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Influence of *Malus domestica* and *Caesalpinia bonducella* Leaf Extracts on the Corrosion Behaviour of Mild Steel in H_2SO_4 Solution

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The electrochemical corrosion behavior of mild steel in 0.5M H_2SO_4 solution in the presence of apple, *Malus domestica* (MD); bonduc, *Caesalpinia bonducella* (CB) leaf extracts were investigated using potentiodynamic polarization curves measurements, electrochemical impedance spectroscopy techniques and Fourier infrared spectroscopy (FTIR) measurements. Polarization curves revealed that both MD and CB leaf extracts act as mixed type inhibitors in sulphuric acid solution. The impedance response consisted of characteristic depressed semicircles clarifying that the corrosion process occurs under charge transfer control. The inhibition efficiency of the leaf extracts increased with increasing the concentration and decreased with temperature. The results showed that CB is more efficient than MD in 0.5M H_2SO_4 solution. The calculated thermodynamic parameters indicated that the adsorption was a spontaneous, endothermic, and accompanied by a decrease in entropy. The adsorption of MD and CB leaves on steel surface obeys Thermodynamic-Kinetic model, Flory-Huggins model and Temkin model. The thermodynamic parameters indicated that the inhibition of mild steel by MD and CB leaf extracts were by physical adsorption mechanism.

Keywords: steel, corrosion, electrochemical, apple and bonduc, leaf extracts.

1. INTRODUCTION

Corrosion of mild steel is a problem in many industries that continuously attracted the attention of researchers. In some industrial processes such as acid cleaning, etching, and pickling using aggressive media such as acids, bases, and salts, leads to corrode the steel. A number of ways such as material selection, cathodic or anodic protection, coatings and the use of corrosion inhibitors has been used to reduce corrosion of the installation industry [1, 2].

Large numbers of organic compounds revealed that N, S and O containing organic compounds acted as promising inhibitors [3, 4]. However, most of these compounds are not only expensive, but also toxic to living beings. It is needless to point out the importance of cheap and safe inhibitors for corrosion of mild steel. So, considerable efforts are made to select corrosion inhibitors which are environmentally safe, readily available and of relatively low cost. Literature show growing trend in the use of natural products known as non-toxic compounds, called also green inhibitors, as corrosion inhibitors. These natural organic compounds are either synthesized or extracted from aromatic herbs, spices and medicinal plants. Plant extracts are viewed as an incredibly rich source of naturally synthesized chemical compounds that can be extracted by simple procedures with low cost and are biodegradable in nature. The use of these natural products such as extracted compounds from leaves or seeds as corrosion inhibitors have been widely reported [5-10].

The aim of the present work is to use electrochemical measurements for studying the effect of leaf extracts of Bonduc, Caesalipinia bonduc (CB) and Malus domestica (MD) on the inhibiting properties and adsorption mechanism of both leaf extracts in 0.5 M H_2SO_4.

2. EXPERIMENTAL

2.1. Solution preparation.

The test solutions were prepared from distilled water and analytical grade reagent H_2SO_4 from BDH chemical company. Stock solution of plant extracts was obtained by drying the plant leaf for 2 h in an oven at 80^{o}C and grinding to powdery form. A 10 g sample of the powder was refluxed in 100 mL distilled water for 1 h. The refluxed solution was filtered to remove any contamination. The concentration of the stock solution was determined by evaporating 10 mL of the filtrate and weighing the residue. Prior each experiment, 4M H_2SO_4 is added to an appropriate volume of the stock solution of plant leaf extract and double distilled water to obtain a solution of 0.5M H_2SO_4 solutions and the required concentration of the extract.

2.2. Electrochemical studies.

Electrochemical impedance and polarization measurements were achieved using frequency response analyzer (FRA) / potentiostat supplied from ACM instruments (UK). The frequency range for electrochemical impedance spectroscopy (EIS) measurements was 0.1 to $3x10^4$ Hz with applied potential signal amplitude of ±10mV around the rest potential. The data were obtained in an electrochemical cell of three-electrode mode; platinum wire and saturated calomel electrodes (SCE) were used as counter and reference electrodes. The material used for constructing the working electrode was mild steel of the following chemical composition (wt. %) (C:0.198 ,Mn:0.57,Si:0.085 ,S:0.038 ,P:0.02 ,and Fe:98.8). The steel plate of rectangular shape was encapsulated in Teflon in such a way that only one surface was left uncovered. The exposed area ($0.36 cm^2$) was mechanically abraded with a series of emery papers of variable grades, starting with a coarse one and proceeding in steps to the finest (800) grade. Before polarization and EIS measurements, the working electrode was left for 30 min to attain the open circuit potential in the used solution. Polarization curve measurements were obtained Polarization curve measurements were obtained at a scan rate of 20 mV/min by polarizing the working electrode from -250 mV cathodically to +250 mV anodically with respect to open circuit potential. All the measurements were done at 30 ± 0.1 0C using WiseCircu water bath (Germany) in solutions open to the atmosphere under unstirred conditions. To obtain the activation parameters the measurements were carried out at $30\text{-}60^oC$. To test the reliability and reproducibility of the measurements, duplicate experiments were performed under the same conditions in each case and found to be within 2% error.

