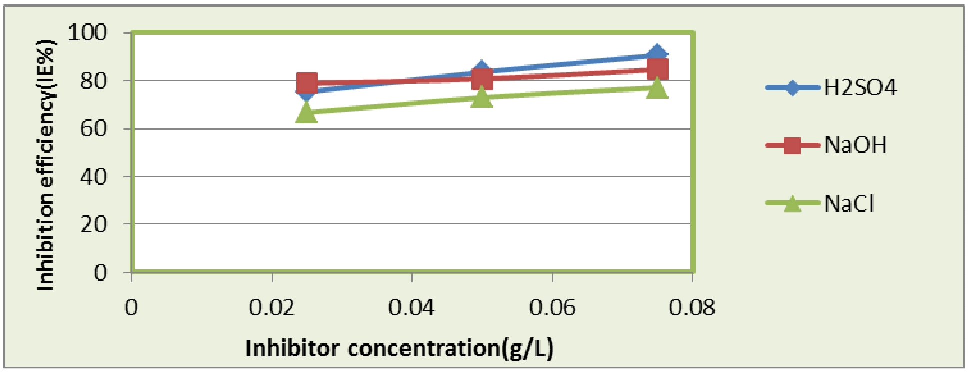

Fig.1.Inhibition efficiency as a function of inhibitor concentration in 1M (H_2SO_4, NaOH, NaCl).at 303^0K.

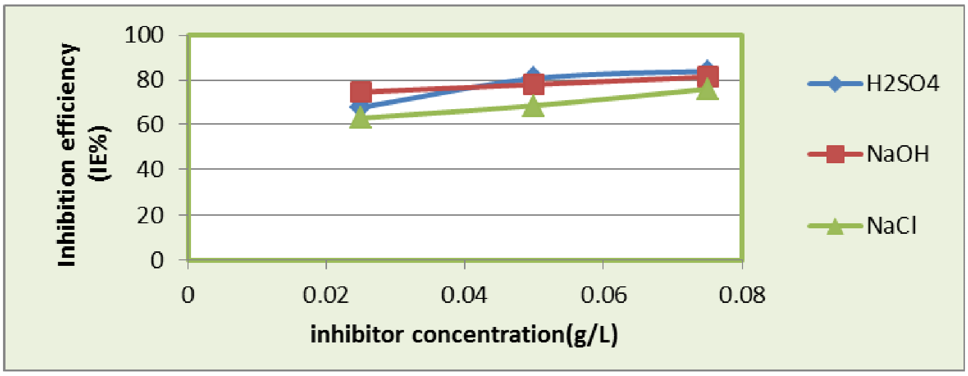

Fig.2.Inhibition efficiency as a function of inhibitor concentration in 1M (H_2SO_4, NaOH, NaCl) at 323^0K.

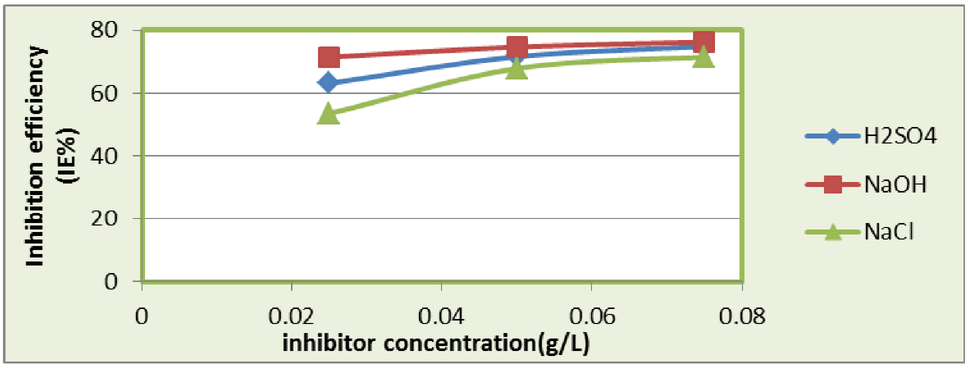

Fig.3.Inhibition efficiency as a function of inhibitor concentration in 1M (H_2SO_4 , NaOH , NaCl) at 333^0K.

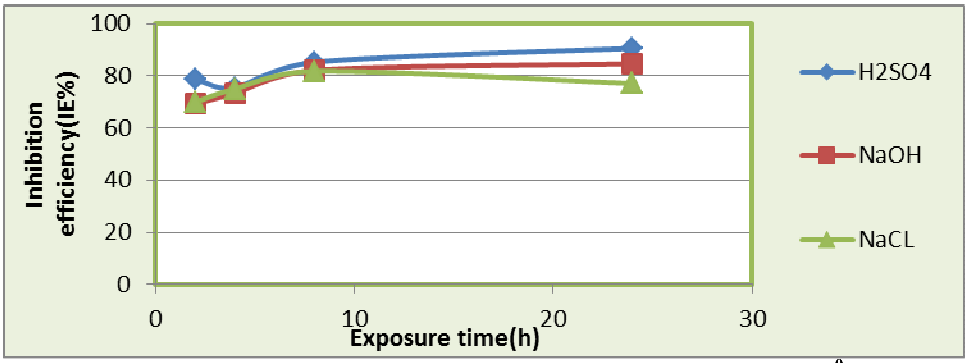

Fig.4. Effect of exposure time in 1M (H_2SO_4, NaOH, NaCl).at 303^0K.

