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## Study of Adsorption Mechanism of Chalcone Derivatives on Mild Steel-Sulfuric Acid Interface

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#### Abstract

Chalcone derivatives namely: (E)-3 (4 methoxyphenyl)-1-(p-tolyl)prop-2-en-1-one (MTP), (E)-1,3-di-p-tolylprop-2-en-1-one (DTP), (E)-3-(4-(diethylamino)phenyl)-1-(pand tolyl)prop-2-en-1-one (DEP) were synthesized and characterized by nuclear magnetic resonance (NMR), Mass recuoscopy (MS) and Infrared spectroscopy (IR). The corrosion mitigation of mild stee. (1.2) in 0.5 M H<sub>2</sub>SO<sub>4</sub> by these compounds has been investigated by weight loss, electrock-inical technique, surface analysis and theoretical studies. The investigations were performed at three optimum concentrations  $(10^{-4}, 10^{-5}, \text{ and } 10^{-6} \text{ M})$  at three temperatures (298, 313 and 328 K) The weight loss Potentiodyanamic polarization (PDP) and Electrochemical impedance spectroscopy (EIS) measurements showed that DEP has the maximum inhibition efficiency (93.3% for highest concentration i.e  $10^{-4}$  M) at 298 K among all three inhibitors. The inhibition efficiencies vary directly and inversely with respect to concentration and temperature respectively for all the additives. Potentiodynamic polarization (PDP) measurements revealed that the chalcones are mixed-type corrosion inhibitors and obeyed the Langmuir adsorption isotherms. Electrochemical impedance spectroscopy (EIS) technique further proposes that the inhibitor molecules mitigate corrosion process by adsorbing

at the metal/electrolyte interfaces. Further the adsorption of chalcones at the metallic surface was supplemented by SEM and AFM studies where the decreased surface roughness of the inhibited mild steel specimens was observed as compared to the uninhibited specimen. Several thermodynamic parameters ( $\Delta G_{ads}^0$ ,  $\Delta H_{ads}^0$  and  $\Delta S_{ads}^0$ ), DFT and MD theoretical parameters were calculated to explain the adsorption behaviour of these compounds on specimen surface.

*Keywords:* Corrosion inhibitor; chalcone; quantum chemical calculations; adsorption isotherm.

### **1** Introduction

Metal corrosion is very old problem as far as human civilization is concerned and has been a matter of investigation since ancient times [1-4]. It is always desirable to understand its proper mechanism along with the solutions that prevent it at a tolerable level. With modernization, use of metal structures increased chormously, the need of corrosion prevention at the level of structural design was strong<sup>1</sup> v fe.t. Enormous utilization of metals has increased the loss share due to corrosion failure in various countries and could be 3-5% of their GDP [5, 6]. Due to the mixed properties <sup>1</sup>:k. fl/xibility high mechanical strength and low cost, mild steel is among the most commonly used materials for building industrial structures [7]. Sulphuric acid is an important miner.' acid which is used in various industries with different uses such as acid pickling, acia bath, descaling etc., therefore the effect of corrosion inhibitors mainly in this medium ren aius the matter of investigation. Corrosion inhibitor is among the most widely used practices to minimize the corrosion induced by mineral acids [8]. Several type of corrosion inhibitors are used but one based on organic compounds are the most operative, effective and economically viable due to their high adsorption nature and synthetic route with ch. aper reactants [9-14]. According to literature, hetero atoms (P, S, O and N) and electron rich centres containing molecules act as good corrosion inhibitors [15-18]. However, most of these organic inhibitors are found to be toxic and less eco-friendly and have restricted use due to volatile nature and less solubility in polar solvents. Maximum surface coverage, economic accessibility and environment friendly nature are the common factors for selecting corrosion inhibitor [19-22].

Fascinating pharmacological properties are reported by Chalcones, flavonoids compounds [23-24]. However, many research groups have reported chalcones derivatives as corrosion inhibitor for different metals in acidic media, but most of the studies are performed in hydrochloric acid medium [25-28]. This is first time that corrosion inhibition abilities of

newly synthesised chalcone compounds with very low concentrations were tested in sulphuric acid medium. The mitigating mechanism of few chalcone derivatives in acidic medium have been reported by Li *et al.* [29,30]. However, the exact inhibition mechanism of many chalcone derivatives is still unknown and a further deep analysis is required. Our research group try to explore the possible inhibitory mode of action of newly synthesised chalcones compound on the mild steel surface in sulfuric acid.

The inhibitive effects of MTP, DTP and DEP have been examined using weight loss, electrochemical techniques and morphological studies. Quantum methods and computational modelling method are also used to correlate theoretical understanding with experimental data.

#### **2** Experimental section

#### 2.1 Materials and methods

Chemicals were purchased from Sigma Aldrich and used without any purification. All Solvents were purified and dried according to standal procedures.

The IR spectra were recorded on a Perkin-EL or model 2000 FT-IR spectrometer by making KBr disk for solid samples. For IR spectra, /mg of the compound is taken. The <sup>1</sup>H NMR and the <sup>13</sup>C NMR spectra were recorded on Jeol Delta 400 MHz and 100.6 MHz spectrometer, respectively using tetramethylsilane (1.45) as internal standard and CDCl<sub>3</sub> as solvent. For the determination of the <sup>1</sup>H NMR arta <sup>13</sup>C NMR spectra, the 5 mg, and 15 mg respectively of compounds are taken and diss. Vec in CDCl<sub>3</sub> to obtain a clear solution. The chemical shift values are on  $\delta$  scale and the compling constant (*J*) are in Hz. HRMS analysis was carried out using Agilent G6530AA LC Q-TOF mass spectrometer. Analytical TLCs were performed on pre-coated Merck silica- $\epsilon$  el 60F<sub>254</sub> plates and the visualization of the developed plates was performed by UV light.