2.3. FTIR analysis

The Infrared spectra of the solid sample were recorded by averaging 32 scans at a resolution of $4cm^{-1}$ using a Perkin-Elmer (2000 FTIR) spectrometer in the spectral region between 4000 and 500 cm^{-1}.

3. RESULTS AND DISCUSSION

3.1. Potentiodynamic polarization curves

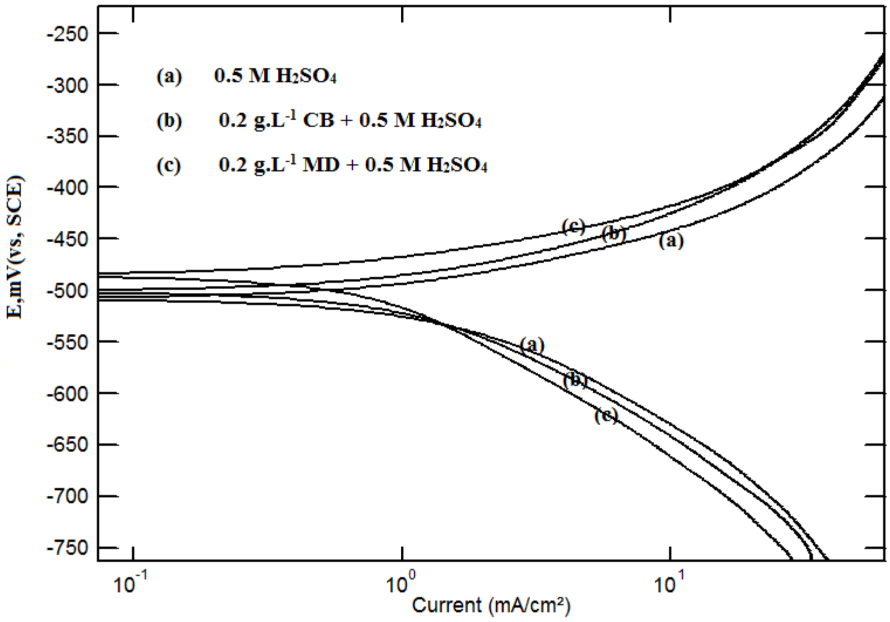


Figure 1. Potentiodynamic polarization curves for steel in 0.5 M H_2SO_4 solutions in the absence and the presence of 0.2g/ CB and MD leaf extracts at 30°C..

Figure 1 demonstrate the potentiodynamic polarization curves for steel in 0.5 M H_2SO_4 solution in the absence and the presence of 0.2g/L Caesalipinia bonduc (CB) and Malus domestica (MD) leaf extracts at 30°C. The curves show that CB and MD retard both the cathodic hydrogen evolution and the anodic metal dissolution indicating that they act as mixed-type inhibitors.

The values of corrosion current density, icorr; corrosion potential, E_{corr}; and cathodic and anodic Tafel slopes (β_c and β_a) along with the percentage of corrosion inhibition efficiency, η, for steel in 0.5 M H_2SO_4 solutions in the absence and the presence of different concentrations of CB and MD leaf extracts at 30°C are presented in Table 1.

The corrosion inhibition efficiency,η, was calculated from polarization measurements using the relation

$\eta= [(i_0-i)/i_0] \times 100$

Where i_o and i, are the corrosion current density in the absence and the presence of both leaf extracts.

Table 1. The electrochemical corrosion parameters for steel in 0.5 M H_2SO_4 solutions in the absence and the presence of different concentrations of CB and MD leaf extracts at 30°C.

Leaf extract	Conc. (g/L)	E_{corr} (mV vs. SCE)	β_a	$-\beta_c$	i_{corr} (mA cm^{-2})	η
			mV/decade			
CB	0	-509	82	154	1.55	-
	0.200	-520	76	136	1.04	34.0
	0.300	-501	70	131	0.80	48.0
	0.400	-493	69	136	0.64	58.7
	0.500	-489	62	138	0.59	61.9
	0.600	-492	64	145	0.45	70.9
	0.700	-480	52	148	0.33	78.7
MD	0.050	-495	86	136	1.20	22.6
	0.100	-483	83	142	0.97	37.4
	0.125	-499	66	136	0.80	48.4
	0.150	-497	62	139	0.71	54.2
	0.175	-492	63	147	0.62	60.0
	0.200	-484	57	138	0.56	64.0
	0.250	-498	96	141	0.44	71.6