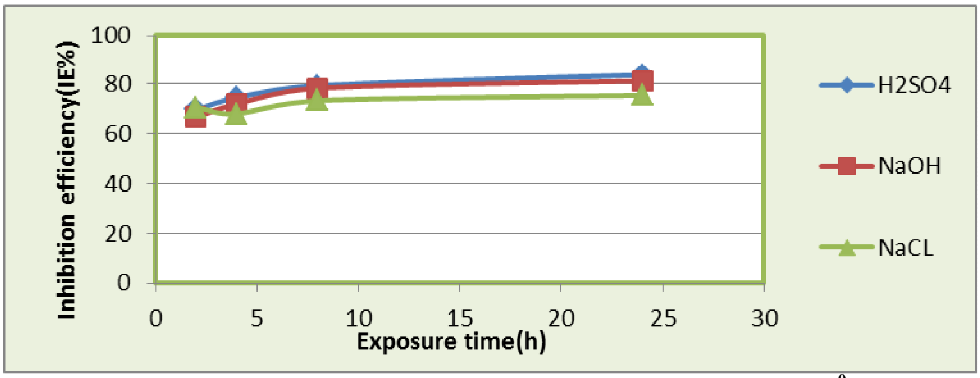

Fig.5. Effect of exposure time in 1M (H_2SO_4,NaOH,NaCl).at 323^0K.

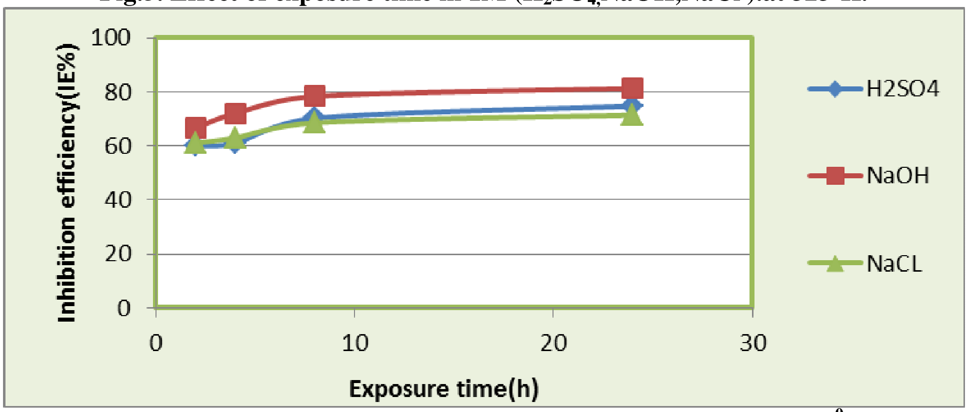

Fig.6. Effect of exposure time in 1M (H_2SO_4, NaOH, NaCl).at 333^0K.

3.4 Kinetic/Thermodynamics and Adsorption Studies

Activation parameters such as the activation energy, Ea, the enthalpy of activation, ΔH^*, and the entropy of activation, ΔS^*, for both corrosion and corrosion inhibition of metal in1 M (H_2SO_4, NaOH, NaCl) in the absence and presence of *Alcohol extract* at different concentrations over a temperature rang between 303-333°K were calculated from an Arrhenius-type plot (Eq. (2) and the transition state (Eq. (4) (Dahmani M et al. 2010 , Singh A. et al. 2010)

$$Rc_{corr} = A \exp(-E_a/RT) \quad \ldots\ldots (2)$$

$$\text{Log}\,(R2_{corr}/R1_{corr}) = (E_a/2.303R) \times (1/T_1 - 1/T_2) \quad \ldots\ldots (3)$$

Where R_{1Corr}, $R_{2Corr}$are the corrosion rates at temperatures T_1 and T2, A is the Arrhenius pre-exponential constant depends on the metal type and electrolyte.

$$Rc_{corr} = RT/Nh \exp(\Delta S^*/R) \exp(-\Delta H^*/RT) \quad \ldots\ldots\ldots (4)$$

Where h is Planck's constant, N is the Avogadro's number, ΔS* is the entropy of activation and ΔH* is the enthalpy of activation.

Figures7 to 9 represents the relation between logs Rc_{corr}. vs. 1/T for metal in 1M H_2SO_4,1M NaOH and 1M NaCl in the absence and presence (0.025g/L ,0.050g/L , 0.075g/L) of the studied inhibitor. Inspection of Table (2) reveals that, the activation energy increases in presence of the inhibitor and consequently the rate of corrosion reaction is decreased. Thus the activation energy values support the fact that the inhibitor was physically adsorbed on the metal surface in all media. The activation energies were also observed to increase with increasing the concentration of the extract, indicating that there is increasing ease of adsorption of the inhibitors with increasing concentration. This is in accordance with the findings of (Nawafleh E.et al. 2012, Prabhu D. and Padmalatha R. 2013, Khalifa O.R.and Abdallah S.M. 2011) . It has been reported that when the values of Ea> 80 kJ/mol it indicates chemical adsorption whereas Ea< 80 kJ/mol infers physical adsorption (Ismail M. et al. 2011, Vijayalakshmi P. R et al 2011). In the present study, a physical adsorption mechanism is proposed since the values of E_a are lower than 80 kJ/ mol.

Table 2: Activation parameters of the dissolution of metal in 1M (H_2SO_4, NaOH, NaCl) in the absence and presence of different concentrations *Citrullus colocynthis* extract.

