Corrosion Inhibition of Mild Steel by Citrus Sinensis (Orange) Leaves Extract in Hcl/H2SO4 Acid Medium

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Abstract: *In this work, citrus sinensis leaves extract was used as inhibitor in 1M HCl and 0.5M H2SO4 solution on mild steel. Potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) tests were carried out on the inhibitor extract at 30°C. The mild steel was analyzed using Scanning Electron Microscopy (SEM). Density Functional Theory (DFT) – based quantum chemical computations involving EHOMO, ELUMO and ELUMO-HOMO were correlated to determine the interaction between the inhibitors and the corroding metals surfaces. Molecular dynamic stimulation of the reaction between the inhibitor molecules and the corroding metal surfaces were performed using Forcite quench molecular dynamics. Potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) showed that the extracts from citrus sinensis L. acts as bio-inhibitor in the acidic media. The results showed that increase in the concentration of the inhibitor up to 50 mg/L at 30°C, increased the efficiency of corrosion inhibition of mild steel. Polarization profiles for mild steel in 1 M HCl and 0.5 M H2SO4 in the absence and presence of citrus sinensis L. extracts showed that cathodic and anodic curves were very much polarized. Both the cathodic βc and anodic βa current values were retarded. This indicated that the citrus sinensis leaves extract influenced both the cathodic and anodic reaction and hence the addition of citrus sinensis leaves extract reduced the metal dissolution and rate of hydrogen evolution reaction on mild steel surface. Nyquist plots for mild steel in 1 M HCl and 0.5 M H2SO4 in the absence and presence of extracts from citrus sinensis L., have shown that the two environments were significantly altered after the addition of extracts from citrus sinensis L. into the test solutions. The diameter of the capacitive loop increased with increase in inhibitor concentration which was significant in the acid solution containing citrus sinensis leaves extract. The inhibiting effect may be attributed to the presence of adsorbed organic compounds from the extract on the surface of the mild steel which formed a protective thin film on the surface of the mild steel.*

Keywords: *Citrus sinensis L., Mild steel, Corrosion, Inhibitor, Acid*

1. INTRODUCTION

Mild steel is one of the most important alloys in existence and has a wild variety of industrial applications. However, it corrodes due to such factors as acidified moisture in the environment. Studies on mild steel surface reactions in acidified moisture has been the subject of investigation due to areas of applications of mild steel for durability in performance and in service (Cheng et al., 2007). Typical situations where inhibitors have been applied in other to mitigate corrosion are in the chemical process industries, textile wet processing plants, marine, oil and gas industries (Benabdellah et al., 2006; Bouklah et al., 2004). Many of synthesized organic compounds, such as amines (Fouda et al., 2005), triazoles (Bentiss et al., 1999), fatty acids (Loto et al., 2012), have been investigated as corrosion inhibitors for steel in acid media. However, plant extracts have continued to attract attention in research where in recent times, corrosion inhibition effect on metals by organic compound extracts from natural sources as plants otherwise called "green inhibitors" have been the focus of researchers. The plant extracts are primarily organic compounds composed of carbon, nitrogen,