Mild steel (MS) specimen having chemical composition (wt%) of C (1.62), Si (0.030), P (0.020), Mn (1.00) and the balance was Fe was used to perform the corrosion inhibition experiments. For Weight loss technique, MS coupons of  $1 \text{cm} \times 1 \text{cm} \times 1 \text{cm}$  were used while for electrochemical techniques coupons having dimension of  $1 \text{cm} \times 1 \text{cm} \times 3 \text{cm}$  whose one end was soldered with a copper wire and covered with epoxy resin araldite except one face with surface area of  $1 \text{ cm}^2$  was used as the working electrode (WE). Prior to a new testing in every technique, the MS specimen was polished with emery papers (grade 150 to 2000), cleaned with acetone (CH<sub>3</sub>COCH<sub>3</sub>), rinsed with distilled water to scrap off impurities. The

structure of investigating compounds (E)-3-(4-methoxyphenyl)-1-(p-tolyl) prop-2-en-1-one (MTP), (E)-1,3-di-p-tolylprop-2-en-1-one (DTP) and (E)-3-(4-(diethylamino)phenyl)-1-(p-tolyl)prop-2-en-1-one (DEP) are shown in Fig. 1 (a-c, respectively). Stock solutions of  $1 \times 10^{-4}$  M concentration of additives in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution were prepared by the calculated amount of the solid compounds MTP, DTP and DEP. The lower concentrations, viz.  $1 \times 10^{-5}$  M and  $1 \times 10^{-6}$  M of these compounds were prepared by diluting the stock solution i.e.  $1 \times 10^{-4}$  M.

### 2.2 Synthesis and characterization

## 2.2.1 Synthesis of (E)-3-(4-methoxyphenyl)-1-(p-tolyl)prop-2-en-1-one (MTP), (E)-1,3-dip-tolylprop-2-en-1-one (DTP), (E)-3-(4-(diethylamino)phc.vl)-1-(p-tolyl)prop-2-en-1one (DEP)

Chalcones were synthesized by previously reported procedure as given in Fig. 2, through base catalyzed condensation of substituted acetophenones and substituted benzaldehydes [31]. To a solution of acetophenone (0.01 mol) in ethanol (40m<sup>1</sup>), be. zaldehyde (0.01 mol) derivative was added. Then solution of aqueous KOH (60 %, 16 r.l) was added with continuous stirring for 30 minutes. The mixing was continued for 7-5 hours at room temperature. After completion of reaction which was confirmed by thin layer chromatography, ice cold HCl (25 ml, 10 %) was added. The solid was obtained which was separated by filtration followed by washing with ice cold water till neutralization. Finallyproduct was recrystallized with ethanol. All three chalcone derivatives were characterized by MRR, IR and Mass Spectroscopy. NMR spectra of all compounds are shown in Fig. 3 (a c) and <sup>13</sup>C NMR, IR and Mass Spectra of these compounds are separately given in SI file.

**MTP:** Mol. Formula: C<sub>1.7</sub>H<sub>16</sub>O<sub>2</sub>; Mol. Wt. 252.1150; Yellow solid; Yield= 94 %; **FT-IR** (CHCl<sub>3</sub>, cm<sup>-1</sup>): 3003, 1652, 810, 737, 672; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.92 (d, 2H), 7.77 (d, 1H), 7.59 (d, 2H), 7.41 (d, 1H), 7.30-7.25 (m, 2H), 6.93 (d, 2H), 3.84 (s, 3H,), 2.42 (s, 3H) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  190.15, 161.67, 144.32, 143.44, 136.00, 130.24, 129.35, 128.65, 127.83, 119.90, 114.48, 55.48, 21.73 ppm; EM m/z (%) : 253 (M+1).

**DTP:** Mol. Formula: C<sub>17</sub>H<sub>16</sub>O; Mol. Wt. 236.1201; Yellow solid; Yield= 95 %; **FT-IR** (CHCl<sub>3</sub>, cm<sup>-1</sup>): 3025, 1660, 807, 759, 735; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.93 (d, 2H), 7.78 (d, 1H), 7.55-7.47 (m, 3H), 7.29 (d, 2H), 7.22 (d, 2H), 2.43 (s, 3H), 2.39 (s, 3H) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 190.24, 144.60, 143.59, 141.03, 135.88, 132.37, 129.77, 129.38,

128.71, 128.52, 121.19, 21.76, 21.61 ppm; EM m/z (%): 237 (M+1).

**DEP:** Mol. Formula: C<sub>20</sub>H<sub>23</sub>NO; Mol. Wt. 293.1780; Yellow solid; Yield= 90 %; **FT-IR** (CHCl<sub>3</sub>, cm<sup>-1</sup>): 3029, 1649, 806, 746, 683; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.91(d, 2H), 7.77 (d, 1H), 7.52 (d, 2H), 7.32-7.25 (m, 3H), 6.65 (d, 2H), 3.40 (q, 4H,), 2.42 (s, 3H), 1.19 (t, 6H) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 190.30, 149.71, 145.58, 142.82, 136.65, 130.76, 129.21, 128.51, 122.04, 116.44, 111.37, 44.52, 21.65, 12.73 ppm; EM m/z (%): 294 (M+1).

#### 2.3 Weight loss technique

The gravimetric study was evaluated at 298, 313 and  $22\% \pm 2$  K for all three studied concentrations of chalcone compounds with average dir oing time of 6 hours. For each set of experiment, a freshly polished coupon with area 1 cm<sup>-</sup> was immersed into 100 mL of test solution, same procedure was repeated in duplicate 'o get reproducible results. The corrosion rate C<sub>R</sub> is calculated by dividing the weight loss, 'W (mg) of specimen by the product of Area, A (cm<sup>2</sup>) of specimen and exposure time, ' (n ours) i.e C<sub>R</sub>=W/At [32]. The inhibition efficiency  $IE_{WL}$  (%) was determined by using the form 'a:

$$IE_{WL}(\%) = \frac{c_R - c_{R(i)}}{c_R} \times 100$$
 (1)

Where  $C_R$  and  $C_R$  (i) are the corrosion rate without and with the addition of the inhibitor in acid solution respectively. The surface coverage ( $\theta$ ) of chalcones molecules on metal surface in all techniques was calculated by using inhibition efficiency values according to the following equation:

 $\theta = IE_{WL}(\%)/100$ 

(2)

Where IE is the inhibition efficiency of a studied additive.

#### 2.4 Electrochemical methods

Three electrodes cell assembly consist of working, auxillary and reference, which was assembled in a luggin capillary, cell assembly were used for electrochemical measurements. The cell assembly was kept in a water thermostat for a fixed time to achieve an open circuit potential (OCP). The measurements were done by using an electrochemical workstation CHI 760C (CH Instruments, Inc, USA). The Tafel graphs potential (E) – logarithm of current (log

I) were obtained by this technique. The plots were recorded in the potential range -0.9 and + 0.0 V at a scan rate 1 mVs<sup>-1</sup>. By the extrapolation of these Tafel plots various corrosion parameters were obtained such as corrosion potential ( $E_{corr}$  in mV), corrosion current ( $I_{corr}$  in mA/cm<sup>2</sup>), two slope values in mV/decade ( $\beta_a$  and  $\beta_c$ , respectively) and tabulated in Table 2.