C(g/L)	Ea(KJ mole^{-1})	ΔH(KJ mole^{-1})	ΔS(KJ mole^{-1})
H_2SO_4 (1M)	3.681	0.995	-0.2168
0.025	14.59	11.90	-0.2245
0.050	10.28	7.594	-0.2245
0.075	25.52	22.83	-0.2264
NaOH (1M)	5.17	2.49	-0.2187
0.025	12.73	10.04	-0.2283
0.050	10.70	8.01	-0.2289
0.075	19.14	16.45	-0.2302
NaCl (1M)	4.81	2.12	-0.2206
0.025	9.15	6.46	-0.2264
0.050	10.94	8.25	-0.2302
0.075	6.75	4.06	-0.2340

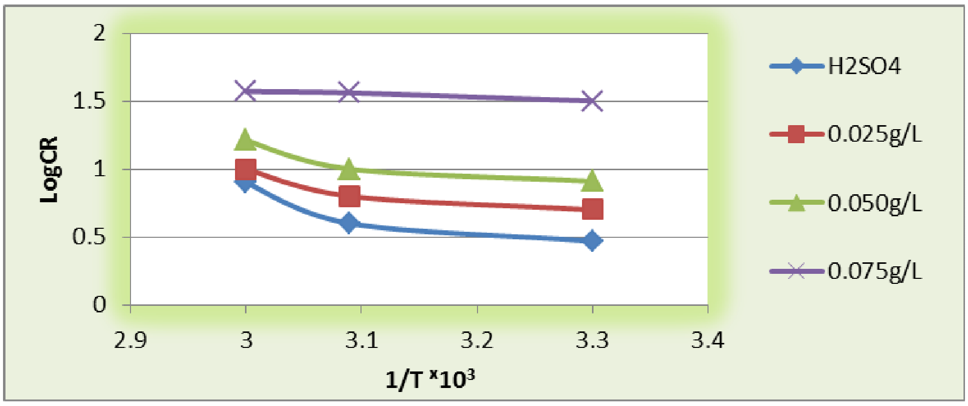

Fig7: Log corrosion rate (mpy) versus 1/T for copper dissolution in 1M H_2SO_4 in the absence and presence of different concentrations of *Citrullus colocynthis* extract.

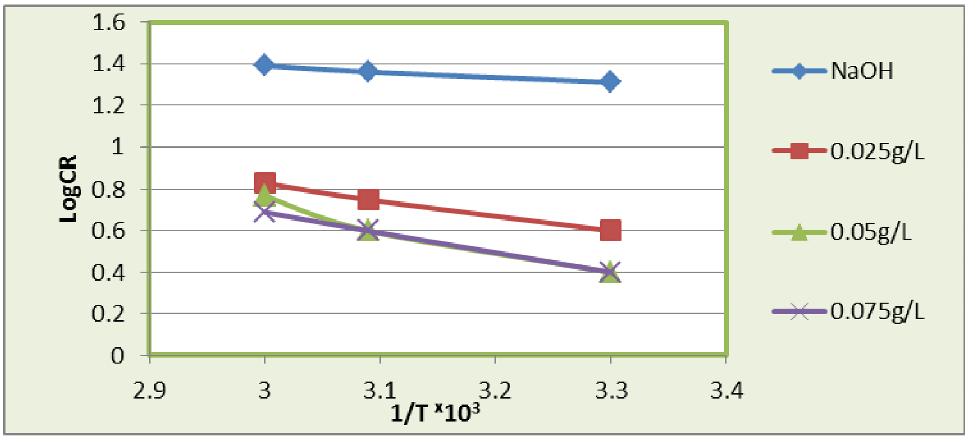

Fig 8: Log corrosion rate (mpy) versus 1/T for copper dissolution in 1M NaOH in the absence and presence of different concentrations *Citrullus colocynthis* extract.

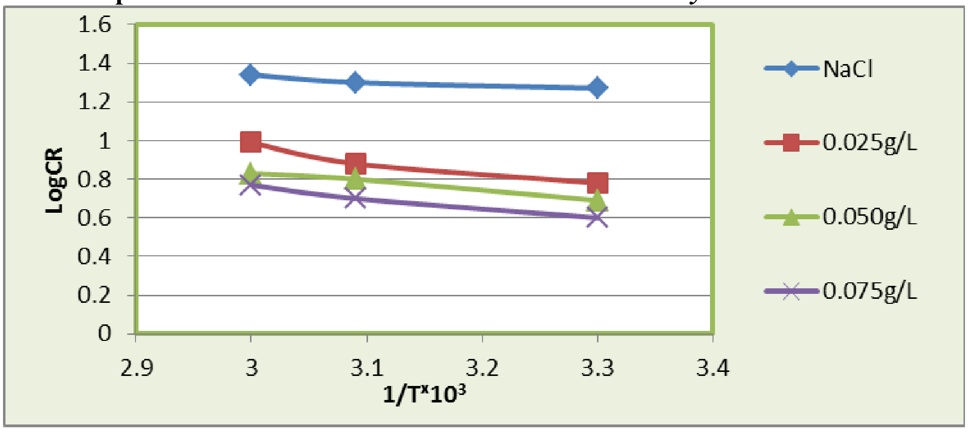

Fig9: Log corrosion rate (mpy) versus 1/T for copper dissolution in 1M NaCl in the absence and presence of different concentrations *Citrullus colocynthis* extract.