Table 1 clarifies that, the values of i_{corr} decrease and η increase with increasing the concentration of CB and MD leaf extracts. However, the slight displacement of E_{corr} upon the addition of both CB and MD leaf extracts indicates that they could be classified as pickling type inhibitor [11]. Tafel slopes (β_c and β_a) are related to the kinetics of the corrosion reaction. The $\beta c = 2.303RT/\alpha nF$ and $\beta a = 2.303RT/(1-\alpha)nF$ where R is the gas constant, 8.314 Joule /mol. K; T is the absolute temperature, α is the " symmetry factor " nominally 0.5, F = 96 540 C/mol is Faraday's constant; and n is number of electrons transferred in the rate determining step [12]. Therefore, at 30°C, βc or $\beta a = 0.120/n$. For the cathodic reactions of hydrogen ion reduction, the value of βc is about 120 mV indicating exchange of one electron during the cathodic reaction. For metal dissolution reactions from active surfaces, values of βa are generally smaller and is about 60 mV indicating exchange of two electrons during metal dissolution process [13]. The variation in in the β_c and β_a values could be related to the adsorption factor.

Figure 2 shows the variations of degree of surface coverage ($\theta = \eta/100$) obtained from potentiodynamic polarization measurements with the leaf extracts concentration. The variation of degree of surface coverage is characterized by an initial rising part followed by an approximately constant saturated part at high concentrations. The curves also indicate that, at low concentrations, MD is more effective than CB in 0.5M H_2SO_4 solution.

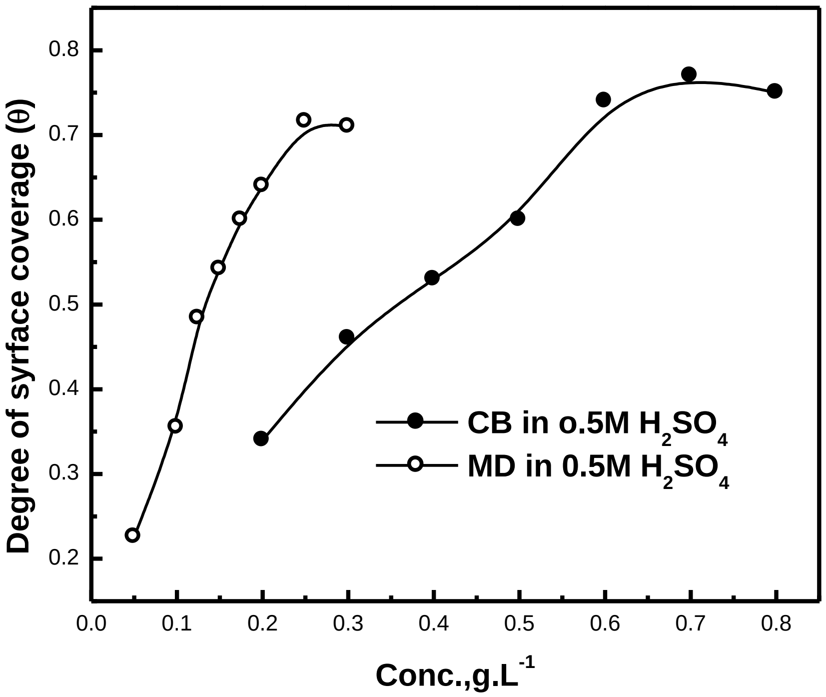


Figure 2. Variations of degree of surface coverage, obtained from polarization measurements, with the leaf extracts concentration.

3.2. Electrochemical impedance spectroscopy measurements

Figure 3 shows the Nyquist impedance plots for steel in 0.5 M H_2SO_4 solution in the absence and the presence of 0.2g/L CB and MD leaf extracts at 30°C. The Nyquist plots show depressed semicircles indicating that the corrosion of steel is mainly controlled by charge transfer. The similarity of the semicircular shape observed in the absence and the presence of CB and MD leaf extract indicated that the corrosion mechanism remained the same irrespective of the presence or absence of the extracts [14, 15].

To analyze the impedance spectra for different Nyquist impedance plots, the equivalent circuit model represented in Figure 4 was employed. The circuit consist of a solution resistance R_s shorted by a constant phase element (CPE) which is placed in parallel to charge transfer resistance element, R_{ct} [16- 18]. The value of (R_{ct}) denotes the electron transfer across the interface and is inversely proportional to corrosion rate.

To compensate for non-homogeneity in the system, the capacitances were implemented as a constant Phase Element (CPE) that is defined by two values, the non ideal double layer capacitance (Q_{dl}) and a constant n. For a non-homogeneous system, n values ranges from 0.9 to 1 [19].