Inhibition Efficiency ( $IE_{GPS}$  %) was computed with concern surface coverage ( $\theta$ ) using the relationships, in equations 3 & 4 [33]:

$$IE_{GPS}(\%) = \frac{I_{corr} - I_{corr(inh)}}{I_{corr}} \times 100 \ \fielde{2}$$

$$\Theta_{GPS} = \mathbf{1} - \left(\frac{I_{corr}(inh)}{I_{corr}}\right) \qquad (4)$$

Where  $I_{corr}$  and  $I_{corr(inh)}$  correspond to the corrosion current aensity (values in mA/cm<sup>2</sup>) in the absence and presence of inhibitors in corrosive solut<sup>2</sup> on, respectively.

The Impedance studies were carried out just after the polarization measurements on the same electrode system without any further surface ne (if cation by using the 10 mV sine wave as the excitation AC signal at the *OCP* in the frequency range from 100 kHz to 0.1Hz. The impedance descriptor charge transfer resistance ( $R_{ct}$  values in  $\Omega \text{cm}^2$ ) was assessed from the semicircle in the Nyquist graphs. The inhibition efficiency for impedance ( $IE_{EIS}$  %) was determined from  $R_{ct}$  according to equation (5) below [34]:

$$IE_{EIS} (\%) = \frac{R_{ct(inh)} - R_{ct(acid)}}{R_{ct(inh)}} \ll 100$$
 (5)

The double layer capacitance  $C_{ll}$  values were calculated according to the equation 6, [15]:

$$f(-Z_{max}) = \frac{1}{2\pi C_{dl}R_{ct}}$$

where  $f(-Z_{max})$  is the maximum frequency on the imaginary impedance axis, and its values are also listed in Table 3. Since the data is made to fit with the corresponding impedance values of an equivalent circuit. The process was performed using the software *ZSimpWin* Version 3.21.

#### 2.5 Morphological study (SEM and AFM)

The specimen coupons were immersed into 50 ml of inhibitors solution (MTP, DTP and DEP) of higher ( $10^{-4}$  M) concentration prepared in 0.5 M H<sub>2</sub>SO<sub>4</sub> for 24 h at room temperature. Study was also done only in the presence of 0.5 M H<sub>2</sub>SO<sub>4</sub>. The coupons were withdrawn, washed with deionised water, kept in a desiccator, and after that the SEM images were

obtained with the JEOL JSM-6610 SEM instrument. The 3-Dimensional AFM analysis was performed with a Nanosurf Easyscan2 instrument, model no. BT-02218.

#### **2.6 Theoretical studies**

The Quantum Chemical Calculations have been carried out by using the Hyperchem 8.0 software and structures optimization by semi-empirical AM1 Method to substantiate the above information at the electronic level. Molecular dynamics (MD) simulation was applied to evaluate the interaction and adsorption performance of selected chalcone derivatives on the surface of Fe (110) using the Forcite module which is implemented in Materials Studio8 [35, 36].

#### **3 Results and discussion**

### **3.1 Effect of concentration on inhibition efficiency**

The variation of corrosion inhibition efficiencies for all studied concentrations of inhibitors at three temperatures are given in Table 1 and p c is are given in Fig. 4(a), (b) and (c). It is observed that percentage of IE increases vith increase in the concentration of inhibitor. Maximum IE% i.e.~89% was shown by L.'P inhibitor as compared to DTP (86%) and MTP (85%) inhibitors at highest concentration (10<sup>-4</sup> M). Hence DEP showed slightly betterinhibition efficiency as compared to other two inhibitors and overall order of inhibition is as follows: DEP > DTP > M.'P. The high value of surface coverage ( $\theta$ ) leads to the fact that adsorption of Chalcone protecules on the active site of mild steel surface is one of the possible mechanisms of inhibition.

### 3.2 Galvanostatic polary ation (GP) study

Polarization graphs for MS with  $(10^{-6} \text{ to } 10^{-4} \text{ M})$  concentrations of MTP, DTP and DEP inhibitors and without inhibitor were recorded at 298 K to 328 K and representative plots at 298 K depicted in Fig. 5 (a), (b) and (c) respectively. The various corrosion parameters were obtained with the help of this study are tabulated in Table 2. The relative deflection of the  $E_{corr}$  values after the addition of an inhibitor as compared to the blank acid is largely gives the indication about the anodic, cathodic or mixed-types behaviour of inhibitors. The swing of  $E_{corr} > 85 \text{ mV}$  towards either of the side is attributed blocking of anodic or cathodic site accordingly by the inhibitor, while a change in  $E_{corr} < 85 \text{ mV}$  implies that the additive is mixed-type inhibitor, it means, it discontinues both mild steel at anodic half-cell and

reduction of  $H^+$  ions at cathodic half-cell of corrosion circuit respectively [37]. The values of corrosion potential obtained from this study are within the range of  $\pm 85$  mV with respect to that of the acid, both anodic and cathodic reaction are affected simultaneously and no particular shift was spotted. This indicates that the all the used inhibitors are act as mixed-type of inhibitors. The values of  $\beta_c$  and  $\beta_a$ , have been found to be irregular which indicates that inhibition of corrosion of MS in acidic medium is not only due to adsorption [38] but there is also involvement of anions and due to synergistic effect. This adsorption process of inhibitor is also indicated by the decrease in current density values. With an increase of an inhibitor concentration inhibition efficiency was also increases. It happens due to the presence of conjugated  $\pi$ -electrons of chalcone which overlaps with the variant d-orbitals of the metal surface and excess of electron density donate back to the vacant  $\pi^*$  orbitals (p-orbital) of inhibitors resulting in a synergistic effect. A comparison of  $I E_{GPS}$  (%) values of MTP, DTP and DEP as shown in Table 2 reveals that DEP exhibits slight better inhibition of mild steel corrosion than MTP, DTP throughout the studied malcentration and temperature range. Generally aromatic compounds have been obser ed better corrosion mitigation properties than O-containing compounds due to the prepence of conjugated  $\pi$ -electron rings which can donate electron-density to vacant d-orbit. 1s Jf Fe [39-42].

