

Inhibitory Impact of Crude Phytochemical compounds of *Symphytum Officinale* (Comfrey) Leaves on the Corrosion of Copper by Hydrogen Tetraoxosulphate (IV) (H_2SO_4) Acid Solution

¹B. U. Ugi*, ²M. E. Obeten

¹Lecturer, Department of Pure and Applied Chemistry, University of Calabar P. M. B. 1115, Calabar – Nigeria

²Lecturere, Department of Chemical Sciences, Cross River University of Technology, P. M. B. 1123, Calabar - Nigeria

Abstract

Crude Alkaloid, Saponins and flavonoids extract of *Symphytum officinale* (CAESO, CSESO and CFESO) leaves were investigated as corrosion inhibitor of copper in 0.5 M H_2SO_4 acid solutions using weight loss, Thermometric, potentiodynamic polarization and electrochemical impedance spectroscopy studies. The weight loss results revealed that the plant extracts are an reliable corrosion inhibitors to the metal tested. Electrochemical polarization data revealed a mixed mode of inhibition and the results of electrochemical impedance spectroscopy have shown that the change in the impedance parameter (charge transfer resistance and double layer capacitance) with the change in concentration of the inhibitors is due to the adsorption of active molecules leading to the formation of a protective layer on the surface of copper. A physical adsorption mechanism was recorded by the inhibitor /metal interface and the Langmuir adsorption isotherm was well obeyed revealing from the good correlation of the data to the isotherm. The inhibitors proved to be a stabled one on the copper surface and a spontaneous reaction process was recorded from the free energy data.

Keywords - *Symphytum officinale*, Langmuir isotherm, weight loss, Gibbs free energy, thermometric method, tafel plots,

I. INTRODUCTION

Corrosion can be viewed as the degradation of a material due to a reaction with its environment [1]. This implies deterioration of physical properties of the material. This can be a weakening of the material due to a loss of a cross sectional area, it can be the shattering of a metal due to hydrogen embrittlement, or it can be the cracking of a polymer due to sunlight exposure [1 –

2]. The consequences of corrosion are many and varied and the effects of these on the safe, reliable and efficient operation of equipment or structures are often more serious than the simple loss of a mass of metal. Failure of various kinds and the need for expensive replacement may occur even though the amount of metal destroyed is quite small. In order to reduce the corrosion of metals, the application of inhibitors is one of the best methods of preventing metals against corrosion [3]. It has been found that most corrosion inhibitors are organic compounds containing polar fractions with nitrogen, sulphur or oxygen in the conjugated system that severely inhibit the corrosion of metals especially steel, aluminium, copper, etc. in acidic and alkaline environments [3 - 4]. Use of inhibitors is one of the most practical methods for protection against corrosion especially in acid solutions to prevent unexpected metal dissolution and acid consumption. Copper corrosion protection has become important particularly in acid media because of the increased industrial applications of acid solutions. The known hazardous effect of most synthetic corrosion inhibitors is the motivation for the use of some natural products. The use of chemical inhibitors has been limited because of the environmental threat and also in recent times due to environmental regulations [5].

Phytochemical compounds extracted from different plants have become important because they are environmentally acceptable, inexpensive, readily available and renewable sources of materials [6]. *Symphytum officinale* contains mixed phytochemicals in varying amounts, including allantoin, pyrrolizidine alkaloids, saponins, tannins, mucilage, among others. Liver toxicity is associated with consuming this plant or its extracts. In modern herbalism, *Symphytum officinale* is commonly used topically. It is still valued for its use in salves and other topical skin preparations and for its

use as animal fodder and fertilizer due to the presence of pyrrolizidine alkaloids (Fig. 1).

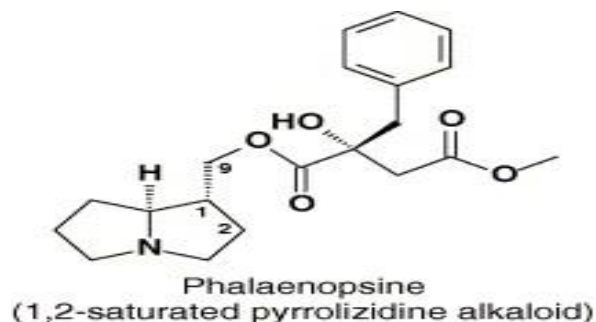


Fig. 1 Major constituents of *Symphytum officinali*

This plant has wide spread usage in medicine both herbal and orthodox. This research is driven by its limited application (especially the phyto compounds) in corrosion study especially in the mitigation of Copper in acidic environment. Hence, this research is investigating the inhibitory impact of crude leaf extracts (Phytochemicals) of *Symphytum officinali* (Comfrey) plant on the corrosion of copper by Hydrogen Tetraoxosulphate (IV) (H_2SO_4) acid solution

II. EXPERIMENTATION

A. Preparation of Copper surface

Prior to corrosion studies, the copper substrate was press cut into coupons of dimensions 2.0 cm x 1.8 cm x 0.08 cm for weight loss and thermometric measurements, and 1 cm x 1 cm for electrochemical impedance and potentiodynamic polarization measurements. The copper coupons were polished using successive grades of silicon carbide paper (#120 – #800), degreased in ethanol to remove the surface dirt arising from the abraded process, rinsed with acetone and air dried. Copper coupons for electrochemical studies were completely insulated leaving one side of the surface (area $\frac{1}{4}$ 1 cm²) exposed. The prepared metal substrates were stored in a desiccator prior to use.

B Preparation of *Symphytum officinali* (Comfrey) sample

The fresh leaves of *Symphytum officinali* (Comfrey) obtained from a farm land in New Jerusalem village in Cross River state, Nigeria were washed and cut into small pieces, then dried in oven at 60°C. After the drying of the leaves, they were put through grinding to obtain a powdered sample with very fine particle size. Conventional mortar and pestle was used for grinding, followed by the use of electric blender to reduce particle size of sample. The powdered sample was extracted in absolute ethanol using suxhlet

extraction process. The crude leave extract and solvent was placed in a water bath for 24 hours to evaporate the solvent leaving a paste (crude ethanol extract) for alkaloids, flavonoids and saponins extraction.