Figures 10 to12 represent the relation between log (R_{Corr} / T) vs. 1/ T for metals in 1M H_2SO_4, 1M NaOH and 1M NaCl in absence and presence of various concentrations the inhibitor. Almost straight lines were obtained with slope equal to (– ΔH* / 2.303) R and an intercept of log [(R/Nh) + (ΔS*/2.303R)]. Enthalpy of activation of absolute values lower than 41.86kJmol^{-1} indicates physical adsorption, and values approaching 100 kJmol^{-1} indicate chemical adsorption(Awad M.I. 2006) . In this study, the values of ΔH* are lower than 41.86 kJmol^{-1} confirming physical adsorption. The positive signs of ΔH* reflect the endothermic nature of the metal corrosion process(Fakrudeen S. P. et al. 2012 , Abdallah M.et al. 2013). The values of the entropy (ΔS*) in the presence of the extract are negative; this indicates that the activated complex in the rate-determining step represents an association rather than dissociation step. This means that the activated molecules were in higher order state than that at the initial state(Obi-Egbedi N.O. et al. 2011)

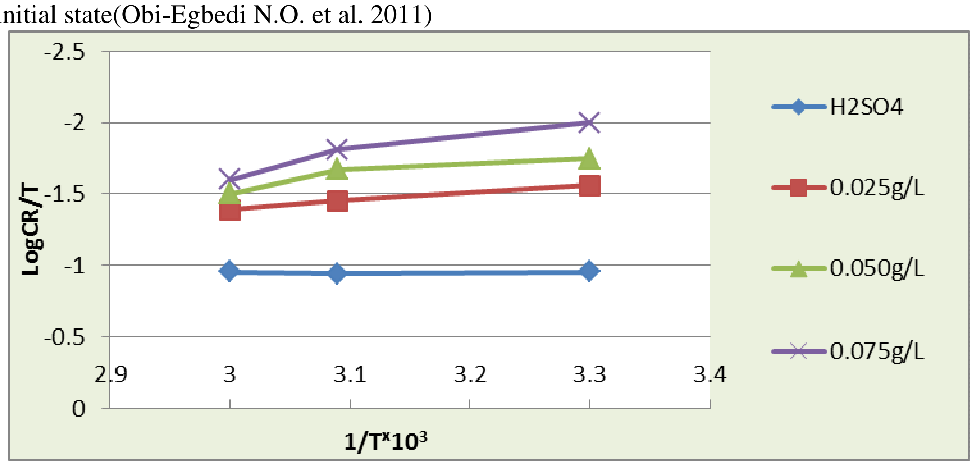

Fig10: Log (corrosion rate (mpy)/T) - 1/T curves for copper dissolution in 1M H_2SO_4 in the absence and presence of the *Citrullus colocynthis* extract.

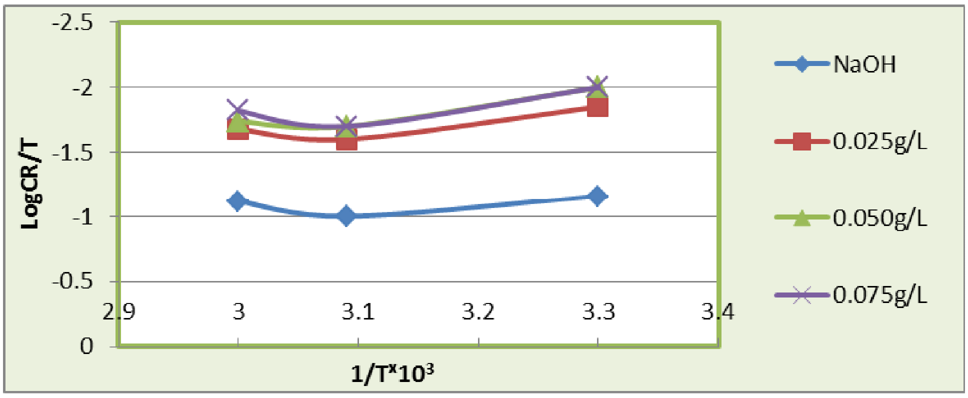

Fig11: Log (corrosion rate (mpy)/T) - 1/T curves for copper dissolution in 1M NaOH in the absence and presence of the *Citrullus colocynthis* extract.

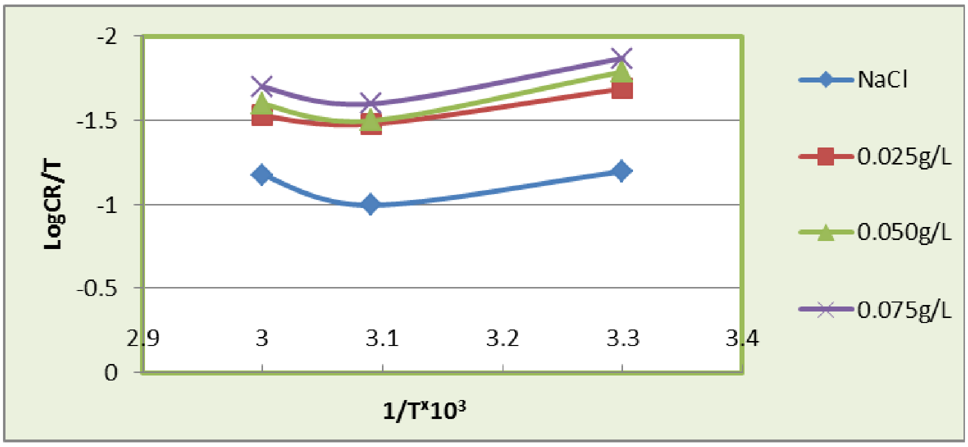

Fig12: Log (corrosion rate (mpy)/T) - 1/T curves for copper dissolution in 1M NaCl in the absence and presence of the *Citrullus colocynthis* extract.