oxygen and sulphur atoms with various degrees of unsaturation. Inhibitors containing multiple bonds play an important role in facilitating the adsorption of these compounds onto metal surfaces (Morad and El-Dean, 2006). El-Etre, (2007), found that aqueous olive (olea europaea L.) leaves extracts worked well as corrosion inhibitor for carbon steel while experimenting on the corrosion inhibition of carbon steel using aqueous extracts from olive leaves in hydrochloric acid solution by weight loss, Tafel polarization and voltammetry methods. The adsorption of the olive leaves extracts on the carbon steel was followed a spontaneous process which followed the Langmuir adsorption isotherm, where the adsorption increased with activation energy of the process. Furthermore, in using shirsh el zallouh (Ferula harmonis) root extracts in corrosion inhibition of c-steel, El-Etre, (2008), used weight loss, potentiostatic polarization and the cyclic voltammetry techniques, and it was found that the addition of the Ferula harmonis root extract reduced the corrosion of the c-steel material at increased temperature. Nazeer et al., (2015), investigated the inhibiting effect of Roselle extract on carbon steel in 0.5 M HCl solution by potentiodynamic polarization, electrochemical impedance spectroscopy (EIS), electrochemical frequency modulation (EFM), scanning electron microscopy (SEM) and energy dispersive x-ray spectroscopy (EDX). Their work revealed that Roselle leaves extract reduced hydrogen gas evolution on the cathode with attendant metal dissolution on the anode. Again, the adsorption of the inhibitor followed the Langmuir adsorption isotherm. Other works on the use of plant leaves extracts as corrosion inhibitors include the report on the inhibitive effect of extracts from Musa acuminate peel (Eddy et al., 2008), extracts from Eucalyptus globulus (Myrtaceae) leaves (Rekkab et al., 2012), and coffee ground extract (Torres et al., 2011) which reported the efficacy of plant extracts as green corrosion inhibitors. The green inhibitors either slowed down the rate of corrosion of mild steel or totally prevented mild steel from corrosion in acidified moisture environment. Various inhibitors in hydrochloric (HCl) acid solution have been studied in the past (Singh et al., 2012), including that of citrus sinensis leaves extract in 1M HCl (M'hiri et al., 2016; Udonne et al., 2015), where it was established that the antioxidants which includes neohesperidin, naringin and ascorbic acid, in the extracts from citrus sinensis L. at any concentration with the spontaneous precipitation of a thin film on the metal surface, played a significant role in corrosion inhibition of steel in acid medium, while in the case of the work by Udonne et al., (2015), extracts from Mangifere indica (Mango) peel proved to be a more efficient inhibitor of corrosion of mild steel in 1M HCl solution when compared with extracts from citrus sinensis L. However, the research gap in the use of mixed acid molar solutions have not been adequately explored, rather studies have been with the use of single acid molar solutions. Reason being that in the natural environment, there may be cases of unmitigated presence of mixed acid solutions in the atmosphere or in aquatic environment where the mild / carbon steel metal is used for structural, marine or automobile applications. Therefore, the objective of this work is to examine the inhibitive efficacy of citrus sinensis leaves extract inhibitor in H2SO4 and HCl mixed acid solution on the corrosion of mild steel using electrochemical impedance spectroscopy and Tafel polarization methods.

2. MATERIALS AND METHODS

2.1. Preparation of Electrodes

Test metal samples of mild steel for electrochemical experiment were machined into cylindrical specimens and fixed in polytetrafluoroethylene (PTFE) rods by epoxy resin in such a way that only one surface of area 1cm2 was left uncovered. The electrodes (cylindrical specimen sample mild steel) used were polished with emery papers (from 800 to 1200), rinsed with distilled water, degreased by ethanol, dried in acetone. Electrochemical experiment were conducted in a three electrode corrosion cell (as shown in Figure 1) using a VERSASTAT 400 complete dc voltametry and corrosion system with V3 studio software for electrochemical impedance spectroscopy and potentiodynamic / Galvanostat corrosion system with E-chem software for potentiodynamic polarization experiments. A platinum sheet was used as counter electrode and a saturated calomel electrode (SCE) was used as reference electrode. The latter was connected via a luggins capillary. Impedance measurement were performed in aerated and unstirred solutions at the end of 3600s at 30±1°C. Impedance measurements were made at corrosion potentials (Ecorr) over a frequency range of 100KHz to 0.1 Hz with a signal amplitude perturbation of 10 mV.

Potentiodynamic polarization studies were carried out in the potential range ± 250 mV versus corrosion potential at a scan rate of 0.5 mVs-1 for mild steel and -250 to 400 mV for aluminum. Each

test was run in triplicate to verify the reproducibility of the data. All experiments were carried out in freshly prepared solution at constant temperature $30 \pm o$ C using a thermostat.

2.2. Electrochemical Impedance Spectroscopy

Electrochemical experiment were conducted in a three electrode corrosion cell as shown in Figure 1, using a VERSASTAT 400 complete dc voltametry and corrosion system with V3 studio software for electrochemical impedance spectroscopy, and Potentiodynamic / Galvanostat corrosion system with E-chem software for potentiodynamic polarization experiments. A platinum sheet was used as counter electrode and a saturated calomel electrode (SCE) was used as reference electrode. The latter was connected via a luggins capillary. Impedance measurement were performed in aerated and unstirred solutions at the end of 3600s at $30\pm1°$C. Impedance measurements were made at corrosion potentials (Ecorr) over a frequency range of 100KHz-0.1 Hz with a signal amplitude perturbation of 10 mV.