C. Preparation of crude saponins, flavonoids and alkaloids inhibitor solutions

The alkaloid fraction was prepared using dilute hydrochloric acid (35.5% w/w) and ammonia solution. HCl used during the experiment was less than 1M, but not weaker than 0.1 M (pH 0-1). Fifty grams of the crude ethanol extract was partitioned between 150 cm³ of chloroform and 100 cm³ of 0.5 M HCl solution using a separating funnel. The HCl solution in the float fraction from the separating funnel was carefully basify with 150 cm³ ammonia solution and this was taken well above pH 7. Two hundred centimeter cube of chloroform was immediately added into the basic solution in the separating funnel to obtain two nice layers with the lower one containing the alkaloids. The chloroform layer was eventually separated from mixture and put aside, the chloroform distilled off, and a small quantity of the crude alkaloids was obtained.

Crude saponins extracts was prepared by heating 20 g of crude *Symphytum officinali* leaves extract in 25 cm³ of methanol for 5 hours using a water bath to reduce volume to at least 15 ml. Then chloroform of 20 cm³ was added to separate organic portion from the aqueous and the organic portion was discarded. The methanolic fraction was then diluted with 10 cm³ buthanol to obtain an n-buthanol/methanol fraction. Both mixtures were then separated to dryness to obtain a crystalline soapy extract used as crude saponins.

In another experiment, 50 g of the dried powdered sample was weighed into a beaker and extracted with 100 cm³ of ethanol at room temperature for 1 hour. The solution was filtered through filter paper. The filtrate was evaporated to dryness over water bath at 50°C. The weight of the dried extract was taken and the amount of flavonoid present was calculated.

10 g each of both the crude saponins, flavonoids and alkaloids extracts were separately soaked in 1000 cm³ of 0.5 M H_2SO_4 solution and kept overnight. The solutions obtained were filtered and stored. From the stock solution, inhibitor test solution of concentrations 0.3 g/L, 0.7 g/L, 1.5 g/L, 2.0 g/L and 3.5 g/L of 0.5 M H_2SO_4 was prepared. The prepared solutions were then used to study the corrosion inhibition impact of the phytochemical compounds.

D. Weight loss method

Gravimetric (weight loss) experiment was carried out to study the effect of addition of different concentrations (0.3 g/L, 0.7 g/L, 1.5 g/L, 2.0 g/L and 3.5 g/L) of phytochemical components of crude *Symphytum officinali* on copper sheet corrosion in 0.5

M H₂SO₄. The polished coupons were weighed and immersed in 100 cm³ electrolytic solution for 60 minutes in the absence and presence of various concentrations of inhibitor at 303K temperatures. After immersion time the coupons of various metals were picked out, cleaned with distilled water, rinsed with ethanol and degreased with acetone and immediately air dried. The specimens were again weighed using electronic balance (sensitivity up to 0.0001gm). The corrosion rate (R_c) in mgcm⁻² h⁻¹ of inhibitor were obtained graphically from a plot of weight loss against time. Inhibition efficiency (%IE) of inhibitors were calculated from equation 1.

$$IE \% = \left(\frac{R_o - R_i}{R_o} \right) \times 100 \quad \dots \dots \dots 1$$

where R_o and R_i are the corrosion rates in the absence and presence of the plant extracts.

E. Thermometric measurements

100 cm³ of the corrodent (1 M HCl) was introduced into a beaker. Thereafter, a copper coupon of dimension 2.0cm x 1.8 cm x 0.08 cm already weighed was dropped into the corrodent and the beaker immersed in a water bath. The volume of the hydrogen gas evolved from the corrosion reaction was regulated by temperature changes in the water bath. At different temperatures of 298 K, 318 K and 328 K, the metal was removed, degreased with ethanol, rinsed with acetone and air dried and then weighed. This procedure was repeated for a set of fresh coupons at different concentrations (0.3 g/L, 0.7 g/L, 1.5 g/L, 2.0 g/L and 3.5 g/L) of crude *Symphytum officinali* extracts

F. Electrochemical determination

Electrochemical measurements were undertaken in a three-electrode cell using Gamry Instrument Potentiostat/Galvanostat/ZRA with a Gamry framework system based on ESA410. copper samples, graphite rod and silver/silver chloride (Ag/AgCl) were used as working, counter and reference electrodes, respectively. All the measurements were taken after the working electrode was immersed for 60 minutes in the different test solutions at room temperature in order to attain a steady-state open-circuit potential (OCP). The frequency range from 100 kHz to 0.01 Hz with amplitude of 10 mV was used in electrochemical impedance experiments. The potentiodynamic polarization curves were recorded from cathodic

potential of -150 mV to anodic potential of +100 mV at a scan rate of 0.5 mV s⁻¹ with respect to free corrosion potential (E_{corr}). The linear Tafel segments of the anodic and cathodic curves were extrapolated to corrosion potential to obtain the corrosion current densities (i_{corr}) and other electrochemical parameters of interest. Inhibition efficiency from electrochemical impedance spectroscopy (EIS), and potentiodynamic polarization (PDP) was computed using Eqs (2) and (3) respectively.

$$IE_{EIS} = 1 - \left(\frac{R_{ct}^0}{R_{ct}} \right) \times 100 \quad \dots \dots \dots (2)$$

where R_{ct}⁰ and R_{ct} are the charge transfer resistances in the absence and presence of the inhibitors respectively.

$$IE_{PDP} = 1 - \left(\frac{i_{corr}}{i_{corr}^0} \right) \times 100 \quad \dots \dots \dots (3)$$

where i_{corr}⁰ and i_{corr} are the corrosion current densities in the absence and presence of inhibitor respectively.

III. RESULT AND DISCUSSION

A. Weight loss Analysis (Effect of Inhibitor concentration on metal dissolution)

The material loss expressed as the corrosion rate for the copper coupons in 0.5 M H₂SO₄ solutions containing different concentrations of crude alkaloid, flavonoid and saponins extracts of *Symphytum officinali* as a function of inhibitor concentration is presented in Table 1. It is observed that the corrosion rates decreased with increase in concentration of both extracts, indicating that the extent of inhibition is dependent upon the amount of extract present [5, 7-10]. Also from Table 1, it is observed that the inhibition efficiencies increase with increase in extracts concentration. This indicates that the phytochemical components of the extracts are adsorbed onto the metal surface resulting in the blocking of the reaction sites, and protection of the copper surface from the attack of the corrosion active ions in the acid medium [11-15]. Comparing the inhibition efficiencies of the extract on the different metals, it is observed that the efficiencies follow the trend: alkaloids (99.7 %) > saponins (94.0 %) > flavonoids (90.3 %). This shows that the yield of the phytochemicals in the plant extracts responsible for the inhibition of the corrosion reactions depend not only on the metal type but also on the type of extract. This finding is in line with previous reports [11].