#### 3.3. Electrochemical impedance speciescopy

The corrosion behaviour of MS in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution in the absence and presence of studied concentrations of all three additives at room temperature was further explored using EIS electrochemical tech mane. The Nyquist plots for MS in 0.5 M H<sub>2</sub>SO<sub>4</sub> without and with various concentrations of the studied Chalcone compounds are shown in Figures 6 (a), (b) and (c). The Nyquist plots show decrease in the radius of semicircles due to non-ideal conduct of electrochemical interface on MS in the aggressive corrosive medium [43]. The diameter of Nyquist plots increases with increase in the amount of inhibitors added in corrosive soultion [44, 45]. This implys that the additives form defensive layer on the MS surface thus rising the impedance of MS interface to the corrosion process. The EIS spectra were fitted into the equivalent circuit shown in Figures 7 (a), (b) and (c), and the electrochemical parameters obtained from the fitting and simulation analysis are listed in

Table 3. The %*IE* The double layer capacitance,  $C_{dl}$  values were calculated according to the equation 5 and 6 respectively and their values are also listed in Table 3. The  $R_{cl}$  value may be infered as the resistance created by inhibitor to the charge transfer ahead of the oxidation of the MS. It is noticeable from the parameters given in Table 3 that with the increase in the concentration of inhibitors the  $R_{cl}$  values increases due to the formation of protective defensive layer of inhibitor molecules on the MS surface thereby reducing the movement of charged species across the interface. The C<sub>dl</sub> values in the presence of the inhibitors are generally lower than that of the blank acid system. This suggest a 4 ecrease in local dielectric constant or an increase in the thickness of capacitive 1ay r, which is attributed to the adsorption of inhibitor molecules on the MS surface [46]. The %IE increases with increasing concentration of the inhibitors but the trend of inhibitor performances obtained from the EIS data cannot be generalized.

#### 3.4 Adsorption isotherm

Various adsorption isotherms [47] vere plotted to investigate the exact mechanism of adsorption of inhibitors. From these isotherms various thermodynamic-kinetic parameters such as  $\Delta G_{ads}^0$ ,  $\Delta H_{ads}^0$  and  $\Delta S_{ads}^0$  were calculated.

By plotting the various is the ms it was obtained that the value of correlation coefficients ( $r^2$ ) for the plots of  $C_{inh}/\theta$  verse,  $c_{inh}$  (Figure 9 (a), (b) &(c)) equal to or nearly 1 which directs that Langmuir adsorption (LA) isotherms are followed by a specific adsorption method at an applicable temperature for all inhibitors viz. MTP, DTP and DEP. The Langmuir adsorption isotherm for an isotherm is denoted by following equation (Eq. 7) [48]:

$$C_{inh}/\theta = \frac{1}{K_{ads}} + C_{inh} \tag{7}$$

The extent of adsorption of inhibitor with respect to total available site is called degree of surface coverage, and is represented by  $\theta$ , which can be obtained by dividing the inhibition efficiency by 100. The value of  $\theta$  lies between 0 and 1, i.e.,  $0 < \theta < 1$ . In equation 7,  $K_{ads}$  indicates the adsorption equilibrium constant whose values were obtained from the intercepts of the above plots. Gibbs Free Energy of Adsorption ( $\Delta G_{ads}^0$ ) values were calculated from the

equation 8;

$$\Delta G_{ads}^{o} = -RTln(55.5K_{ads}) \tag{8}$$

Where; R and T denote the universal Gas Constant having value 8.314 JK<sup>-1</sup>mol<sup>-1</sup> and the absolute temperature in Kelvin respectively.

Physisorption ( $\Delta G_{ads}^0 \sim -20$  kJ/mol) or chemisorption ( $\Delta G_{ads}^0 \sim -40$  kJ/mol), adsorption behaviour of inhibitor molecules on metal surface is indicated by  $\Delta G_{ads}^0$  values having negative sign which explain the spontaneity of the process. All inhibitors MTP, DTP and DEP are showing chemisorption (values ranges from -40 to -50 kJ.mol<sup>-1</sup>)  $\sim$  mitigate corrosion on the MS surface.

With the help of Van't Hoff equation (Eq. 9) other therr on ynamic parameters like enthalpy (  $\Delta H_{ads}^{0}$ ) and entropy ( $\Delta S_{ads}^{0}$ ) of adsorption were obtained.

$$lnK_{ads} = \frac{-\Delta H^{\circ}_{ads}}{RT} + const.$$
(9)

Enthalpy of adsorption were evaluated by taking the slope  $(\Delta H_{ads}^0/R)$  of the graph plotted between natural logarithm of  $K_{ads}$  against the reciprocal of T. The entropy of adsorption  $\Delta S_{ads}^0$ further calculated by putting the values of  $\Delta G_{ads}^0$  and  $\Delta H_{ads}^0$  in the following equations:

$$\Delta G^0_{ads} = -\Delta H^0_{ads} - T\Delta S^0_{ads} \tag{10}$$

$$\Delta S_{ads}^{\circ} = \frac{\Delta H_{ads}^{\circ} - \Delta G_{ads}^{\circ}}{T}$$
(11)

Generally, enthalpy values less than -40kJ/mol, is an indication of physiorption mechanism whereas for chemisorption behaviour, the values are around -100kJ/mol and negative sign shows the exothermic nature of this process. Calculated values of enthalpies of adsorption are -78 kJ/mol, -62 kJ/mol and -63 kJ/mol for MTP, DTP and DEP, respectively, therefore all inhibitors obey physiorption on the specimen. This may be explained due to electrostatic attraction between positively charged oxidised metal surface and negatively charged species formed due to the inhibitor molecules. The negative values of  $\Delta S_{ads}^0$  leads to the fact that the intermediate species is formed due to adsorption than desorption process, which signifies that no disordering occur in the reaction path [49]. The thermodynamic parameters such as  $\Delta G_{ads}^0$ .

 $\Delta H_{ads}^0$  and  $\Delta S_{ads}^0$  obtained from Langmuir adsorption isotherm for MTP, DTP and DEP are reported in Table 5. Further Arrhenius relationship was used to calculate the activation energy ( $E_{act}$ ) related with current rate [50, 51]:

$$log I_{corr} = log A - \left(\frac{-E_{act}}{2.303RT}\right)$$
(12)

The Arrhenius graphs of log of current density against 1000/T and plot of activation energy versus concentrations of inhibitors MTP, DTP and DEP, respectively are plotted. The activation energy has been calculated by the slopes of plotted graphs and the values are tabulated in Table 5. The two modes via which an inhibitor protection the surface of the metal are either by "blocking the geometry" effect that is by blocking the area available for reaction, or by adjusting the activation energy of anodic and cathod's process on the uninhibited surface during the inhibited corrosion reaction. Table 5 shows hat  $E_{act}$  values are higher after the addition of MTP, DTP and DEP inhibitors than in corrosive 0.5 M H<sub>2</sub>SO<sub>4</sub> solution only shows the reduced corrosion rates in the existence of inhibitors in corrosive medium.