The inhibition efficiency was calculated from the results obtained by using the following equations (Hussin and Kassim, 2010)

$$IE\% = \left(\frac{R_{ct(inh)} - R_{ct}}{R_{ct(inh)}}\right) \times 100 \tag{1}$$

Where Rct and Rct (inh) denotes charge transfer resistance in the absence and presence of the inhibitor.

2.3. Potentiodynamic Polarization Technique

Potentiodynamic polarization studies were carried out in the potential range $\pm$ 250 mV versus corrosion potential at a scan rate of 0.5 mVs-1 for mild steel and -250 to 400 mV for aluminum. Each test was run in triplicate to verify the reproducibility of the data. All experiments were carried out in freshly prepared solution at constant temperature $\pm30°$C using a thermostat.

The inhibition efficiency was determined using the equation:

$$IE\% = \left(\frac{I_{corr(bl)} - I_{corr(inh)}}{I_{corr(bl)}}\right) \times 100 \tag{2}$$

Where; Icorr(bl) and Icorr(inh) represents the corrosion current density in the absence and presence of the inhibitor, respectively.
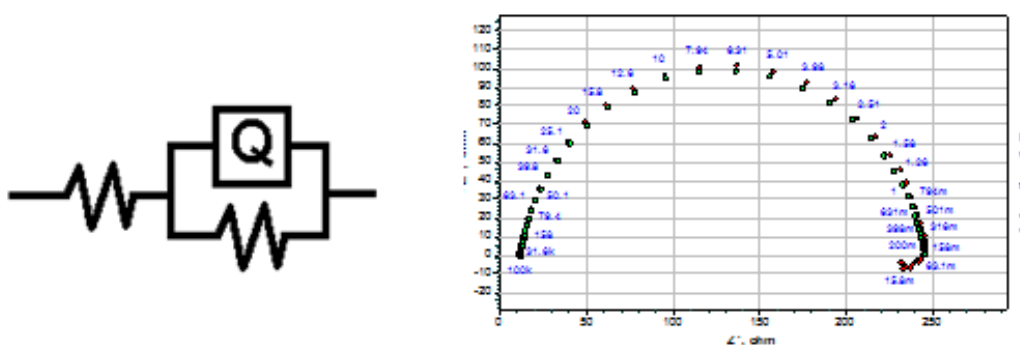

Figure1. *Equivalent Circuit Model for Mild Steel*

3. RESULTS AND DISCUSSION

3.1. Potentiodynamic Polarization Measurements for Citrus Sinensis Leaves Extract

Polarization profiles for mild steel in 1 M HCl and 0.5 M H_2SO_4 in the absence and presence of *citrus sinensis* leaves extract at 30°C are shown in Figure 1. The cathodic and anodic curves were very much polarized. Both the cathodicβc and anodic βa current values was retarded.

This indicated that the *citrus sinensis* leaves extract influenced both the cathodic and anodic reaction and hence the addition of *citrus sinensis* leaves extract reduced the metal dissolution and rate of hydrogen evolution reaction on mild steel surface. Electrochemical corrosion parameters, such as corrosion potential (*E*corr), cathodic and anodic Tafel slopes (*β*a and *β*c), corrosion current (*i*corr) and inhibition efficiency (IE *%*) obtained by extrapolation of the Tafel lines are shown in Table 1.