Table 1
Weight loss analysis result showing the corrosion rate of copper, surface coverage and inhibition efficiency of inhibitors in 0.5 M H₂SO₄ solutions at different concentrations

CFESO	CAESO	CESO
-------	-------	------

Conc. (g/L)	CR (mg/cm ² /h)	θ	%IE	CR (mg/cm ² /h)	θ	%IE	CR (mg/cm ² /h)	θ	%IE
Blank (0.5 M H ₂ SO ₄)	3.294	-	-	3.294	-	-	3.294	-	-
0.3 g/L	0.687	0.791	79.1	0.388	0.882	88.2	0.506	0.846	84.6
0.7 g/L	0.467	0.858	85.8	0.310	0.906	90.6	0.401	0.878	87.8
1.5 g/L	0.410	0.876	87.6	0.201	0.939	93.9	0.320	0.903	90.3
2.0 g/L	0.399	0.879	87.9	0.038	0.988	98.8	0.261	0.921	92.1
3.5 g/L	0.321	0.903	90.3	0.011	0.997	99.7	0.198	0.940	94.0

B. Thermometric analysis (Effect of temperature on inhibitor concentration)

The influence of temperature on the corrosion inhibitive behavior of the two tested inhibitors were investigated from the thermometric method data in the temperature range of 298, 318 and 328 K. Results obtained as shown in Table 2 revealed that corrosion rate increased with increase in temperature in the absence and presence of the inhibitors but decreased with increased inhibitor concentration. On the other hand, inhibition efficiency of the two inhibitors decreased as temperature was increased and increase

with inhibitor concentration. The apparent decrease in % IE as temperature was raised from 298, 318 and 328 K for CAESO, CSESO and CFESO could be related to change of adsorption mode from chemisorption to physisorption caused by desorption of adsorbed inhibitor as a result of increased solution agitation due to higher rate of hydrogen gas evolution [6, 9, 12]. This is verified from the higher values of inhibition efficiency noticed at the lowest temperature (298 K) against the highest (328 K).

Table 2
Thermometric analysis result showing temperature effect on the corrosion rate of copper, surface coverage and inhibition efficiency of inhibitors in 0.5 M H₂SO₄ solutions at different concentrations

	Conc. (g/L)	CR (mg/cm ² /h)			θ			% IE		
		298K	318K	328K	298K	318K	328K	298K	318K	328K
CSESO	Blank (0.5 M H ₂ SO ₄)	0.891	2.471	9.115	-	-	-	-	-	-
	0.3 g/L	0.389	1.195	4.496	0.563	0.516	0.507	56.3	51.6	50.7
	0.7 g/L	0.320	0.877	4.237	0.641	0.645	0.535	64.1	64.5	53.5
	1.5 g/L	0.257	0.802	4.001	0.712	0.675	0.561	71.2	67.5	56.1
	2.0 g/L	0.107	.533	3.572	0.880	0.784	0.608	88.0	78.4	60.8
	3.5 g/L	0.049	0.289	1.966	0.945	0.883	0.784	94.5	88.3	78.4
CAESO	Blank (0.5 M H ₂ SO ₄)	0.891	2.471	9.115	-	-	-	-	-	-
	0.3 g/L	0.305	0.966	3.877	0.658	0.609	0.575	65.8	60.9	57.5
	0.7 g/L	0.210	0.731	3.142	0.764	0.704	0.655	76.4	70.4	65.5
	1.5 g/L	0.111	0.591	2.835	0.875	0.761	0.689	87.5	76.1	68.9
	2.0 g/L	0.034	0.369	2.164	0.962	0.851	0.763	96.2	85.1	76.3
	3.5 g/L	0.006	0.147	1.469	0.993	0.941	0.839	99.3	94.1	83.9
CFESO	Blank (0.5 M H ₂ SO ₄)	0.891	2.471	9.115	-	-	-	-	-	-
	0.3 g/L	0.439	1.358	5.071	0.507	0.450	0.444	50.7	45.0	44.4
	0.7 g/L	0.385	1.211	4.629	0.568	0.510	0.492	56.8	51.0	49.2
	1.5 g/L	0.300	1.028	4.019	0.663	0.584	0.559	66.3	58.4	55.9
	2.0 g/L	0.159	0.687	3.669	0.822	0.722	0.597	82.2	72.2	59.7
	3.5 g/L	0.107	0.427	2.521	0.880	0.827	0.723	88.0	82.7	72.3

C. Electrochemical impedance spectroscopic result

Fig. 1a-c shows the Nyquist plot of one capacitive loop exhibiting an extended semicircle in the complex

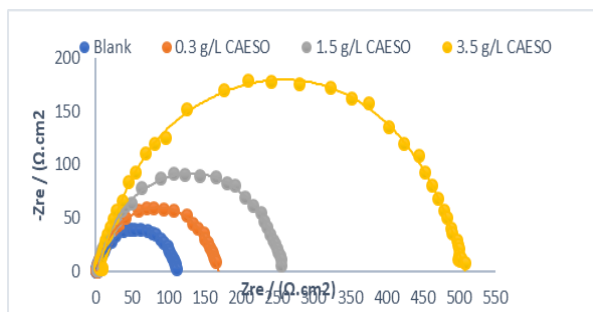
impedance plane both in uninhibited and inhibited solutions, an indication that corrosion rate is controlled by charge transfer resistance [13 - 15]. The impedance

diagrams obtained increases in diameter as inhibitor concentration increases indicating that the presence of inhibitor molecules strengthens the inhibitive film occurring through defects of this film with increase in *Symphytum officinali* concentration [9, 13] (Fig. 2). Table 3 shows that C_{dl} values decreased when the concentration of the inhibitor molecules increased. The decrease in C_{dl} might arise from a decrease in local

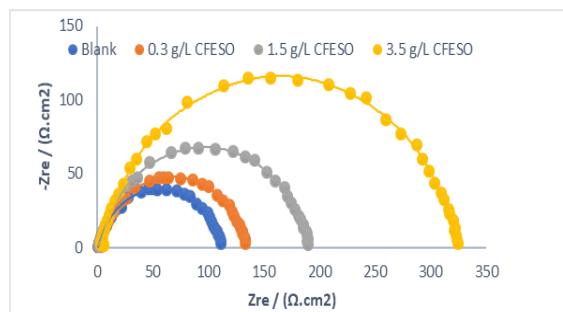
dielectric constant and/or an increase of the electrical double layer thickness which might arise from substitution of preadsorbed water molecules on the metal/electrolyte interface by adsorbed organic constituents of *Symphytum officinali* extract, suggesting that inhibitor molecules function by adsorption at the metal/solution interface [14].