### 3.5 Scanning electron microscopy (f TM)

Two dimensional SEM images of properly grinded metal coupons surface, and the surface of specimens recovered from consider solution before and after the addition of highest concentration i.e.  $1 \times 10^{-4}$  M c<sup>+</sup> MTP, DTP and DEP, respectively, are shown in Figure 10 (a-e). The well grinded Flans specimen surface (Figure 10a) shows that it is homogeneous and is free from roughness and pits whereas in the presence of acidic solution (Figure 10b) MS coupon reveals destruction of uniform surface having pits and holes which is due to MS dissolution and formation of plenty of corrosion products. However, a protective layer of inhibitors with confined roughness on MS surface appeared which shows a significant reduction in the addition of DEP {Figure 10 (e)} than to seen in the presence of MTP and DTP {Figure 10 (c-d)}. The corrosion inhibition is not only due to the conjugated pi-electrons of phenyl rings, and electron donating tendency of heteroatom; here oxygen but also due to the occurrence of synergistic ion also assists. Further it is concluded that inhibition effect of DEP is higher than the other studied additives.

#### 3.6 Atomic force microscopy (AFM)

Three dimensional images of polished MS, in the absence and presence of inhibitor in studied corrosive medium are shown in Figure 11 (a–e). The MS surface morphology was tested by assessing roughness of specimen (RMS) and these values are tabulated in Table 6. The RMS values of plane sample (Figure 11 a) and sample in acidic corrosive solution (Figure 11b) were find out to be as 112.8 and 648.2nm, respectively. Noticeably showing that the roughness of the 0.5 N H<sub>2</sub>SO<sub>4</sub> exposed metal surface is very high and it shows an uneven surface having rough lots due to extensive corrosion. Further it is observed that in the presence of MTP, DTP and DEP mitigation of corrosion take place. The images depicted in Figures 11 (c-e) shows that the inhibitors are forming protect. The images on the MS surface with adsorption as limited corrosion products formed after a tdition of 10<sup>-4</sup> M inhibitors [52, 53]. The values of RMS are presented in Table 6 for MTP, LTP and DEP (184.3, 167.6 nm and 141.2 nm) at 10<sup>-4</sup> M, respectively, the trends obtain. It give the confirmation for the DEP in comparison to MTP and DTP.

### 3.7 Quantum chemical (QC) calculation

In the light of experimental results for the selection of good inhibitor for MS, the quantum chemical calculations have been carned out by using the Hyperchem 8.0 software and structures optimization by semi-empiric I AM1 Method to substantiate the above information at the electronic level. Optimize,' geometries of inhibitors (Ball and stick model), mulliken charges,  $E_{HOMO}$ , the energy of highest occupied molecular orbital (E<sub>LUMO</sub>), the energy of lowest unoccupied molecular orbital are shown in Figures 12-14, the gap energy ( $\Delta E$ ), the dipole moment ( $\mu$ ) were calculated for the MTP, DTP and DEP inhibitors, respectively and tabulated in Table 7. ELOMO tells the susceptibility of the inhibitor molecules towards hitting by nucleophiles and frequently related to electron affinity (A). Smaller the  $E_{LUMO}$  values are the more will be the electron gaining tendencies of inhibitors.  $E_{HOMO}$  is linked with electron contributing capability of inhibitor molecules and the negative of  $E_{HOMO}$  related to ionization potential (I). The little energy difference between  $E_{LUMO}$  and  $E_{HOMO}$  i.e.  $\Delta E$  makes the possibility of transferring of the electrons from the inhibitor molecules to the atoms of the iron very probable [54, 55]. The potential inhibition efficiencies increase if the MTP, DTP and DEP have higher  $E_{HOMO}$  energies and lower  $E_{LUMO}$  energies and small  $\Delta E$  as reported in Table 7.

The calculated entire atomic Mullikan's charges for all additives MTP, DTP and DEP

molecules are depicted in Figure 12 (b), 10 (b) and Figure 14(b). By careful examination of Figs., we reveal that the values of the electronegative charges of the oxygen, carbon atoms of phenyl rings and ions which are present in the solution act as an active sites, whichjustify the relationship between the donating electrons and inhibition efficiency [57,58]. The total energy with negative sign (-70019.1, -62639.4 and -78482.6kcal/mol) clearly indicate that chalcone compounds (MTP, DTP and DEP, respectively) are thermally stable and comparatively less prone to break.

For the protonation of the molecules studied, the results obtained by the MarvinSketch software show that the compound DEP is the only molecule that is favourable for protonation in the nitrogen atom in the acidic medium. As shown in Table 7 that the protonation of the DEP results in an increase of molecular reactivity, this is very clear, and  $\Delta E$ ,  $E_{LUMO}$  and total energy values are decreased. The effect of protonation has a negative influence on the electrons donor power by the studied molecules to vara, the iron surface, therefore,  $E_{HOMO}$  value are decreased.

### 3.8 MD simulations

Molecular dynamics (MD) simulation was applied to evaluate the interaction and adsorption performance of selected chalcone deravatives on the surface of Fe (110) using the Forcite module [59]. The MD simulation was executed in a  $32.270^*$   $32.270^*$   $34.134\text{Å}^3$  simulation box with periodic boundary conditions, which was composed of the chemical species (with inhibitory monomer +  $20\text{H}_3\text{O}^+$  +  $10\text{SO}_4^{2^2}$  +  $500\text{H}_2\text{O}$ ) and slab of Fe (110). The COMPASS force field has been uncer [60]. All systems surveyed were carried out in the presence Andersen thermostat at 298 K, NVT ensemble, with a simulation time of 400 ps and a time step of 1.0 fs [61].

The results of the simulation are represented in Figure 12 and reported in Table 8. The superior and lateral views displayed in Figure 15 show that the three chalcones derivatives adhere to the metal surface through any part of the molecular structure, covering a large area of iron. This result confirms that the molecules studied carry several electron donor and acceptor sites, which facilitates their adsorption on the surface of the metal substrate. This behaviour protects the metal surface against corrosion in the  $H_2SO_4$  medium.

The two energy descriptors, i.e. interaction energy (E interaction) and binding energy (E binding),

are calculated using the two equations below [62]:

$$\boldsymbol{E}_{interaction} = \boldsymbol{E}_{total} - (\boldsymbol{E}_{surface+solution} + \boldsymbol{E}_{inhibitor})$$
(13)

$$\boldsymbol{E_{binding}} = -\boldsymbol{E_{interaction}} \tag{14}$$

The values of these descriptors are shown in Table 8, where it is noted that the negative values of the E interaction reflect the spontaneity of the adsorption process [63]. Generally, the minimum value of E interaction reflects a higher interaction between the inhibitory molecule and the metal surface, therefore the DEP molecule is well verified this finding [64]. This shows that this molecule is considered to be a more efficient inhibitor against corrosion of the steel being investigated. This inhibitory potential is possibly the to the existence of the metal surface donor electron group (N(CH<sub>3</sub>)<sub>2</sub>). The adsorption of this descriptor indicates much larger adsorption [65] The increasing order of E binding is MTP<DTP<DEP, indicating that the DEP inhibitor is a good and very effective condition to best protect the metal surface.