Analysis of these data shows that the *citrus sinensis* leaves extract act as a very effective corrosion inhibitor for mild steel in 1 M HCl and 0.5 M H_2SO_4 solution. The percentage inhibition efficiency increased with increase in concentration of the inhibitor. Furthermore, the concentration of inhibitor introduced for the study was effective even at a small concentrations and indicated the great deal of activeness of *citrus sinensis* leaves extract to mild steel surface. The effectiveness were probably due to the presence of heteroatom in the active constituents in *citrus sinensis* leaves extract. The maximum inhibition efficiency of 94.7% was obtained in 1 M HCl and at a concentration of 1000 mg/L, whereas in 0.5 M H_2SO_4 maximum inhibition efficiency is 77.5% at a concentration of 1000 mg/L.
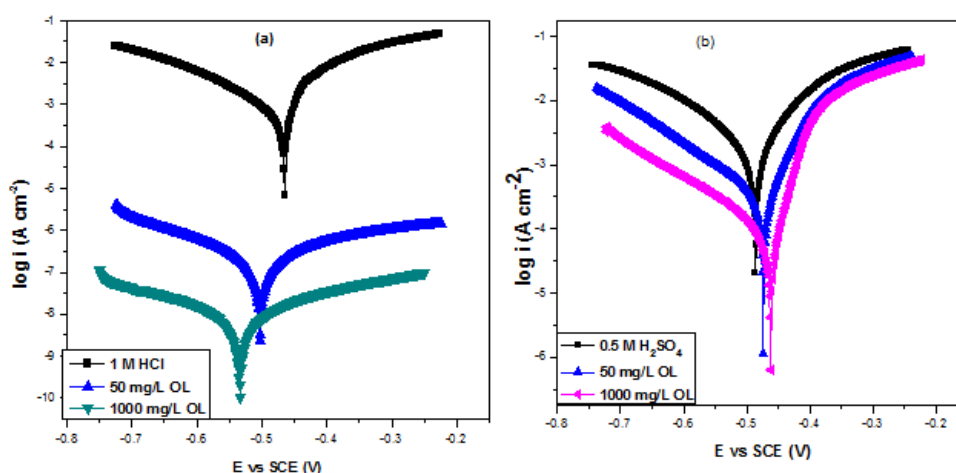

Figure2. *Potentiodynamic polarization curves for mild steel in: (a) 1 M HCl and (b) 0.5 M H_2SO_4 in the presence and absence of different concentrations of citrus sinensis leaves extract.*

Table1. *Polarization parameters for mild steel in 1 M HCl and 0.5 M H2SO4 in the absence and presence of citrus sinensis leaves extact.*

System	E_{corr}	I_{corr}	b_a	b_c	IE (%)
I M HCl	-466.4	183	100.6	122.7	
50 mg/ OL	-454.9	21.3	75.1	115.1	88.4
1000 mg/L OL	-461	9.6	71.4	104.2	94.7
0.5 M H_2SO_4	-454.3	1340	119.5	181.2	
50 mg /L OL	-452.4	803	116.2	202.4	40.1
100 mg/L OL	-450.6	301.4	61.2	165.7	77.5

3.2. Electrochemical Impedance Spectroscopy for Citrus Sinensis Leaves Extract

Nyquist plots for mild steel in 1 M HCl and 0.5 M H2SO4 in the absence and presence of citrus sinensis leaves extract are shown in Figure 2. It was evident from these plots that the impedance response of mild steel in the two environments has significantly altered with the addition of citrus sinensis leaves extract into the test solutions. The results obtained can be interpreted in terms of the equivalent circuit of the electrical double layer shown earlier which has been used previously to model the steel/acid interface. The plots were similar in the acid environment. The semicircle in all cases corresponds to a capacitive loop. The semicircle radii depends on the inhibitor concentration. The diameter of the capacitive loop increased with increase of inhibitor concentration, increasing significantly in the solution containing citrus sinensis leaves extract. Polarization resistance is unequivocally correlated to the corrosion current density in relatively simple corrosion systems characterized by a charge transfer controlled process. The results show that citrus sinensis leaves extract values increased with increase of inhibitor concentration. As citrus sinensis leaves extract is inversely proportional to the corrosion current, which was used to determine the inhibitor efficiency (IE%), from the relation given earlier: The electrochemical impedance parameters derived from the Nyquist plots and the inhibitors efficiencies (IE%) are shown in Table 2. The Nyquist plots obtained in the real system represents a general behavior where the double layer on the interface of metal/solution does not behave as a real capacitor. On the metal side, electrons control the charge distribution whereas on the solution side, it is controlled by ions. As ions are much larger than the electrons, the equivalent ions to the charge on the metal would occupy quite a large volume on the