In order to obtain the adsorption isotherm, The θ value for inhibitor concentration at different temperatures has been calculated according to equation (5) The experimental results were best fit with Langmuir adsorption isotherm , The Langmuir adsorption isotherm is given by Eq. (5)(Keles H.et al. 2008 , Noor E.A. et al. 2008)

$$C/\theta = (1/K_{ads}) + C \qquad \dots\dots\dots(5)$$

Where C: is the inhibitor concentration, Θ: is the degree of surface coverage of the inhibitor, K_{ads}. Is the equilibrium constant of the adsorption process, The *K* value is related to the Gibbs free energy of adsorption. $\Delta G°_{ads}$, according to the following equation (Sounthari P. et al. 2013):

$$K_{ads} = (1/55.5)\ exp - \Delta Go_{ads}/RT \qquad \dots\dots(6)$$

Where 55.5 is the molar concentration of water in the bulk solution in mol L^{-1}, R is the universal gas constant and T is the absolute temperature.

As shown in Figures13 to15, the plot of C/ Θversus C for metals in the corrosive medium with different inhibitor concentrations yields a straight line showing that the adsorption of these inhibitors is well described by the Langmuir isotherm. The calculated values of K and ΔG° of the adsorption reaction of metal are shown in Tables 3.

Table 3: Adsorption parameters from Langmuir isotherm for the *Citrullus colocynthis* extract in 1M (H_2SO_4, NaOH, and NaCl) for metal corrosion at 303,323 and 333 K.

Medium	T(°K)	Kads(mole^{-1})	ΔG°_{ads} (kJ/ mol)
H_2SO_4	303	127.0	-22.31
	323	68.97	-22.12
	333	39.36	-21.28
NaOH	303	73.24	-20.93
	323	57.96	-21.68
	333	42.45	-21.49
	303	44.63	-19.68
NaCl	323	41.99	-20.81
	333	33.28	-20.81

The extract of *Citrullus colocynthis* contains the alkaloids, saponins and flavonoids compounds, these compounds having many active centres such as oxygen and nitrogen, are adsorbed on the metal surface and the effectiveness of these inhibitors on the corrosion of copper may be due to the electron densities on the active centres. Generally, the values of ΔG°_{ads} around -20kJ/mol or lower are consistent with physisorption, while those around -40kJ/mol or higher involve chemisorption (Eddy N. O. and Ekop A. S. 2007, Ihebrodike M. M. et al. 2010, Saratha R. Et al 2011)

The results are presented in table (3), the values$\Delta G_{ads}$are negative and less than -40 kJmol^{-1}. This implies that the adsorption of the inhibitor on metal surface is spontaneous and confirms physical adsorption mechanism (Abiola O. K. et al. 2007, Elewady G.Y et al. 2008, Vimala J. R. Et al. 2011). The positive values of adsorption equilibrium constant K_{ads} imply a better adsorption, which leads to an increase in the inhibition efficiency (Abboud Y. Et al. 2009)

The adsorption equilibrium constant K_{ads}decreases with increase in experimental temperature (Table 3) indicating that the interactions between the adsorbed molecules and the metal surface are weakens and consequently, the adsorbed molecules could become easily removable. Such data explains the decrease in the inhibition efficiency with increasing temperature (Onuegbu T. U. Et al 2013, Obot I.B. et al. 2010)

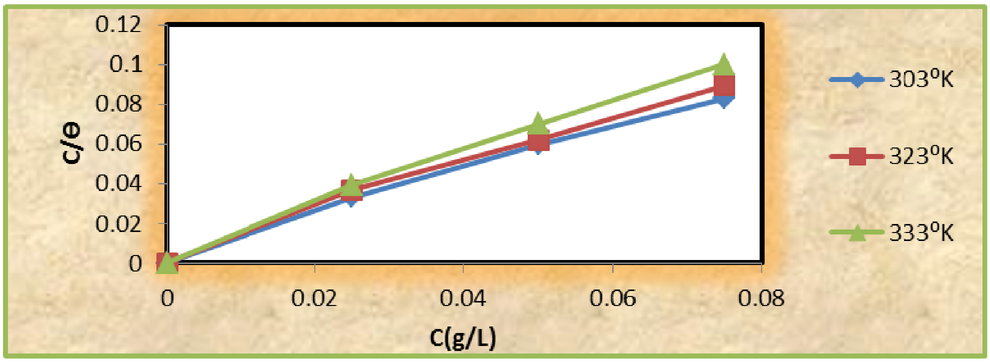

Fig 13: Langmuir adsorption isotherms for the adsorption of the *Citrullus colocynthis* extract on copper in 1M H_2SO_4 at different temperatures

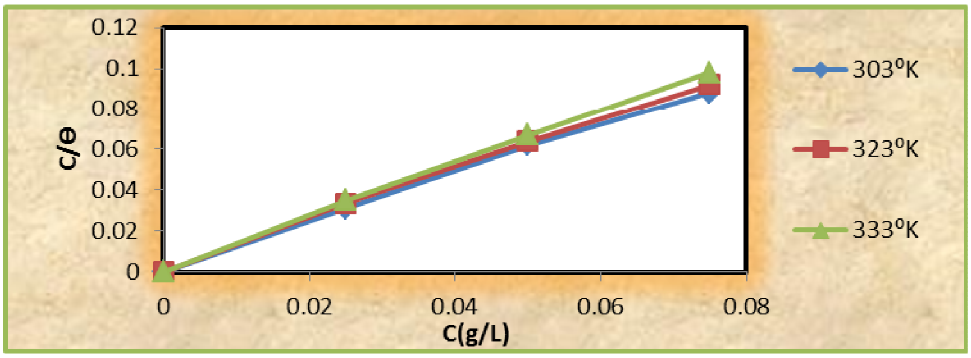

Fig.14: Langmuir adsorption isotherms for the adsorption of the *Citrullus colocynthis* extract on copper in 1M NaOH at different temperatures