Organic molecules carrying note 5 atoms are able to protonate in acidic media [66]. In our situation, the DEP molecule is the only one among the studied chalcone derivatives that protone in the nitrogen at m in the chosen medium. Using MD simulation, we can assess the degree of reactivity of protonated DEP with the atoms of the first layer of iron. Figure 15 represents the best adsorption configuration of protonated DEP on the Fe (110) surface. It is clear from the side and top views that the entire structure of the DEP molecule adsorbs on the surface of the iron, i.e. there is no change in the adsorption state compared to the neutral form. This means that protonation does not change the conformation and configuration of the DEP molecule, which shows that this molecule retains its molecular reactivity in relation to the iron surface. Simulation results show that the E interaction value (-696.721/mol) is closer to

that obtained for the neutral form of the adsorbed DEP molecule (-700.871 kJ/mol). This indicates protonation does not affect the interaction behaviour of DEP/Fe (110) surface.

#### 4. Mechanism of corrosion inhibition

By correlating literature with the results obtained from all techniques we can conclude that the MTP, DTP and DEP act as mixed type of inhibitor by mitigating both anodic as well cathodic mechanisms for MS corrosion in H<sub>2</sub>SO<sub>4</sub> medium. This is an established fact that organic compounds impede the metal corrosion due to adsorption on the surface. The adsorption phenomena are mostly interpreted on the structure of the inhibitor molecule, charge on the metal surface and the formation of metal solution interface. Therefore, the expected mechanism for the adsorption of chalcones derivatives on the MS surface can be proposed as follows: (a) the physisorption contacts the expectation, (b) the chemisorption behaviour of lone electron pair of heteroatoms (N and  $2^{\circ}$ ) vacant *d*-orbitals of iron atoms, (c) donor-acceptor exchanges of the  $\pi$  -electrons of  $\sigma$  o natic ring of inhibitor to empty *d* orbital of iron atoms.

Experimental outcomes give clear idea  $u_{1,2}^{e_1}$  the chalcone compounds act as effective against the mild steel corrosion in 0.5 M H<sub>2</sub>CO<sub>4</sub>. This can be explained because chalcones possess double bonds, aromatic rings and be explained and these electron rich centres donate their electron density to vacant d-orbit ils of iron. Another possible interaction which can be denied is interaction of protonated chargeness with the steel surface since MS carries positive charge in acid solution so similar charge is of protonated inhibitor and substrate repel each other.

Low degree of hydration due to the large size of sulfate ions, so number of water molecules attached will be less, the efore electrostatic attractions of negatively charged end of water dipoles attached with sulfate ions with positively charged MS surface is limited. Thus, overall adsorption is due the combined effect of sulfate ions and inhibitor molecules. In addition, these chalcones can adsorb on the mild steel via chemisorption, donating electrons from nitrogen and oxygen atoms to iron surface by replacing water molecules.

#### **5** Conclusions

Chalcone derivatives namely MTP, DTP and DEP are assessed as new and competent inhibitors against the mild steel corrosion in  $0.5 \text{ M H}_2\text{SO}_4$  solution through electrochemical, morphological and quantum chemical analysis. The results obtained from these techniques direct to the following outcomes:

- MTP, DTP and DEP show that inhibition efficiency is directly proportional to the concentration.
- MTP, DTP and DEP act effectively as a mixed type inhibitor.
- Weight loss outcomes are in a good agreement with electrochemical measurements.
- Langmuir adsorption (LA) isotherm is obeyed by all inhibitors. The interaction of hetero atoms and  $\pi$ -electrons of phenyl rings with the mild steel surface is the main cause of adsorption.
- SEM and AFM techniques showed the retardation of corrosion with addition of inhibitor. Experimental and theoretical results complement each other to indicate that DEP is the best inhibitor in the series studied.

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**Figure1.** Molecular structure of studied chalcones  $(\mathbf{a})(E)$ -3-(4-methoxyphenyl)-1-(p-tolyl)prop-2-en-1-one (MTP) $(\mathbf{b})(E)$ -1,5 di-p-tolylprop-2-en-1-one (DTP) and  $(\mathbf{c})(E)$ -3-(4-(diethylamino)phenyl)-1-(p-tolyl)prop-2-en-1-one (DEP).



Figure 2. Schematic diagrams for the synthetic route of the chalcones derivatives.







**Figure 3.**<sup>1</sup>H NMR of chalcone derivatives (\*) MTP (b) DTP and (c) DEP.





**Figure 4.** Effect of inhibitor concentration on corrosion inhibition efficiency for (a) MTP (b) DTP and (c) DEP and at 298 K





**Figure 5.** Galvanostatic polarization curves for MS in 0.5 M H<sub>2</sub>SO<sub>4</sub> without and with various concentrations: (...0.5 M H<sub>2</sub>SC 4), (...10<sup>-4</sup> M),(...10<sup>-5</sup> M) and (...10<sup>-6</sup> M) of (a) MTP, (b) DTP and (c) DEP at temperatures 2.28 K.





**Figure 6.** Nquist Diagrams for MS in 0.5 M H<sub>2</sub>SO<sub>4</sub> with out and with various concentrations: (...0.5 M H<sub>2</sub>SO<sub>4</sub>), (...10<sup>-4</sup> M),(...10<sup>-5</sup> M)and (...10<sup>-6</sup> M) of (a) MTP, (b) DTP and (c) DEP at temperatures 298 K.





**Figure 7.** Nyquist Fitting of Experimental Data (MS in 0.5 M H<sub>2</sub>SO<sub>4</sub> in the presence of  $10^{-2}$  M of (a) MTP, (b) DTP, nd (c) DEP at temperatures 298 K.



**Figure 8.** The Common Equivalent Circuit Corresponding to Exp rimental Data (MS in 0.5 M  $H_2SO_4$  in the presence of  $10^{-2}$  M of (a) MTP, (b) DTP and (c)  $DL_4$ 





Figure 9. Representative Langmuir adsorption isothe rms for MS in 0.5 M  $H_2SO_4$  containing various concentrations of (a) MTP (b) DTP and (c) DE<sub>1</sub> at 298-328 K.