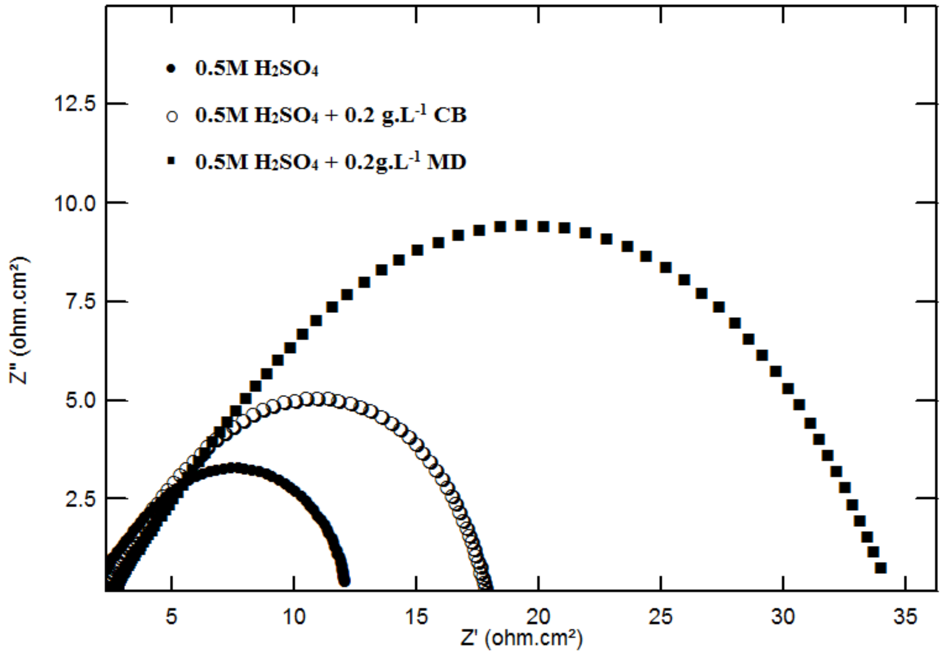


Figure 3. Nyquist impedance plots for steel in 0.5 M H_2SO_4 solution in the absence and the presence of 0.2g/L CB and MD leaf extracts at 30°C.

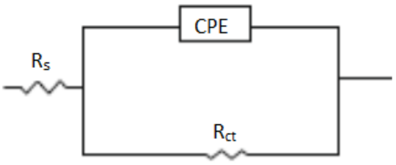


Figure 4. schematic for the equivalent circuit model

The values of electrochemical impedance parameters; R_{ct}, Q_{dl} and n values obtained from fitting the experimental data to the proposed model together with η are given in Table 2.

The percentage inhibition efficiency (η) can be calculated from impedance measurements according to the equation:

$\eta = [(R_{ct} - R_{ct0})]/R_{ct} \times 100$

Where R_{ct0} and R_{ct} are the values of the charge transfer resistance (Ω cm^2) in the absence and the presence of leaf extract, respectively.

It is obvious from the results in the table that the presence of CB leaf extracts increases R_{ct} and decreases Q_{dl} which were also concentration dependent indicating that the inhibiting action of CB leaf extracts take place by adsorption mechanism. The change in the R_{ct} and Q_{dl} values is due to the gradual replacement of water molecules by the anions of the acid and by the adsorption of the organic molecules on the metal surface thus decreasing the extent of the metal dissolution [20]. On the other hand, the increase in the Q_{dl} values of MD leaf extract suggests that the active ingredient of the leaf extract function by adsorption/desorption mechanism at the metal/solution interface. The adsorption/desorption equilibrium is most probably shifted towards desorption. But the concentration of the inhibitor is high enough to sustain an inhibiting adsorption layer [21]. It may be assumed that the density of the layer of adsorbed particles within outer Helmholtz layer (OHL) decreases while the diffuse part of double electrical layer increases. The inhibition efficiencies calculated from EIS are in good agreement with those obtained from potentiodynamic polarization curves.

Table 2. Impedance parameters for mild steel in 0.5M H_2SO_4 containing different concentrations of CB and MD leaf extracts at 30°C.

Leaf extract	Conc. (g/L)	R_{ct} (Ω cm^2)	Q_{dl} (μF)	n	η
CB	0	11.52	142	0.77	0
	0.200	16.95	165	0.72	32.0
	0.300	23.04	170	0.70	50.0
	0.400	27.69	158	0.68	58.0
	0.500	32.80	150	0.71	65.0
	0.600	42.01	180	0.65	72.0
	0.700	52.31	168	0.67	78.0
	0.800	39.73	137	0.72	71.0
	0.900	35.22	119	0.72	67.0
MD	0.050	15.28	129	0.72	24.6
	0.100	19.17	142	0.77	39.9
	0.125	23.15	144	0.72	50.2
	0.150	26.82	101	0.74	57.1
	0.175	30.20	147	0.71	61.8
	0.200	34.53	157	0.70	66.6
	0.250	38.70	144	0.72	70.2

3.3. Spectrophotometric analysis

Figure 5 and Figure 6 shows the FTIR spectrums of CB and MD leaf extracts. The IR spectrum in Figure 5 showed absorption bands for OH (3337.4 cm$^{-1)}$, C-H sp stretching vibration (2916.7cm^{-1}), C-H sp^2 stretching vibration (2848.9 cm^{-1}), C=C aromatic (1650.2 and 1449.1 cm^{-1}), C=O (1706.6 cm^{-1}), C-O aromatic ether (1373.6 and 1243.0 cm^{-1}). The strong band 1042.1 cm^{-1} is assigned to C-O single bond of OMe.