Table 3
Results from IES experiment for the adsorption of copper coupons in 0.5 M H₂SO₄ solutions containing different extract concentrations of *Symphytum officinali* leaves

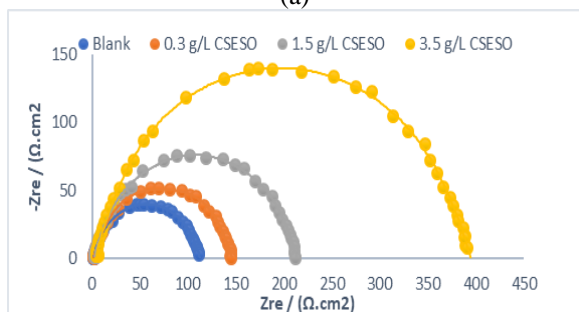
	Conc. (g/L)	Rct (Ωcm^{-2})	Cdl (μFcm^{-2})	IE _R %
	Blank (0.5 M H ₂ SO ₄)	104	7.7 x 10 ⁻⁴	-
CAESO	0.3 g/L	182	3.9 x 10 ⁻⁴	42.9
	1.5 g/L	281	1.8 x 10 ⁻⁴	63.1
	3.5 g/L	527	6.6 x 10 ⁻⁵	80.3
CSESO	0.3 g/L	172	6.2 x 10 ⁻⁴	40.0
	1.5 g/L	215	5.4 x 10 ⁻⁴	53.4
	3.5 g/L	396	2.7 x 10 ⁻⁴	73.7
CFESO	0.3 g/L	159	6.9 x 10 ⁻⁴	34.6
	1.5 g/L	197	4.1 x 10 ⁻³	47.2
	3.5 g/L	341	3.0 x 10 ⁻⁴	69.5



(a)



(c)



(b)

Fig. 2. Nyquist plots for the adsorption of (a)CAESO (b) CSESO and (c) CFESO on copper coupon in 0.5 M H₂SO₄ solutions

D. Potentio-dynamic polarization results

The polarization behaviour of copper electrodes in 0.5 M H₂SO₄ solutions in the absence and presence of different concentrations of crude alkaloid, saponins and

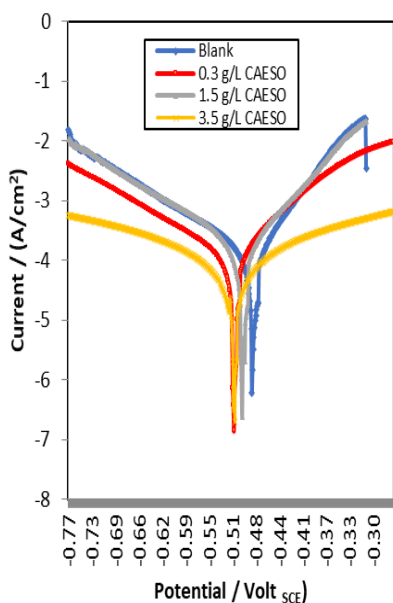
flavonoids extracts of *Symphytum officinali* leaves are shown in Fig. 3a - c. The polarization curves show that in presence of the extracts of *Symphytum officinali* leaves the cathodic and anodic branches of the

polarization curves are shifted towards lower currents, probably due to the consequence of the blocking effect of the adsorbed inhibitor molecules [15 – 16]. As it can be observed from Table 4, the anodic and cathodic reactions are affected by the inhibitors implying that the addition of the inhibitors reduces the anodic dissolution of all the copper and also retards the cathodic hydrogen evolution reactions. It follows from Fig. 3a - c. that the shapes of the polarization plots for inhibited electrodes are not substantially different from those of uninhibited

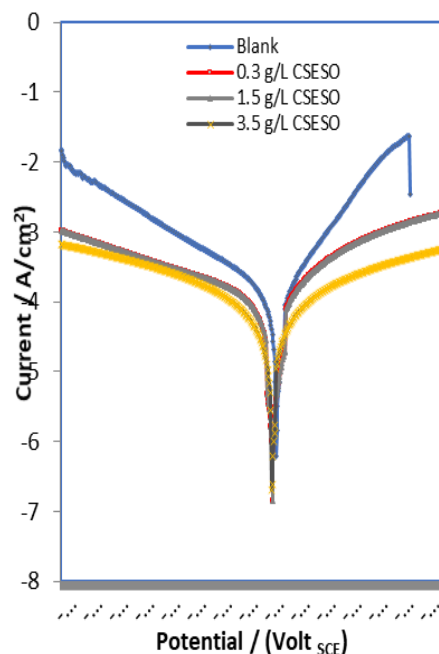
electrodes. The presence of each inhibitor decreases the corrosion rate but does not change other aspects of the behaviour. This means that the inhibitor does not alter the electrochemical reactions responsible for corrosion [10,17]. The inhibitive action of these inhibitors on copper metal therefore may be related to its adsorption and formation of a barrier film on the electrode surface, protecting them from corrosion [12].