solution side of the double layer. From Table 2, it is clear that polarization resistance values were increased and the capacitance values decreased with increasing inhibitors' concentration. Decrease in the capacitance, which may result from a decrease in local dielectric constant and/or an increase in the thickness of the electrical double layer, suggests that the inhibitor molecules act by adsorption at the metal/solution interface. This indicated the formation of a surface film on the mild steel. The inhibitor was effective to a reasonable extent in the studied environments.
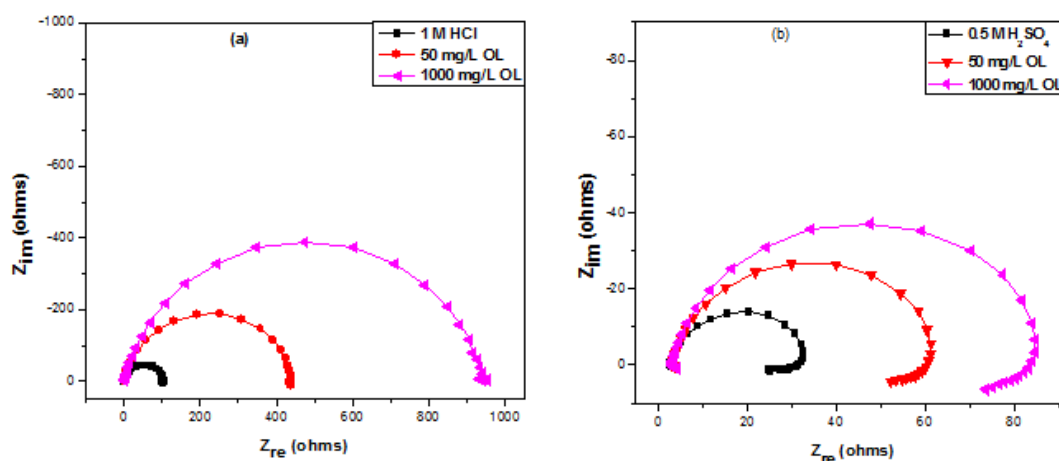

Figure3. *Electrochemical impedance curves for mild steel in: (a) 1 M HCl and (b) 0.5 M H_2SO_4 in the presence and absence of different concentrations of citrus sinensis leaves extract.*

Table2. *Electrochemical Impedance Parameters of Mild Steel in 1 M HCl and 0.5 M H2SO4 in the Absence and Presence of citrus sinensis leaves extract at 30oC.*

System	R_s (Ω cm^2)	R_{ct} (Ω cm^2)	N	C_{dl} (F cm^{-2})	IE (%)
1 M HCl	1.659	102.7	0.89	6.908E-5	
50 mg/L OL	2.865	418.7	0.89	6.794E-5	75.5
1000 mg/L OL	3.428	928.4	0.89	5.021E-5	88.9
0.5 M H_2SO_4	2.063	28.02	0.89	1.131E-4	
50 mg/L OL	2.481	59.5	0.89	5.144E-5	59.2
1000 mg/L OL	2.723	83.7	0.89	2.972E-5	66.5

3.3. SEM Analysis

The SEM images of the corroded and non-corroded mild steel surfaces are presented in Figures 1 to 4. The micrograph of corroded mild steel in the corrosive media in the presence and absence of citrus sinensis leaves extract inhibitor is presented in Figures 1 - 4. Considering corroded mild steel metals for all the used media, there were difference in the morphology of the metals surface in the presence and absence of the *citrus sinensis* leaves inhibitor. The scanning electron micrographs revealed that the surface was damaged owing to corrosion in the absence of the inhibitor, but in the presence of the inhibitor, there was moderate surface damage. This is attributed to the formation of thin film layer of protective coating on the metal surface. This is in agreement with the previous study by Loto *et al.*, 2012. The surface-nature of the corroded metals in the presence and absence of the inhibitors shows that the inhibitors were mixed inhibitors.

Figure1. *Micrograph of corroded mild steel surface in HCl with citrus sinensis leaves extract.*
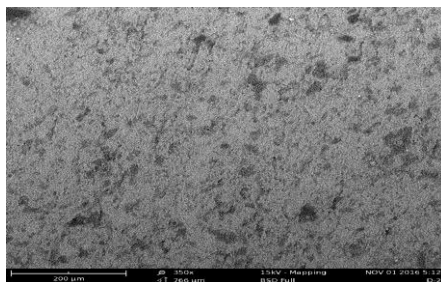
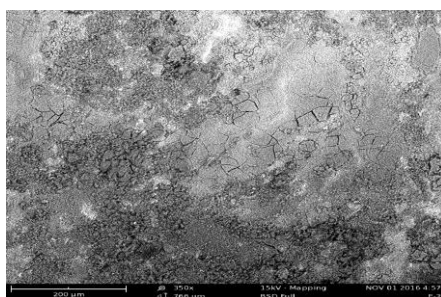**Figure2.** *Micrograph of corroded mild steel surface in HCl without citrus sinensis leaves extract inhibitor*