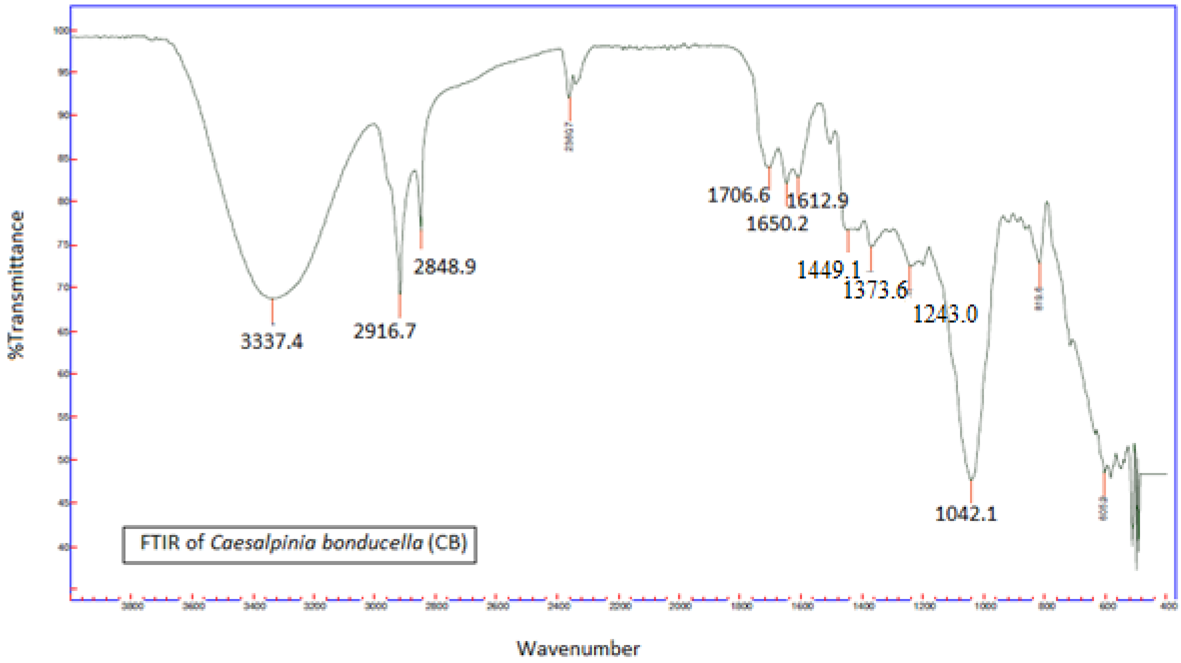


Figure 5. IR spectrum of CB leaf extract.

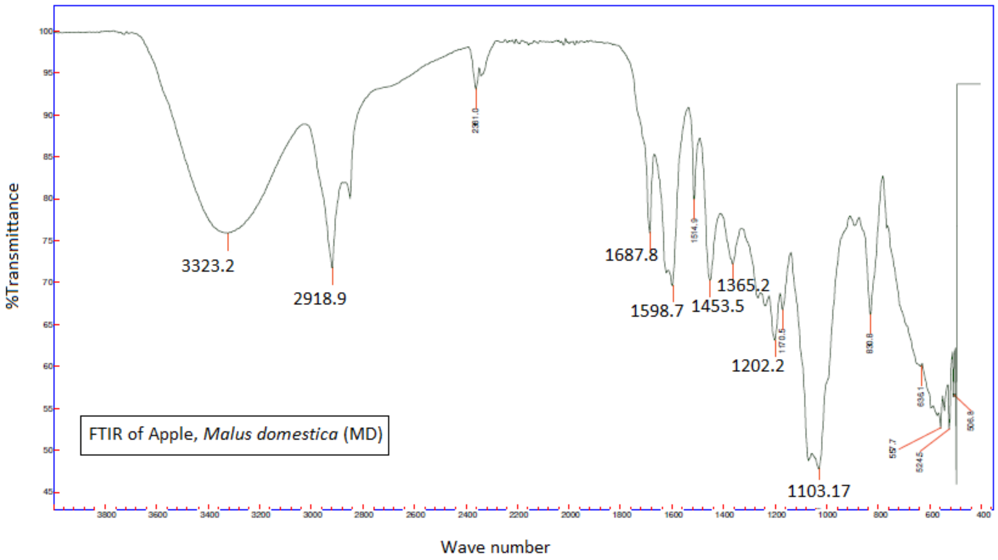
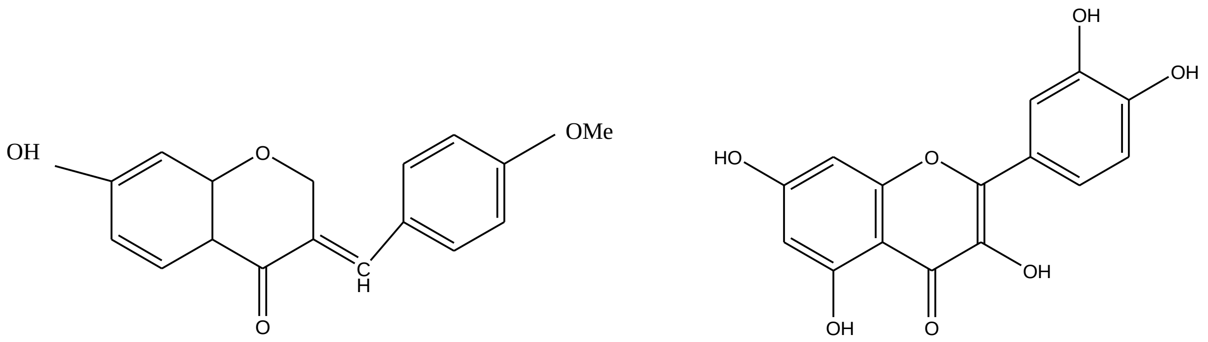