Table 4
Results from PDP experiment showing parameters for the adsorption of copper coupons in 0.5 M H₂SO₄ solutions containing different extract concentrations of *Symphytum officinali* leaves

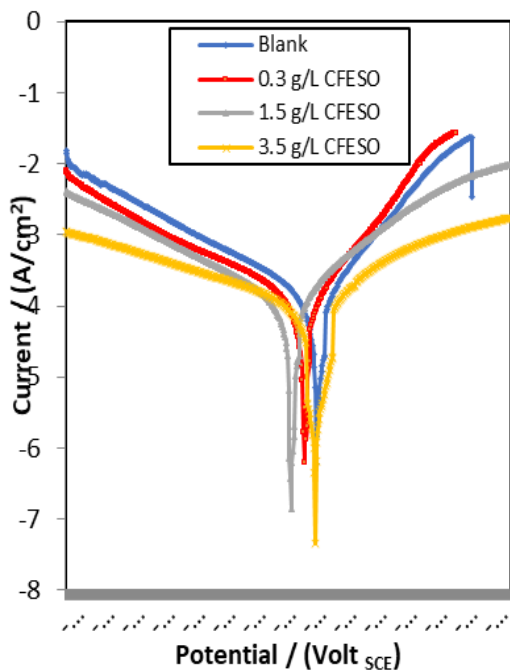
	Conc. (g/L)	I _{corr} (mAcm ⁻²)	β _c (mV/dec)	β _a (mV/dec)	IEi (%)
	Blank (0.5 M H ₂ SO ₄)	3.078	109	192	-
CAESO	0.3 g/L	1.037	89	93	66.3
	1.5 g/L	0.411	55	84	86.7
	3.5 g/L	0.107	23	47	96.5
CSESO	0.3 g/L	1.175	99	134	61.8
	1.5 g/L	0.840	71	106	72.7
	3.5 g/L	0.299	34	82	90.3
CFESO	0.3 g/L	3.161	101	159	46.6
	1.5 g/L	2.906	86	117	50.9
	3.5 g/L	2.726	54	90	53.9



(a)



(b)



(c)
Fig. 3 Tafel plots for the adsorption of (a)CAESO (b) CSESO and (c) CFESO on copper coupon in 0.5 M H₂SO₄ solutions

E. Thermodynamic Effects

The temperature of the system was varied across the inhibitor concentrations from which the activation energy for the corrosion of copper in solutions of 0.5 M H₂SO₄ was evaluated using the Arrhenius equation given by equation 4

$$\ln R_c = \ln A - \frac{E_a}{RT}$$

where R_c is the corrosion rate, E_a is the apparent effective activation energy, R is the general gas constant, and A is the Arrhenius pre-exponential factor. Calculated values of activation energy were obtained from the slope of Fig. 4 and presented in Table 5. The values obtained are higher than the value obtained for the blank, an indication that alkaloid, saponins and flavonoid extracts of *Symphytum officinali* retards the corrosion of copper in 0.5 M H₂SO₄ solutions [18]. Since the activation energy which is the energy required to oxidize metal is increased with inhibitor concentration, it implies that more energy has to be supplied to the system for the corrosion to take place, thus the observed decrease in corrosion rate. The values are also consistent with the data expected for the mechanism of physical adsorption (<80KJmol⁻¹).

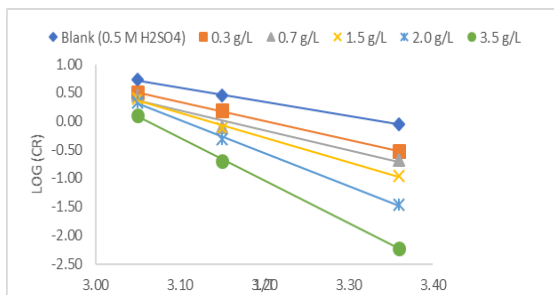
Table 5
Thermodynamic parameters for the adsorption of copper coupons in 0.5 M H₂SO₄ solutions containing different extract concentrations of *Symphytum officinali* leaves

	Conc. (g/L)	E _a	R ₂	lnA	ΔH	R ₂	ΔS
CAESO	Blank (0.5 M H ₂ SO ₄)	9.98	0.9975	21.31	10.24	0.9955	-10.80
	0.3 g/L	12.36	0.9996	23.56	16.45	0.9173	-28.53
	0.7 g/L	14.13	0.9662	24.03	15.31	0.9659	-24.66
	1.5 g/L	15.84	0.9953	26.03	17.02	0.9811	-27.87
	2.0 g/L	16.44	0.9985	28.75	18.07	0.9981	-29.09
	3.5 g/L	19.07	0.9992	31.31	21.13	0.9998	-87.98
CSESO	Blank (0.5 M H ₂ SO ₄)	9.98	0.9975	21.31	10.24	0.9955	-10.80
	0.3 g/L	13.98	0.9996	23.64	14.75	0.9995	-32.37
	0.7 g/L	13.42	0.9999	21.91	13.79	0.9987	-29.13
	1.5 g/L	13.57	0.9977	22.29	13.96	0.9992	-26.49
	2.0 g/L	14.42	0.9997	24.38	13.79	0.9997	-26.13
	3.5 g/L	15.16	0.9999	25.75	14.61	0.9998	-28.14
CFESO	Blank (0.5 M H ₂ SO ₄)	9.98	0.9975	21.31	10.24	0.9955	-10.80
	0.3 g/L	14.15	0.9992	24.19	15.32	0.9975	-34.54
	0.7 g/L	14.58	0.9986	24.16	13.52	0.9999	-27.93
	1.5 g/L	14.36	0.9996	24.54	13.84	0.9848	-27.73
	2.0 g/L	15.07	0.9989	25.94	13.06	0.9999	-25.70
	3.5 g/L	15.28	0.9977	26.21	19.16	0.9996	-40.25

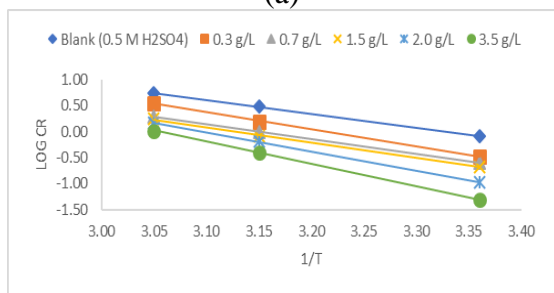
Thermodynamic parameters, Enthalpy of adsorption (ΔH_{ads}), Entropy of adsorption (ΔS_{ads}) of alkaloid, saponins and flavonoid extracts of *Symphytum officinali* on copper in 0.5 M H_2SO_4 solutions was calculated using equation 5 (transition state equation), which can be written [13,19]

$$\frac{CR}{T} = \log \frac{R}{Nh} + \frac{\Delta S}{2.303R} - \frac{\Delta H}{2.303RT} \quad 5$$

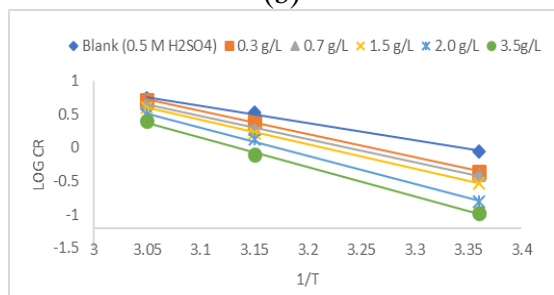
From equation 5, values of $\log(C_R/T)$ were plotted against $1/T$ as shown in Fig. 5a - c and from the slope and intercept of the plots, values of enthalpy and entropy of adsorption were calculated as shown in Table 5. From the calculated values of ΔH_{ads} , it can be deduced that the adsorption of the inhibitor on copper surface is exothermic and the reaction becomes less exothermic with increase in inhibitor concentration [11,20]. The negative values for ΔS_{ads} shows the non-spontaneous dissolution of the metal and the increase in its value suggests decrease in disordering in the rate determining step, hence increase stability of inhibitors on steel surface [21].