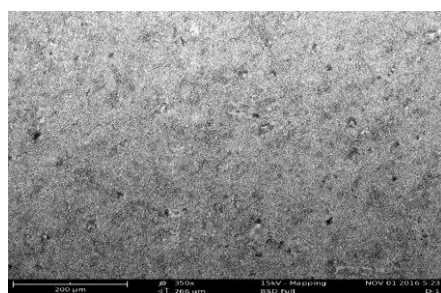**Figure3.** *Micrograph of corroded mild steel surface in H2SO4 without citrus sinensis leaves extract inhibitor*

Figure4. *Micrograph of corroded mild steel surface in H2SO4 without citrus sinensis leaves extract inhibitor*

4. THEORETICAL COMPUTATION

4.1. Quantum Chemical Computation

The inhibition effectiveness of inhibitors with different chemical structures have been correlated with the quantum chemical parameters such as energy of Highest Occupied Molecular Orbital (HOMO), Lowest Unoccupied Molecular Orbital (LUMO) and the energy gap between the LUMO and HOMO ($\Delta E = E_{LUMO} - E_{HOMO}$) (Rodríguez-Valdez et al., 2006). High HOMO (less negative) is associated with the capacity of a molecule to donate electrons to an appropriated acceptor with empty molecular orbital that facilitate the adsorption process and therefore indicates better performance of the corrosion inhibitor (Khalil, 2003; Liu *et al.,* 2011; Nkiko *et al.,* 2018). E_{LUMO} corresponds to a tendency for electro acceptance. Based on this, the calculated difference ($E_{LUMO} - E_{HOMO}$) demonstrated inherent electron donating ability and measures the interaction of the inhibitor molecule with the metal surface.

According to the frontier molecular orbital theory of chemical reactivity, transition of electron is due to an interaction between the frontier orbitals, HOMO and LUMO of reacting species. The energy of HOMO is directly related to the ionization potential and characterizes the susceptibility of the molecule toward attack by electrophiles. The energy of LUMO is directly related to the electron affinity and characterizes the susceptibility of the molecule toward attack by nucleophile. The lower the values of E_{LUMO} are, the stronger the electron accepting abilities of the molecules. Table 4 shows the calculated values of quantum chemical properties for the most stable conformations of inhibitors.

The electronic structures of the inhibitors, the distribution of frontier molecular orbitals and Fukui indices have been modeled in order to establish the active sites as well as local reactivity of the inhibiting molecules. This was achieved using the DFT electronic structure program DMol[3] using a Mulliken population analysis. Electronic parameters for the stimulation include restricted spin polarization using the DND basis set as the Perdrew Wang (PW) local correlation density function.

Table 5 shows the calculated Mulliken atomic charges and Fukui indices for nucleophilic (F^+) and electrophilic (F^-) attacks by extracts from *citrus sinensis L.* molecules.

Table4. *Calculated values of quantum chemical properties for the most stable conformations of the inhibitors.*

Property	Citrus sinensis L/E
E_{HOMO} (eV)	-7.462
E_{LUMO} (eV)	-7.383
$E_{LUMO-HOMO}$ (eV)	0.079
Maximum F^+ (Muliken)	0.218
Maximum F^- (Muliken)	0.218
Maximum(Atomic Charge)	1.378

Table5. *Calculated Mulliken atomic charges and Fukui indices for nucleophlicic (F+) and electrophilic (F-) attacks by citrus sinensis leaves extract molecule.*