Figure 6. IR spectrum of MD leaf extract.

Figure 6 showed absorption bands for OH (3323.2 cm^{-1}), C-H stretching vibration (2918.9cm^{-1}), C=C aromatic (1598.7 and 1453.5 cm^{-1}), C=O (1687.8 cm^{-1}), C-O aromatic ether (1202.2 and 1103.17cm^{-1}).

It was reported that [22] CB leaf extract contains a substance known as Bonducellin, and that of MD leaf extract contains [23] Quercetin as a major constituent (Figure 7). The expected spectrum bands of the hydrolyzed form of both chemical compounds are in a good agreement with that obtained from FTIR spectroscopy measurement.



Bonducellin Quercetin

Figure 7. The chemical structure of Quercetin and Bonducellin.

3.4. Adsorption isotherms

Adsorption at the metal-solution interface has been considered as the primary step in the action of most corrosion inhibitors in acidic environment. The mode of interaction of plant leaf extract with the mild steel surface could be better understood using adsorption isotherms [24].

Attempts were made to fit (θ= %P/100) values to different isotherms including the Langmuir, thermodynamic-kinetic model, Florry- Huggins, and Temkin [25-29].

It was found that the experimental data does not fit to Langmuir adsorption isotherm indicating non-ideal behavior for the adsorption of the plant leaf extract on the metal surface. The adsorption parameters obtained from Kinetic – Thermodynamic model, Flory-Huggins isotherm, and Temkin models for CB and MD leaf extracts in 0.5M H_2SO_4 at 30°C are given in Table 3. The values of correlation coefficient (R^2) were used to judge the best-fit isotherm. In the present study, the strong correlation ($R^2 > 0.97$) suggests that the adsorption of CB and MD on the surface obeyed the used isotherms and models. Different information is obtained from each isotherm. The efficiency of both plant leaf extracts is essentially a function of the both the magnitude of its binding constant K. Large values of K mean better and stronger interaction, while small values of K mean that the interaction between the inhibitor molecules and the metal is weaker [30]. Hence, according to the numerical values of K obtained, the inhibition efficiency of MD leaf extracts in 0.5M H_2SO_4 is higher than that of CB. The values of 1/y, the number active sites occupied by one-inhibitor molecules, for CB and MD leaf extracts is less than unity indicating multilayer adsorption. The value of x, the number of adsorbed water molecules substituted by a given inhibitor molecule, indicates that the active chemical ingredient of CB and MD leaf extracts has small size compared to that of water. On the other hand, it is evident from Temkin isotherm; that positive values of the adsorption parameter (f) suggest the occurrence of mutual repulsion of that the active chemical ingredient of CB and MD leaf extract [31, 32].

Table 3. Linear fitting parameters of CB and MD leaf extract according to the mentioned models in 0.5M H_2SO_4 at 30°C.

Plant leaf	Kinetic Model			Florry Huggins			Temkin		
	K	1/y	R^2	K	x	R^2	K	f	R^2
CB	3.13	0.65	0.99	5.32	0.37	0.96	12.76	2.81	0.99
MD	7.98	0.77	0.99	9.31	0.61	0.97	42.81	3.32	0.99

3.5. Effect of temperature

Figures 8 shows the potentiodynamic polarization curves for steel in the presence of 0.25 g.L^{-1} MD leaf extract in 0.5M H_2SO_4 at different temperature.