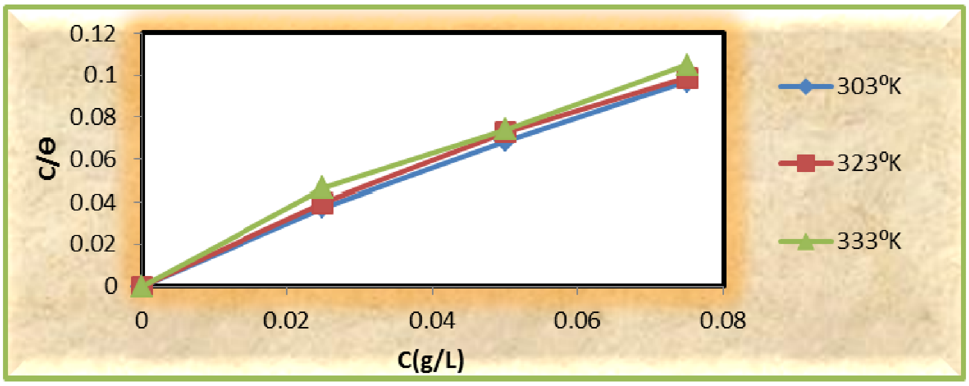

Fig.15: Langmuir adsorption isotherms for the adsorption of the *Citrullus colocynthis* extract on copper in 1M NaCl at different temperatures

3-5.Potentiodynamic polarization data

The effects of sulphuric acid, sodium hydroxide and sodium chloride media on the corrosion rate of copper sample were studied using Tafel polarization technique as shown in Figs. 16 -18-20)

The corrosion current of the copper plate in 1M H_2SO_4 decreases from 303.24 μA cm^2 to 4.81 μA $cm^2$with the addition of 0.075 g/L probably *Citrullus colocynthis* extract .As shown in the following fig.17 The decrease in I_{corr} values is due to the decreased SO_4^{-2} ions attack on the copper surface(Xometl O. O. Et al. 2013)In addition, the corrosion potentials of the polarization curves are shifted towards more negative potentials in the presence of inhibitors due to the decrease in the rate of the cathodic reaction. The cathodic reaction for copper in open air 1 M H_2SO_4 solution is the oxygen reduction as follows(Abd-El-Nabey B.A. et al. 2013)

$$4H^+ + O_2 + 4e^- \rightarrow 2H_2O \quad \ldots\ldots (7)$$

On the other hand, the anodic reaction of copper in 1 M (NaCl, H_2SO_4, and NaOH) solutions is the dissolution of Cu to Cu^{+2} as follows

$$Cu_{(s)} \rightarrow Cu^{+2} + 2e^- \quad \ldots\ldots (8)$$

The corrosion current of the copper plate 1M NaOH decreases from 52.17 μA cm^2 to 1.56 μA cm^2 with the addition of 0.075 g/L for the *Citrullus colocynthis* extract .As shown in the following fig.19 .On the other hand, The corrosion current of the copper plate 1M NaCl decreases from 13.76 μA cm^2 to 1.88 μA cm^2 with the addition of 0.075 g/L for the *Citrullus colocynthis* extract. The corrosion potentials of the polarization curves are shifted towards less negative potentials in the presence of inhibitors and the values of Icorr decrease in NaOH, NaCl solution. This indicates that inhibitors cause anodic polarization (M. Abdallah M. 2000) . As shown in the following figures19 and figures21

Tafel plots that are produced by electrochemical test are used in calculating the cathodic (β_C) and anodic(β_A) Tafel constants .The Tafel constants measured contributes in calculating the corrosion rate. The slope of the straight line fits the linear regions of the anodic and cathodic Tafel gives the Tafel constants, β_A and β_C (Flis J. and Zakroczymski T. 1996)

$$I_{corr} = \beta_A \beta_C / 2.303 R_p (\beta A + \beta_C) \quad \ldots\ldots (9)$$

R_p is the resistance polarization (Ramesh S.V. and Adhikari A.V. 2009)

Table4shows the electrochemical corrosion parameters, as corrosion potential (E_{corr}), cathodic Tafel slopes (βc), corrosion current density (I_{corr}), obtained by extrapolation of the Tafel lines and the inhibition efficiency %IE which was evaluated from the relation:

$$\%IE = [(I_{corr})_0 - (I_{corr})/(I_{corr})_0] \times 100 \quad \ldots\ldots (10)$$

$$\theta = (I_{corr})_0 - (I_{corr}) / (I_{corr})_0 \ldots\ldots (11)$$

Where $(I_{corr})_o$ and I_{corr} are the corrosion current densities, in the absence and the presence of inhibitor and θ is the surface coverage.