**Figure 10.**SEM images of (a) plain MS surface, (b) MS in 0.5 M  $H_2SO_4$ , (c) MS in 0.5 M  $H_2SO_4 + 10^{-4}$  M MTP, (d) MS in 0.5 M  $H_2SO_4 + 10^{-4}$  M DTP, and (e) MS in 0.5 M  $H_2SO_4 + 10^{-4}$  M DEP, after 24 h exposure at the x1000 magnification.







**Figure 11.**AFM three dimensional images of (a) plain MS surface, (b) MS in 0.5 M H<sub>2</sub>SO<sub>4</sub>, (c) MS in 0.5 M H<sub>2</sub>SO<sub>4</sub> +  $10^{-4}$  M MTP, (d) MS in 0.5 M H<sub>2</sub>SO<sub>4</sub> -  $10^{-4}$ M DTP, and (e) MS in 0.5 M H<sub>2</sub>SO<sub>4</sub> +  $10^{-4}$  M DEP, after 24 h exposure.



**Figure 12.** Computed quantum optimized structure parameters for MTP; (a) Ball and Stick modal, (b) Mulliken charges (c) HOMO frontier orbital energy distribution (d) LUMO frontier orbital energy distribution.





**Figure 13.** Computed quantum optimized structure parameters for DTP; (a) Ball and Stick modal (b) Mulliken charges (c) HOMO frontier orbital energy distribution (d) LUMO frontier orbital energy distribution.





**Figure 14.** Computed quantum optimized structure parameters for DEP; (a) Ball and Stick modal, (b) Mulliken charges (c) HOMO frontier orbital energy distribution (d) LUMO frontier orbital energy distribution.





**Figure 15.** Side and top views of the final adsorption of neutral molecules MTP (a), DTP (b) and DEP (c) on the Fe (110) surface in solution.



Figure 16. Side and top views of the final adsorption of DEP protonated on the Fe (110) surface in solution ( $H_2SO_4$ ).

**Table 1.** Corrosion parameters calculated by Weight Loss method of MS in  $0.5 \text{ M H}_2\text{SO}_4$  in the presence of inhibitors MTP, DTP and DEP.

Temp.	Conc.	Initial	Final	Weight	C <sub>R</sub>	IE (%)
<b>(K</b> )		Weight	Weight F <sub>w</sub>	Loss (g)	$(mgcm^{-2}h^{-1})$	
( <b>K</b> )	(111)	$\mathbf{I}_{\mathbf{w}}(\mathbf{g})$	(g)		(ingen n )	
				~		
			$\mathbf{H}_{2}$	SO <sub>4</sub>	<u>.                                    </u>	
298	0.5	12.6694	12.6573	י12 <sup>1</sup> .	2.01	
313	0.5	10.2678	10.2496	0.0191	3.18	
328	0.5	10.3072	10.2860	0.0206	3.43	
			M	ТР		
	4	<b>_</b>		r	1 1	
	10-4	12.5002	1. 4984	0.0018	0.30	85.12
298	10 <sup>-5</sup>	10.4789	.0.4748	0.0041	0.68	66.11
	10 <sup>-6</sup>	12.69 <sup>-</sup> U	12.6920	0.0050	0.83	58.67
	10 <sup>-4</sup>	11 35.73	11.3364	0.0029	0.48	84.81
313	10 <sup>-5</sup>	12.5061	12.5592	0.0069	1.15	63.87
	10 <sup>-6</sup>	11.6923	11.6840	0.0083	1.38	56.54
	10 <sup>-4</sup>	11.9770	11.9721	0.0049	0.81	76.21
328	10 <sup>-5</sup>	11.8921	11.8834	0.0087	1.45	57.76
	10 <sup>-6</sup>	10.8360	10.8259	0.0101	1.68	50.97
	DTP					
	10 <sup>-4</sup>	11.1844	11.1827	0.0017	0.28	86.18
298	10 <sup>-5</sup>	11.4465	11.4444	0.0021	0.34	82.93
	10 <sup>-6</sup>	11.2500	11.2468	0.0032	0.53	73.98

	10 <sup>-4</sup>	11.4466	11.4437	0.0029	0.48	83.70
313	10 <sup>-5</sup>	10.9762	10.9719	0.0043	0.71	75.84
	10 <sup>-6</sup>	10.9739	10.9682	0.0057	0.95	66.97
	10 <sup>-4</sup>	11.0367	11.0316	0.0051	0.85	74.37
328	10 <sup>-5</sup>	11.6817	11.6748	0.0069	1.15	65.33
	10 <sup>-6</sup>	11.2495	11.2404	0.0091	1.52	54.27
			D	EP		·
	10 <sup>-4</sup>	11.1476	11.1461	0.0015	0.25	89.49
298	10 <sup>-5</sup>	10.7927	10.7896	0.0021	0.52	78.17
	10 <sup>-6</sup>	11.5253	11.5198	ס.טֹירדע	0.92	61.27
	10 <sup>-4</sup>	11.5669	11.5650	L.0019	0.32	88.34
313	10 <sup>-5</sup>	11.8665	11.8612	0.0052	0.87	66.01
	10 <sup>-6</sup>	12.3321	17.5.`58	0.0063	1.05	58.82
	10 <sup>-4</sup>	10.7575	.7522	0.0053	0.88	77.06
328	10 <sup>-5</sup>	11.5198	11.5111	0.0087	1.45	62.38
	10 <sup>-6</sup>	10.7685	10.7575	0.011	1.83	52.38
<u> </u>			•			•

**Table 2.** Potentiodynam<sup>\*</sup>, Potarization derived Corrosion parameters of MS in 0.5 M  $H_2SO_4$  in the presence of MTF, DTP and DEP.