As seen, increasing temperature, enhance both anodic metal dissolution and cathodic hydrogen evolution processes. This behavior can be interpreted on the basis that the increases in temperature results in desorption of the inhibitor from the surface of mild steel [33].

Figure 9 shows Nyquist Impedance plots for mild steel in 0.5M H_2SO_4 in the presence of 0.25g.L^{-1} MD leaf extract at different temperatures. As seen, increasing the temperature decreases the size of the depressed semicircles indicating increase of the corrosion rate (reciprocal of the charge transfer resistance).

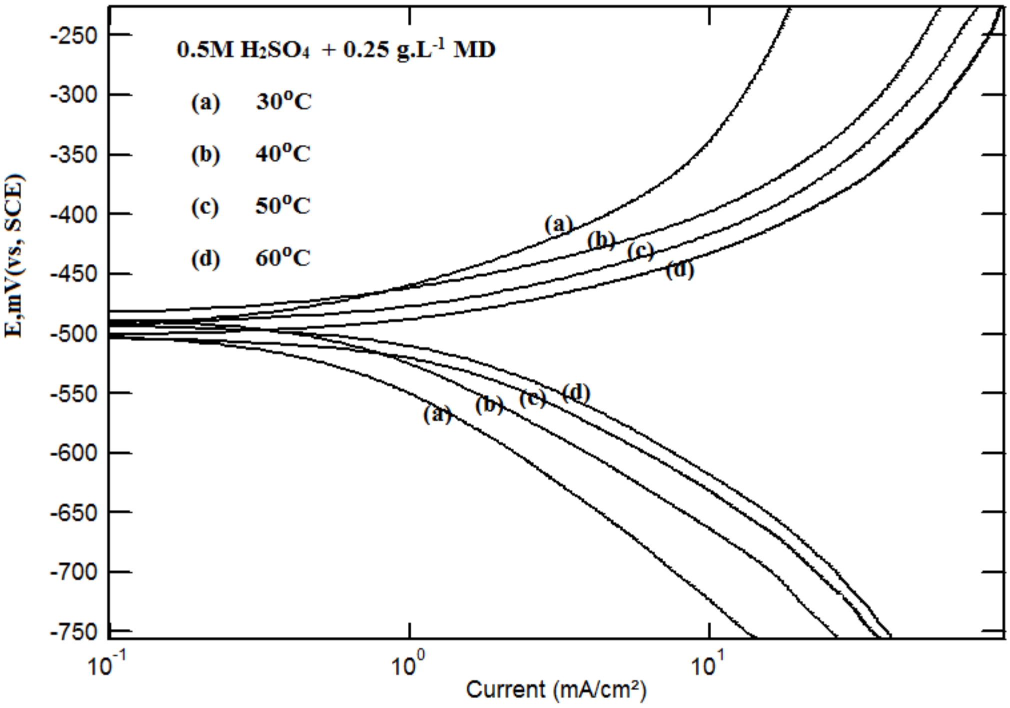


Figure 8. Potentiodynamic polarization curves for mild steel in 0.5M H_2SO_4 in the presence of 0.25 g.L^{-1} MD leaf extract at different temperatures.

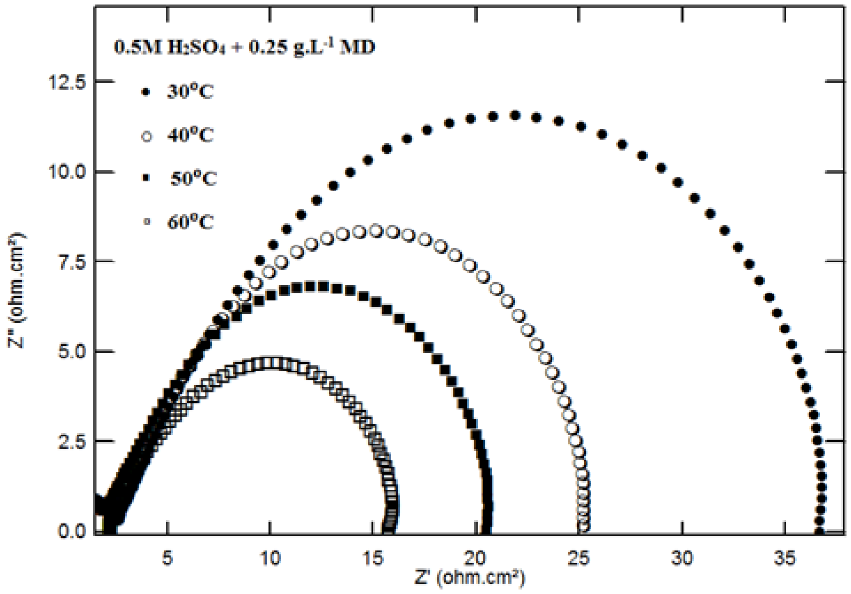


Figure 9. Nyquist Impedance plots for mild steel in 0.5M H_2SO_4 in the presence of $0.25g.L^{1}$*MD* leaf extract at different temperatures.