It is clearly seen from figures 17, 19 and 21 that the cathodic slope value was changed with the addition of extracts in aggressive solutions. This result indicates the influence of the inhibitor on the kinetics of the hydrogen evolution reaction. The decrease in the corrosion current can attributed to the inhibition efficiency of extracts of *Citrullus colocynth* fruits on the cathodic part of polarization curves through the reduction of hydrogen ions H^+ and also its effectiveness on the anodic part due to adsorption of the extract components on the surface of copper sample which contain a barrier hinders the process of hydrogen gas evolution and metal dissolution (Arab S.T.and Emran K.M. 2008). The functional groups of the inhibitor are playing important role during the adsorption process. The process of adsorption is the process of replacing between extract molecules and water. A molecule on the electrode surface is as follows.

$$Ex_{(sol)} + XH_2O_{(ads)} \rightarrow Ex_{(ads)} + H_2O_{(sol.)} \ldots\ldots (12)$$

Where $Ex_{(sol)}$ and $Ex_{(ads)}$ refer to the extract molecules in solution and extract molecules adsorbed on the metal surface, respectively, $H_2O_{(ads)}$ water molecule adsorb on the metal surface and X is the number of water molecules which replaced by one molecule of the extract(Polo Bastidas J.l. et al. 2000).

It is interesting to note that the values of % IE measured by polarization measurement are higher than those obtained from weight loss measurement. These results may be due to the fact that the electrochemical measurements were carried out on freshly prepared solutions (Fouda A.S. et al. 2011)

Table 4: Electrochemical kinetic parameters from polarization curves for copper in1M (NaOH, H_2SO_4, NaCl) without and with (0.075 g/L) of the inhibitor at 303 ^oK.

Medium	Icorr µA cm-²	Ecorr mV	βc mV dec.-¹	βa mV dec.-¹	%IE	Θ
H_2SO_4	303.24	-16.40	-118.5	88.70		
Citrullus colocynthis extract	4.8100	-26.30	-143.2	66.30	98.41	0.984
NaOH	52.170	-268.4	-203.7	58.10		
Citrullus colocynthis extract	1.5600	-146.4	-52.30	48.60	97.00	0.970
NaCl	13.760	-158.0	-194.8	405.8		
Citrullus colocynthis extract	1.8800	-42.30	-112.4	62.40	86.33	0.863

The above results indicated that Citrullus colocynthis extract as good inhibitor for corrosion of the three Medias

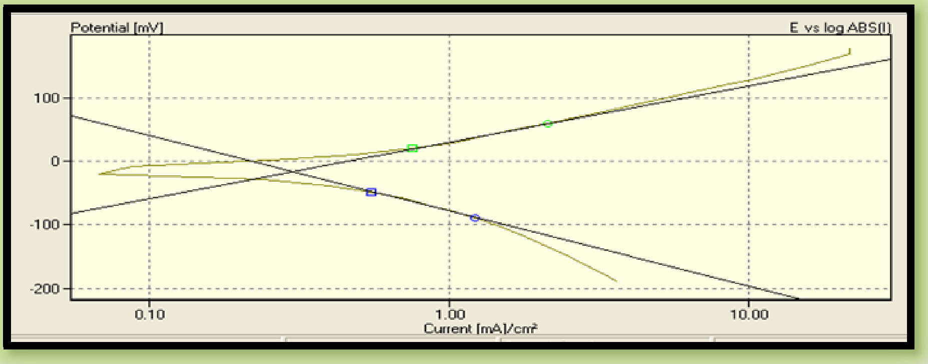

Figure 16: Tafel polarization for copper in 1M H_2SO_4 at 303 0K in absence of inhibitor

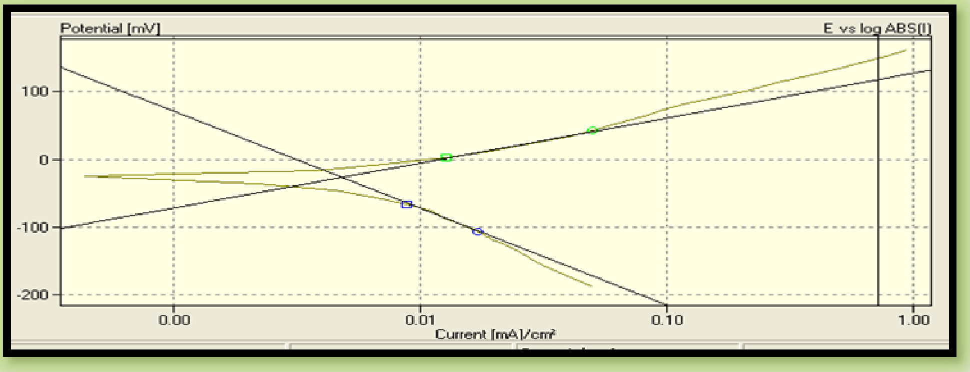

Figure 17: Tafel polarization curve for copper in 1M H_2SO_4 at 303 0K in presence of the *Citrullus colocynthis* extract

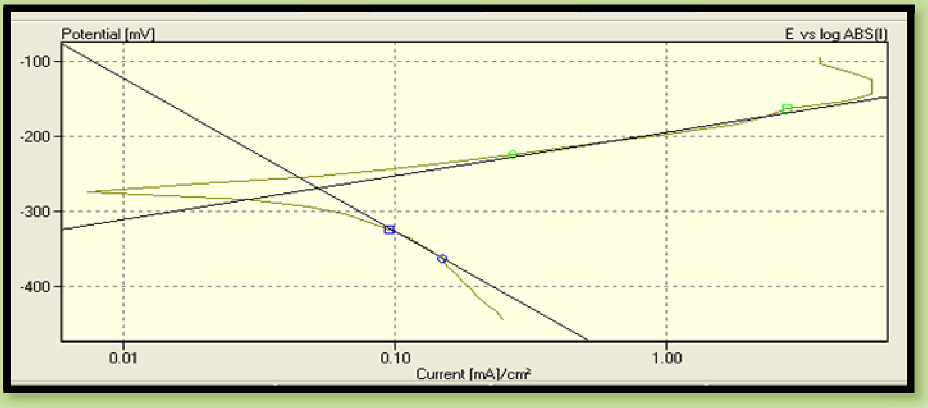

Figure 18: Tafel polarization curve for copper in 1M NaOH at 303 0K in absence of inhibitor.