Atom	Atomic Charge	F^+	F^-
C (1)	0.203	0.009	0.009
C (2)	0.031	0.008	0.008
C (3)	-0.244	0.007	0.007
C (4)	-0.468	0.056	0.056
C (5)	-0.527	0.036	0.036
C (6)	0.429	0.007	0.007
C (7)	-0.119	0.009	0.019
C (8)	-0.143	0.008	0.007
C (9)	-0.337	0.007	0.027
C (10)	-0.180	0.056	0.010
O (11)	-0.972	0.036	0.002
H (12)	0.649	0.007	0.000
N (13)	0.418	0.009	0.007
N (14)	0.434	0.008	0.010
C (15)	0.102	0.007	0.006
C (16)	-0.194	0.056	0.006
C (17)	-0.301	0.008	0.008
C (18)	0.228	0.051	0.051
C (19)	-0.309	0.006	0.006
C (20)	-0.216	0.008	0.008
S (21)	1.305	0.014	0.014
O (22)	-0.469	0.085	0.085
O (23)	-0.292	0.218	0.218
O (24)	-0.208	0.137	0.137
Na (25)	0.976	0.001	0.001
S (26)	1.378	0.013	0.013
O (27)	-0.420	0.053	0.052
O (28)	-0.201	0.113	0.113
O (29)	-0.872	0.078	0.078
Na (30)	0.978	0.000	0.000

4.2. Molecular dynamics (MD) simulation

Molecular dynamics (MD) stimulation was also performed to understudy the interaction between a single inhibitor molecule and the corroding metal surface to probe the inhibitor adsorption process at the molecular level. Simulations were performed using Forcite quench molecular dynamics in the MS modeling 4.0 software, to sample many different low energy minima and to determine the global energy minimum. The representative metal surfaces for the stimulation was steel. The metal slab were cleaved along the (1 1 0) plane. Calculations was carried out in a 12 × 10 supercell using the COMPASS force field and the Smart algorithm. Temperature was fixed at 298 K, with NVE ensemble, with a step of 1 fs and stimulation time 5 ps. The system was quenched every 250 steps with metal (1 1 0) surface atoms constrained. Also, the parameters presented in Table 4 include the total energy and binding energy of the substrate-adsorbate configuration. The total energy is defined as the sum of the energies of the adsorbate components, the rigid adsorption energy and the deformation energy. In this study, the substrate energy (mild steel,) is taken as zero. In addition,

binding energy reports energy released (or required) when the relaxed adsorbate components (inhibitors) are adsorbed on the substrate. The binding energy is defined as the sum of the rigid adsorbate energy and the deformation energy reports the energy released when the unrelaxed adsorbed components are relaxed on the substrate surface.

In order to make computation less cumbersome, solvent and charge effects were neglected. This is because both compounds being compared are subjected to identical conditions and the overall effect will be the same and virtually cancel out. In agreement with the electronic distribution model, a lateral orientation was observed for each molecule on the metal surface.

The binding energy (EBind) between the inhibitor molecule and the metal surfaces was estimated using the following equation (Bartley et al., 2003):

$$E_{Bind} = E_{total} - (E_{inh} + E_{metal}) \tag{3}$$

In all cases, the binding energies were calculated by averaging the energies of the six structures of lowest energy. The obtained values are shown in Table 6.

Table6. *Calculated value of binding energy and total energy between the inhibitor molecules and metal surfaces*

Inhibitor/metal system	$E_{Binding}$ (eV)	Total Energy (Ha)
Citrus sinensis	-157.85354	-2356.151446

It is clear from Table 6 that the binding energy has a negative value indicating exothermic reaction. As the value of the binding energy increased, the more easily the inhibitor adsorbs on the metal surface, and consequently the inhibition efficiency is enhanced.

5. CONCLUSION

Electrochemical measurements and theoretical computations were employed to investigate the corrosion inhibition and adsorption behavior of citrus sinensis leaves extract on mild steel. The inhibition efficiency was dependent on inhibitor concentration. Hence, the higher the inhibitor concentration, the better the inhibitive performance. The inhibitive efficacy of citrus sinensis L. extract is probably due to electrostatic bonding between the inhibitors and the metal surfaces as well as the aromatic structure of the inhibitors, covering surface area of metal. Potentiodynamic polarization measurements have shown that citrus sinensis leaves extract inhibited both the cathodic and anodic reaction processes and thus classified it as a mixed- type inhibitor. EIS measurements show higher Rct values obtained in the presence of inhibitors and represents corrosion inhibition. The theoretical study demonstrated that the inhibition efficiency increased with increase in EHOMO and decrease in ELUMO and energy gap, ΔE.

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