Temp. (K)	Conc. (M)	-E <sub>corr</sub> (mV)	b <sub>c</sub> (mV/dec)	b <sub>a</sub> (mV/dec)	I <sub>corr</sub> (μA/cm <sup>2</sup> )	IE (%)	θ
			H	I <sub>2</sub> SO <sub>4</sub>		·	
298	0.5	473	166.1	139.5	008805.00	-	-
313	0.5	475	189.3	168.8	014990.0	-	-
328	0.5	490	212.5	172.4	18230.0	-	-
MTP							

298	10-4	484	125.2	107.2	001207.10	86.29	0.862
	10-5	475	111.6	99.62	001618.32	81.62	0.816
	10-6	458	102.0	82.84	002505.41	71.54	0.715
	10-4	493	104.5	135.9	7312.25	51.21	0.5121
313	10-5	462	118.0	76.82	8648.50	42.30	0.4230
	10-6	475	178.0	174.5	11208.0	45.77	0.4577
	10 <sup>-4</sup>	501	104.5	128.7	9024.21	50.49	0.5049
328	10-5	481	168.7	179.8	11270.1	38.17	0.3817
	10-6	479	181.4	167.9	16670.2	08.55	00.085
	I		I	DTP	0	1	
	10-4	498	119.2	91.87	00986.10	88.80	0.888
298	10-5	492	87.68	84.8.)	01183.02	86.56	0.865
	10-6	483	79.92	81.20	02421.00	72.10	0.721
	10-4	493	104.5	135.9	04394.8	70.68	0.7068
313	10-5	462	119.0	37.8	06521.2	56.49	0.5649
	10-6	476	17.9.0	146.5	08128.0	45.77	0.4577
	10-4	502	104.2	128.1	08551.3	53.09	0.5309
328	10-5	473	162.7	179.8	10135.2	44.40	0.4440
	10-6	476	181.2	176.1	13880.0	23.86	0.2386
	·			DEP			
	10-4	<u>4</u> 93	110.2	096.5	00589.40	93.3	0.933
298	10-5	-`51	100.4	91.80	00724.90	91.7	0.917
	10-6	455	94.6	92.20	01001.20	88.6	0.886
	10-4	479	165.7	169.7	04212.0	71.90	0.719
313	10-5	473	167.1	178.8	06584.2	56.07	0.560
	10-6	467	175.6	155.5	07928.0	47.11	0.471
	10-4	502	104.2	128.1	06551.2	64.06	0.6406
328	10-5	473	169.7	179.8	07184.0	60.59	0.6059
	10-6	461	166.8	169.8	12630.0	30.71	0.3071

Compound	Concentration	$R_{ct}$ ( $\Omega$ cm <sup>2</sup> )	<i>f</i> <sub>max</sub>	$C_{dl}$ (µF cm <sup>-2</sup> )	IE (%)
	( <b>M</b> )				
$H_2SO_4$	0.5	4.937	2.03	15888	-
MTP	10 <sup>-4</sup>	46.82	17.9	190.00	89.45
	10-5	32.31	13.1	376.21	84.71
	10-6	24.42	7.06	923.61	79.78
DTP	10 <sup>-4</sup>	145.1	45.5	24.119	96.59
	10-5	111.9	3,71	38.048	95.98
	10-6	98.73	26.6	60.633	94.99
DEP	10 <sup>-4</sup>	262.5	83.6	7.2561	98.11
	10-5	268.1	74.7	10.214	97.63
	10-6	1 1.1	46.6	24.217	96.50

**Table 3.** Electrochemical Impedance derived Corrosion parameters of MS in  $0.5 \text{ M H}_2\text{SO}_4$  in the presence of various concentrations of MTP, DTP and DEP.

Table 4. Adsorption paramete. \* studied for MTP, DTP and DEP at different temperatures

Temperature	$K_{ads} < 10^4 (M^{-1})$	$\Delta G^{\circ}_{ads}$ (kJ mol <sup>-1</sup> )	$\Delta H^{\circ}_{ads}$ (kJ mol <sup>-1</sup> )	$\Delta S^{\circ}_{ads}(JK^{-1} \text{ mol}^{-1})$	
(K)	5				
MTP					
298	200.34	-45.89		-108.3	
313	50.14	-44.59	-78.18	-107.2	
328	11.15	-42.63	-70.10	-108.3	
		DTP			
298	333.2	-47.16		-53.04	
313	50.16	-44.59	<b>60.07</b>	-58.69	
328	33.37	-45.63	-62.97	-52.86	
DEP					
298	1000	-49.88		-47.09	

313	50.07	-44.59	-63.91	-61.72
328	100.6	-48.62		-46.62

**Table 5.** Activation thermodynamic parameters for MS in 0.5 M  $H_2SO_4$  in the presence of various concentrations of MTP, DTP and DEP

Compound	Concentration (M)	$E_{act}$ (kJ/mol)
H <sub>2</sub> SO <sub>4</sub>	0.5	21.27
	10 <sup>-4</sup>	37.71
MTP	10-5	12.82
	10-6	40.55
	10-4	44.34
DTP	10-5	33.35
	10-6	29.18
	10	39.90
DEP	10	35.62
	10-6	36.37

**Table 6.** Roughness data from AFM 1. Pasurements for MS surface in 0.5 M  $H_2SO_4$  without and with  $10^{-4}$  and  $10^{-6}$  M concentrations of MTP, DTP and DEP.

Compound	Conc.(M)	Average Area RMS (nm)
Plain MS	-	112.8
H <sub>2</sub> SO <sub>4</sub>	0.5	648.2
МТР	10 <sup>-4</sup>	184.3
	10 <sup>-6</sup>	412.7
DTP	10 <sup>-4</sup>	167.6
	10-6	385.2
DEP	10 <sup>-4</sup>	141.2
	10-6	317.1

Parameters/Compounds	MTP	DTP	DEP	Protonated
↓ ↓				DEP
Total energy (kcal mol <sup>-1</sup> )	-70019.1	-62639.4	-78482.6	-568175.437
E <sub>HOMO</sub> (eV)	-8.8377	-9.0483	-8.0545	-11.302
E <sub>LUMO</sub> (eV)	-0.7131	-0.7407	-0.51442	-4.167
$\Delta E (eV)$	8.1246	8.3076	7.54008	7.135
μ (Debye)	4.058	2.987	4.869	19.958

**Table 7.** Quantum chemical parameters of studied chalcones MTP, DTP and DEP using AM<sub>1</sub> semi-empirical method, Hyper Chem 8.0.

**Table 8.** Selected energy parameters in kJ/mol obtained from MD simulations for adsorption

 of the neutral molecules on Fe (110) surface.

Systems	<b>E</b> ateraction	E binding
Fe(110)/MTP	-553.459	653.459
Fe(110)/DTP	-645.736	645.736
Fe(110)/DEP	-700.871	700.871

#### **Declaration of competing interests**

 $\boxtimes$  The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

### **Highlights**

- Chalcone derivatives are reported as corrosion inhibitors.
- ♦ Chalcone derivatives were synthesized and characterized by NMR, MS and IR.
- ◆ Electrochemical, theoretical and surface morphological techniques were used.
- ✤ The results were supported by MD, SEM, AFM and QC Calculations.

















Figure 4







Figure 5







#### Figure 6









Figure 8









Figure 10







Figure 11





