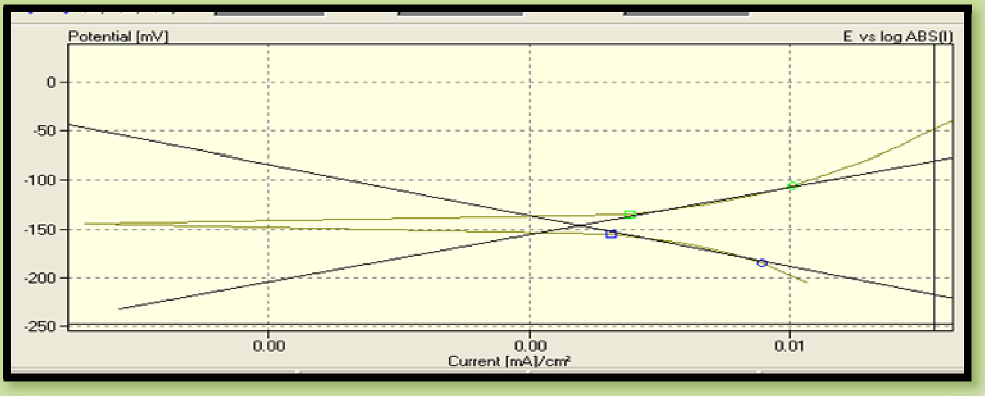

Figure 19: Tafel polarization curve for copper in 1M NaOH at 303 0K in presence of the *Citrullus colocynthis* extract

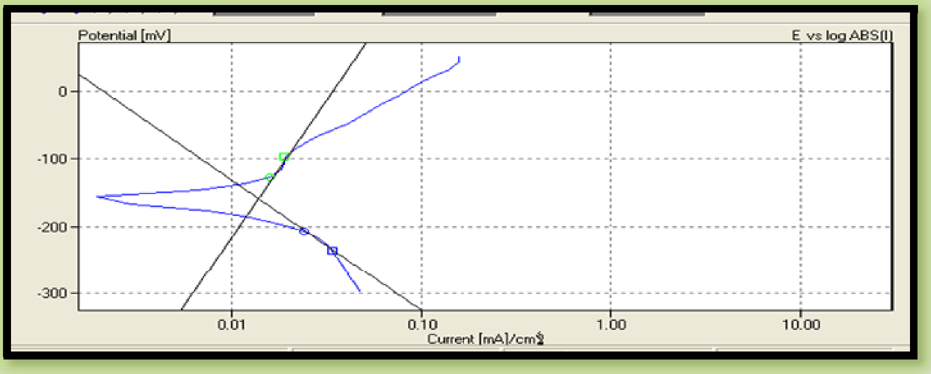

Figure 20: Tafel polarization curve for copper in 1M NaCl at 303 0K in absence of inhibitor.

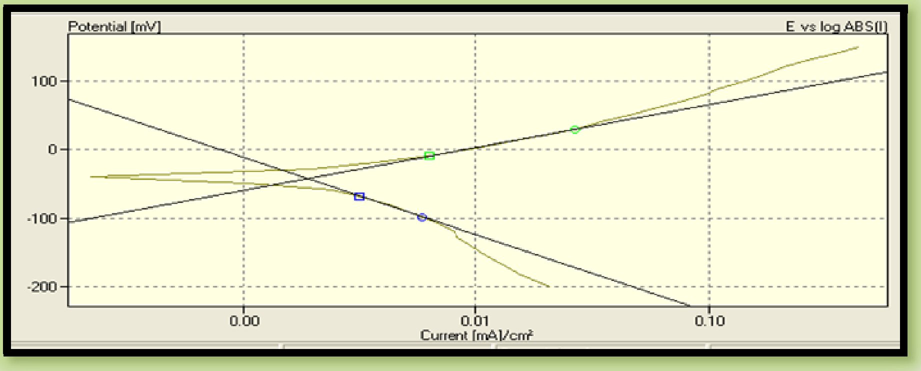

Figure 21: Tafel polarization curve for copper in 1M NaCl at 303 0K in presence the *Citrullus colocynthis* extract

CONCLUSIONS

The *Citrullus colocynthis* extract was found to be an efficient natural corrosion inhibitor for copper in1M (H_2SO_4, NaOH, NaCl) solutions by using Potentiodynamic polarization and weight loss techniques. The negative values of ΔG indicate that the adsorption of the inhibitors on the metal surface is spontaneous. Ea and ΔH values of the corrosion process also support this observation. All values of ΔS^*_{ads} are negative for the blank and inhibited solution which implies that the activation complex in the rate determining step represents association rather than dissociation step. The adsorption characteristics of *Citrullus colocynthis* extract on the metal surface were approximated by Langmuir adsorption isotherm, and it obeyed and fitted this model. The results obtained from Potentiodynamic polarization and weight loss measurements are in good agreement, although the Potentiodynamicpolarization gave rather high inhibition efficiency. The investigated extracts were of mixed-type inhibitors, i.e. they affect both anodic dissolution of copper, and hydrogen evolution reactions.

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