(a)

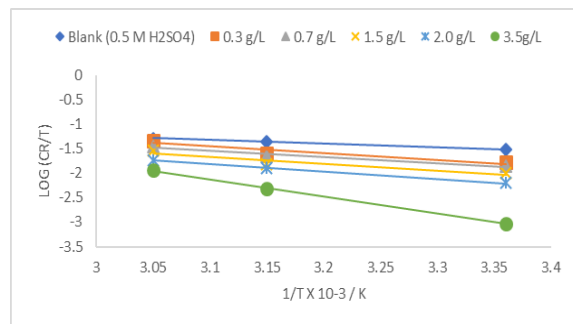


(b)

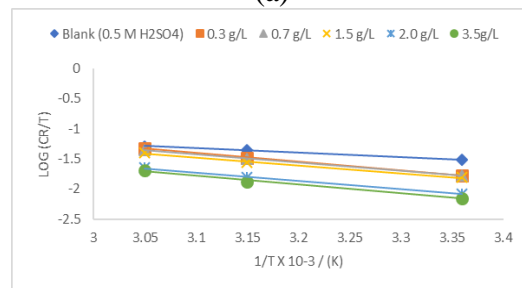


(c)

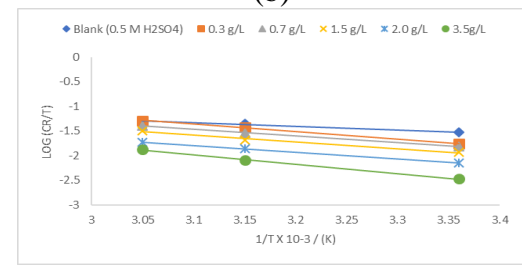
Fig. 4 Arrhenius plots for the adsorption of (a) CAESO (b) CSESO and (c) CFESO on copper coupon in 0.5 M H_2SO_4 solutions



(a)



(b)



(c)

Fig. 5 Transition state plots for the adsorption of (a)CAESO (b) CSESO and (c) CFESO on copper coupon in 0.5 M H_2SO_4 solutions

F. Adsorption consideration

If it is assumed that the blocking effect of the adsorbed species is solely responsible for corrosion inhibition effect, then the degree of surface coverage is

indispensable in the construction of adsorption isotherm. The values obtained from thermometric analysis were theoretically fitted into Langmuir adsorption isotherm model and the correlation coefficient (R^2) value was

used to determine the best fit [18, 20-22]. Langmuir isotherm was found to be one of the best fit adsorption isotherm model to describe the adsorption of both CAESO, CSESO and CFESO on copper coupon in 0.5 M H₂SO₄ solutions. Langmuir isotherm is characterized by Eqn. 6 [31 – 33]:

$$\frac{C}{\theta} = \frac{1}{K} + C \quad \dots \quad 6$$

where C is the inhibitor concentration and K is the equilibrium constant of the adsorption–desorption process. Fig. 6 presents the plot of $\frac{C}{\theta}$ against C using θ values obtained for thermometric technique at various temperatures. In all cases, linear plots were obtained and the R² values are close to unity (Table 3), suggesting that the adsorption of CAESO, CSESO and CFESO molecules on copper surface obeys Langmuir adsorption isotherm [6,23 - 30]. From the values of Kads, the standard free energy of adsorption for both

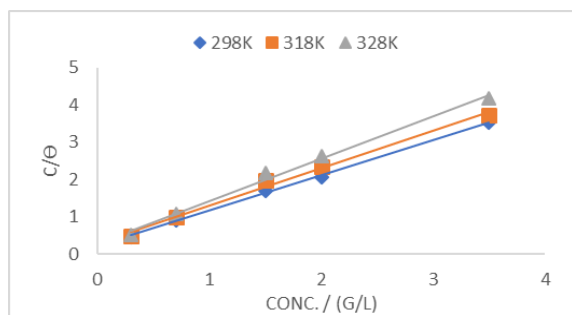
AEOTL and FEOTL at different temperatures were obtained as follows (Eqn. 7):

$$\Delta G^0_{ads} = RT \ln (55.5K_{ads}) \dots \quad 7$$

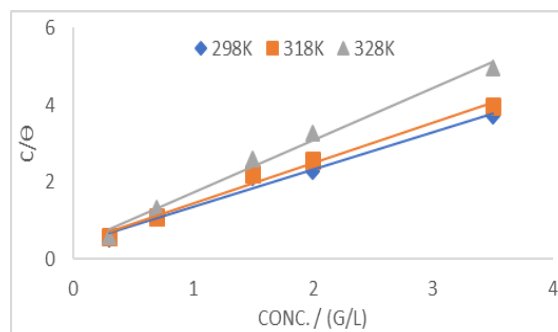
where R is the universal constant, T is the absolute temperature and 55.5 is the concentration of water molecules expressed in mg L⁻¹ or ppm. The computed values of ΔG^0_{ads} listed in Table 3 are less negative than -40 kJ mol⁻¹ and more negative than -20 kJ mol⁻¹. In the literature, the value of ΔG^0_{ads} equal to -20 kJ mol⁻¹ or less is taken to indicate physisorption involving electrostatic interaction between charged molecules whereas those in the order of -40 kJ mol⁻¹ or more is interpreted as chemisorption involving charge sharing or transfer from the inhibitors to the metal surface to form a kind of co-ordinate bond [21, 34 -36]. From the values of ΔG^0_{ads} obtained in this present work, it can be deduced that adsorption mechanism of both inhibitors on copper surface may involve physisorption,

Table 6
Langmuir adsorption parameters for the adsorption of copper coupons in 0.5 M H₂SO₄ solutions containing different extract concentrations of *Symphytum officinali* leaves