Similar observations were recorded from polarization and Nyquist plots for mild steel in 0.5M H_2SO_4 in the presence of $0.70g.L^{1}$*CB* leaf extract at different temperatures, not shown.

The values of thermodynamic were calculated using Arrhenius equation and transition state equation [35]:

$$\ln\upsilon = \ln A - (E_a/RT)$$

Where υ is the corrosion rate and is taken as reciprocal of the charge transfer resistance (R_{ct}) obtained from the Nyquist plots, E_a is apparent activation energy, A; the pre-exponential factor, and R is the universal gas constant. An alternative formulation of the Arrhenius equation is the transition state equation [34]:

$$\upsilon=(RT/Nh)\ \exp((\Delta S^*/R)\exp(-\Delta H_*/RT)$$

Where ΔH_* is the apparent enthalpy of activation, ΔS^* is the apparent entropy of activation, h is the Planck’s constant and N is the Avogadro`s number, respectively.

This binding constant K, obtained from Kinetic model, is related to the standard free energy of adsorption (ΔG_{ads}), with the following equation [31].

$$K_{ads} = 1/55.5\ e^{(-\Delta Gads/RT)}$$

Where R is the molar gas constant, T is the absolute temperature in Kelvin and 55.5 is the concentration of water in solution expressed in molar.

The activation parameters for steel in 0.5M H_2SO_4 in the absence and presence of 0.7 $g.L^{-1}$ of CB and of $0.25g.L^{1}$ MD leaf extract were obtained from the linear square fitting of log (ν) and log(ν/T) data vs. (1/T. The calculated values for the activation parameters together with ΔG_{ads} are given in Table 4.

Table 4. The activation parameters of mild steel in 0.5M H_2SO_4 in the absence and presence of 0.7 g.L^{-1} *CB* and 0.25 g.L^{-1} *MD* leaf Extracts respectively.

Plant leaf extract	E_a kJ.mol^{-1}	ΔH* kJ.mol^{-1}	ΔS* J.mol^{-1}.K^{-1}	ΔG_{ads} kJ.mol^{-1}
-	13.864	11.225	-228.45	-
CB	32.75	30.11	-178.41	-12.99
MD	25.86	23.22	-196.55	-12.86

It is clear from the table that E_a values in the presence of the CB and MD leaf extract are higher than the E_a value for the blank solution. The increase in activation energy may be attributed to the geometric blocking effect of the adsorbed inhibitive species on the metal surface [35]. This observation further supports physisorption mechanism. Moreover, the average difference values of the (E_a -ΔH*) are 2.63, 3.3, and 2.65 kJ/mol which are approximately equal to the average value of RT (2.63 kJ/mol) at 30°C. This indicates that the corrosion process is unimolecular reaction as it is characterized by the following equation [36]:

Ea - ΔH* =RT.

It is also seen in Table 4 that Ea and ΔH* vary in the same manner but however, the values of ΔH* are lower than that of Ea. This indicates that the corrosion process must involve a gaseous reaction, simply hydrogen evolution reaction associated with decrease in total reaction volume.

The positive values of ΔH* of both leaf extract indicates that the formation of the activated complex is endothermic process. The values of ΔS* in the absence and presence of the extracts are negative. This indicates that the activated complex in the rate determining step represents an association rather than dissociation step meaning that a decrease in disordering takes place on going from reactants to the activated complex [37-39].

The negative values of the ΔG_{ads} reflect the spontaneity of the adsorption process of CB and MD leaf extracts and the stability of the adsorbed layers on the mild steel surface in both plant leaves. Furthermore, values of ΔG_{ads} up to -20 kJ.mol^{-1} are consistent with electrostatic interactions between the charged molecules and the charged metal (physisorption) while those more negative than -40kJ moL^{-1} involve sharing or transfer of electrons from the inhibitor molecules to the metal surface to form a coordinate type of bond (chemisorptions) [30, 40-41]. In the present study, the values of ΔG_{ads} are less than -20 kJ.mol^{-1} .This result means that the adsorption mechanism of CB and MD leaf extract on mild steel surface is physisorption rather than chemisorptions.

4. CONCLUSION

CB and EB leaf extract showed inhibitive effect on corrosion of mild steel in 0.5M H_2SO_4. The adsorption of extracts followed kinetic-thermodynamic, Flory-Huggis, and Temkin model's. CB extract showed greater inhibition efficiency than that of MD.

Adsorption of CB and MD extracts on the surface of the steel is spontaneous and occurred by physical adsorption. Activation energy was found to be greater in the presence of CB and MD leaf extracts which suggests that the adsorbed organic matter has provided a physical barrier to charge and mass transfer leading to reduction in the rate of corrosion. Thus, the *Caesalpinia bonducella* (CB) and *Malus domestica* (MD) leaf extracts were proved to be eco friendly and low cost inhibitor with average effeciency.

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