	Temp. (K)	k (g/L)	R ²	Slope	ΔG^*_{ads} (kJ/mol)
CAESO	298	4.50	0.9983	0.9465	-13.68
	318	3.26	0.9921	0.9996	-13.74
	328	0.35	0.9929	0.9929	-8.06
CSESO	298	2.52	0.9829	0.9652	-12.24
	318	2.50	0.9964	1.0506	-13.05
	328	2.46	0.9893	1.0350	-13.41
CFESO	298	2.10	0.9913	1.0080	-11.79
	318	1.69	0.9992	1.0810	-12.00
	328	1.89	0.9808	1.2905	-12.69



(a)



(b)

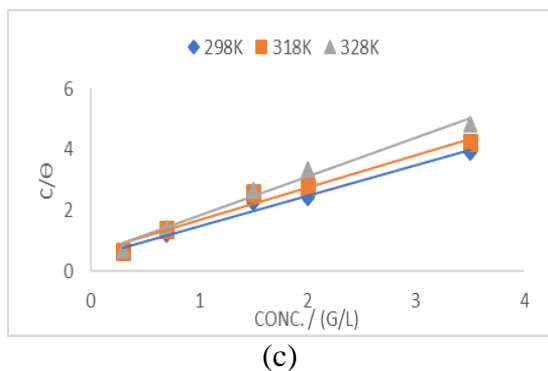


Fig. 6 Langmuir isotherm plots for the adsorption of (a)CAESO (b) CESO and (c) CFESO on copper coupon in 0.5 M H₂SO₄ solutions

IV. CONCLUSION

The following conclusions were drawn from the concluded research investigating the inhibitory impact of crude leaf extracts (Phytochemical compounds) of *Symphytum officinali* (Comfrey) plant on the corrosion of copper by Hydrogen tetraoxosulphate (IV) (H₂SO₄) acid solution.

1. That the results from both techniques were in agreement as both techniques proved both phytochemical compounds from *Symphytum officinali* (Comfrey) as excellent and reliable corrosion inhibitors of copper in Hydrogen Tetraoxosulphate (IV) (H₂SO₄) acid solution.
2. The research also suggested that the crude alkaloid extracts of *Symphytum officinali* leaves is a better inhibitor compared to the crude saponins and flavonoids extracts (alkaloids (99.7 %) > saponins (94.0 %) > flavonoids (90.3 %) which might be due to the strong adsorption of pyrrolidizine molecules on the surface.
3. The effectiveness of the compounds as inhibitors was ascribed to the adsorption of the molecules on the metal surface. CAESO was more effective than other two due to additional electrostatic interaction and the presence of oxygen atom which contributes an adsorption site for the interaction of the molecule on the copper surface.
4. The thermodynamic data suggests that the inhibitors are reliable, spontaneous and stable on the copper surface.
5. The adsorption statistics suggested a physical adsorption mechanism and a monolayer adsorption process, hence obedience of the Langmuir adsorption isotherm.
6. Electrochemical results revealed corrosion retardation of both the anodic dissolution of the metal and cathodic hydrogen evolution, hence mixed type inhibitors.

REFERENCES

- [1] H.Uhlig, W. Revie, Corrosion and Corrosion Control, New York, (2008)
- [2] R.S.Treseder, NACE Corrosion Engineer's Reference Book, Hoston, (2002).
- [3] A.Sharmila, A.A. Prema, P.A. Sahayaraj, Influence of Murraya koenigii (curry leaves) extracts on the corrosion inhibition of carbon steel in HCl solution, Rasayan J. Chem, 3 (2010) 81.
- [4] H.Hassannejad, A. Nouri, Sunflower seed hull extract as a novel green corrosion inhibitor for mild steel in HCl solution, J. Mol. Liq. 254 (2018) 382.
- [5] Y.Qiang, S. Zhang, B. Tan, S. Chen, Evaluation of Ginkgo leaf extract as an eco-friendly corrosion inhibitor of X70 steel in HCl solution, Corros. Sci., 133 (2018) 16
- [6] L.A.Nnanna, B.W. Onwuagba, I.M. Mejeha, K.B. Okeoma, Inhibition effects of some plant extracts on the acid corrosion of Aluminium alloy", Afri J. Pure and Appl Chem, 4 (2010) 016.
- [7] I.B.Obot, A.S. Umoren, N.O. Obi-Egbedi, Corrosion inhibition and adsorption behaviour for aluminium by extract of Aningeria robusta in HCl solution: synergistic effect of iodide ions." J. Mater and Environ Sci., 2 (2011) 71
- [8] E.E.Oguzie, C.O. Akalezi, S.C. Okoro, A.A. Ayuk, E.N. Ejike, Adsorption and corrosion inhibiting effect of Dacryodis edulis extracts on low-carbon-steel corrosion in acidic medium", J. Colloid and Interface Sci, 349 (2010) 292.
- [9] A.H.Kadhum, A.B. Mohamad, L.A. Hamed, A.A. Al-Amiery, N.H. San, Y.A. Musa, Inhibition of mild steel corrosion in hydrochloric acid solution by new coumarin. Materials Sci., 7 (2014) 4348.
- [10] C.Kamal, L.M. Gopolarishma, (2012) Caulerpin-A bis-indole as a green inhibitor for the corrosion of mild steel in 1M HCl solution from the marine alga Caulerpa racemosa. Ind. Eng. Chem. Res. 51 (2012) 10407.
- [11] A.Habib, S. Mirzaee, T. Rostamikia, R. Bagheri, Pomegranate (Punica granatum) peel extract as a green corrosion inhibitor for mild steel in hydrochloric acid solution. International Journal of Corrosion, (2015) Article ID 197587
- [12] C.Hui, F. Zhenghao, S. Jinling, S. Wenyan, X. Qi, Corrosion inhibition of mild steel by Aloe extract in HCl solution medium. Int. J.electrochem. Sci., 8 (2013) 734.
- [13] M.A.Chidiebere, E.E. Oguzie, L. Liu, Y. Li, F. Wang, (2015). Adsorption and corrosion inhibiting effect of riboflavin on Q235 mild steel corrosion in acidic environments. Mater. Chem. Phys. 156 (2015) 104
- [14] E.S.Ferreira, C. Giacomelli, F.C. Giacomelli, A. Spinelli, Evaluation of the inhibitor effect of l-ascorbic acid on the corrosion of mild steel. Mater. Chem. Phys. 83 (2004), 134.
- [15] K.Ghulamullah, M. Kazi, N. Newaz, J. Wan, H. Basiru, M.A. Binti, L.F. Fadhil, M.K. Ghulam, Application of natural product extracts as green corrosion inhibitors for metals and alloys in acid pickling processes - A review. International Journal of Electrochemical Science, 10 (2015) 6134.
- [16] I.K.Shalabi, Y.M. Abdallah, H.M. Hassan, A.S. Fouda, Adsorption and corrosion inhibition of Atropa belladonna extract on carbon steel in 1M HCl solution. International Journal of Electrochemical Science. 9 (2014) 1487.
- [17] K.S.Sharma, P. Anjali, I.B. Obot, Potential of Azadirachtaindica as a green corrosion inhibitor against mild steel, aluminium and tin: A review. Journal of Analytical Science and Technology. 6 (2015) 41.
- [18] I.E.Uwah, B.U. Ugi, P.C. Okafor, A.I. Ikeuba AI, Comparative study of corrosion inhibition and adsorption characteristics of ethanol extracts of Andrographis paniculata (King bitters) and Vernonia amygdalina (Bitter leaf) on mild steel in HCl solution. International Journal of Applied Chemistry, 9 (2013) 88.
- [19] H.L.Y.Sin, A.A. Rahim, C.Y. Gan, B. Saad, M.I. Salleh, M. Umeda, Aquilaria subintergra leaves extracts as sustainable

- mild steel corrosion inhibitors in HCl, Measurement 109 (2017) 345.
- [20] E.Alibakhshi, M. Ramezanzadeh, G. Bahlakeh, B. Ramezanzadeh, M. Mahdavian, M. Motamedi, Glycyrrhiza glabra leaves extract as a green corrosion inhibitor for mild steel in 1 M hydrochloric acid solution: Experimental, molecular dynamics, Monte Carlo and quantum mechanics study, J. Mol. Liq. 255 (2018) 198.
- [21] A.A.Al-Amiery, A. Abdul, H. Kadhum, A. Kadhim, A.B. Mohamad, C.K. How, S. Junaedi, Inhibition of mild steel corrosion in sulfuric acid solution by new Schiff base, Materials, 7 (2014) 804.
- [22] K.Ghulamullah, M. Kazi, N. Newaz, J. Wan, H. Basiru, M.A. Binti, L.F. Fadhil, M.K. Ghulam, Application of
- [23] natural product extracts as green corrosion inhibitors for metals and alloys in acid pickling processes - A review, International Journal of Electrochemical Science. 10 (2015) 6134.
- [24] Z.V.Murthy, K. Vijayaragavan, Mild steel corrosion inhibition by acid extract of leaves of Hibiscus sabdariffa as a green corrosion inhibitor and sorption behavior. Green Chemistry Letters and Reviews, 7 (2014) 219.
- [25] B.U.Ugi, M.E. Obeten, Ekerete Jackson, Crude alkaloid and saponin extracts of Agrimonia eupatoria plant as control measure in stainless steel corrosion in hydrogen tetraoxosulphate (VI) acid rich area, J. Env. Sci. Pollut. Res., 4 (2018) 249.
- [26] E.Ituen, O. Akaranta, A. James, S. Sun, Green and sustainable local biomaterials for oilfield chemicals: Griffonia simplicifolia extract as steel corrosion inhibitor in hydrochloric acid, Sustain, Mater. Technol., 11 (2017) 18.
- [27] S.A.Umoren, M.M. Solomon, Effect of halide ions on the corrosion inhibition efficiency of different organic species—a review, J. Ind. Eng. Chem., 21 (2015) 100.
- [28] J.Gopal, A. Shadma, S. Shanthi, P. Rajiv, Musa paradisiac peel extract as green corrosion inhibitor for mild steel in HCl solution, Corros. Sci., 90 (2015) 117.
- [29] A.I.Ikeuba, B.I. Ita, R.A. Etiuma, V.M. Bassey, B.U. Ugi, E.B. Kporokpo, Green corrosion inhibitors for mild steel in H₂SO₄ solution: Comparative study of flavonoids extracted from Gongronema latifolium with crude extract, Jour. Chem. Proc. Eng., 34 (2015) 9.
- [30] H.Louis, J. Japari, A. Sadia, M. Philip, A. Bamanga, Photochemical screening and corrosion inhibition of Poupartia birrea bark extract as a potential green inhibitor for mild steel in 0.5 M H₂SO₄ solution, World News Nat. Sci., 10 (2017) 100.
- [31] A.O.Okewale, A. Olaitan, The use of rubber leaf extract as a corrosion inhibitor for mild steel in acidic solution, Int. J. Mater. Chem., 7 (2017) 13.
- [32] O.Olawale, J.O. Bello, Akinbami, P. A study on corrosion inhibition of mild – steel in hydrochloric acid using cashew waste, Int. J. Mod. Eng. Res. 2 (2015) 64.
- [33] S.J.Olesegun, E.A. Okoronkwo, A.E. Okotete, O.A. Ajayi, Gravimetric and electrochemical studies of corrosion inhibition potential of acid and ethanol extract of siam weed on mild steel, Leonardo J. Sci., 9 (2016) 42.
- [34] B.U.Ugi, I.E. Uwah, P.C. Okafor, J. Ekerete, S.E. Ejim, N.E. Nya, Sulphuric acid corrosion of mild steel in the stem extracts of Cnidocolus aconitifolius plant, J. Appl. Chem. Sci. Int., 5 (2016) 216.
- [35] M.Srivastava, P. Tiwari, S.K. Srivastava, A. Kumar, G. Ji, R. Prakash, Low cost aqueous extract of Pisum sativum peels for inhibition of mild steel corrosion, J. Mol. Liq., 254 (2018) 368.
- [36] A.Saxena, D. Prasad, R. Haldhar, G. Singh, A. Kumar, Use of Saraca ashoka extract as green corrosion inhibitor for mild steel in 0.5 M H₂SO₄, J. Mol. Liq., 258 (2018) 97.
- [37] P.E.Alvarez, M.V. Fiori-Bimbi, A. Neske, S.A. Brandán, C.A. Gervasi, Rollinia occidentalis extract as green corrosion inhibitor for carbon steel in HCl solution, J. Ind. Eng. Chem., 58 (2018) 99.