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# FULL LENTH ARTICLE

# Corrosion inhibition of aluminum in 1 M HCl by novel pyrimidine derivatives, EFM measurements, DFT calculations and MD simulation



# N.S. Abdelshafi<sup>a,\*</sup>, M.A. Sadik<sup>b</sup>, Madiha A. Shoeib<sup>c</sup>, Shimaa Abdel Halim<sup>a</sup>

<sup>a</sup> Chemistry Department, Faculty of Education, Ain Shams University, Roxy 11711, Cairo, Egypt

<sup>b</sup> October High Institute for Engineering and Technology, Giza, Egypt

<sup>c</sup> Corrosion Control & Surface Protection Department, Central Metallurgical Research and Development Institute, CMRDI, Cairo, Egypt

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# KEYWORDS

Corrosion inhibitor; Pyrimidine derivatives; Aluminum; EFM; DFT; MD modeling **Abstract** Four pyridine-pyrimidine derivatives, namely pyridine-2,6-diamine (PD), pyrimidine-2amine (PA), 6-amino-3,4-dihydropyrimidine-2(1H)-thione (ADT) and ethyl (R)-6-(4-chlorophe nyl)-2-mercapto-4-methyl-1,6-dihydropyrimidine-5-carboxylate (EMMD) are used as effective inhibitors for aluminum corrosion in 1 M HCl solution. The anti-corrosive potential of these heterocyclic compounds has been evaluated by electrochemical frequency modulation (EFM) method, The inhibition efficiency of these inhibitors was strongly associated to the concentration  $(10^{-7} 10^{-3}$ M) and the structure of the molecules; reached a maximum of 95.68% for EMMD at  $10^{-3}$ M owing to more anchoring functional groups. The effect of temperature on the corrosion behaviour was assessed at solution temperature range 298–323 K. The four inhibitors adsorbed according to the Langmuir's adsorption isotherm. Thermodynamic activation parameters for the dissolution process of aluminum in 1 M HCl and inhibited solutions were calculated and discussed. Surface analysis (SEM, EDX, and AFM) confirmed the formation of a protective layer adsorbed on the aluminum surface. In addition, theoretical studies by DFT and MD revealed the correlation between the molecular chemical structure of studied inhibitors and their inhibition efficiency. The adsorption mechanism is revealed by theoretical calculations.

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\* Corresponding author.

E-mail address: nashwasaad@edu.asu.edu.eg (N.S. Abdelshafi). Peer review under responsibility of King Saud University.



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# 1. Introduction

Aluminum and its alloys have excellent electrical and thermal conductivity and can be widely used in a variety of industries because of their advantages (Wang et al., 2016). The surface oxide coating on aluminum's surface is responsible for its corrosion resistance (Zhang and Hua, 2010). Exposing of aluminum to aggressive acidic media during acid pickling induces rapid dissolution of the amphoteric oxide coating which results in corrosion. As a result, numerous treatments and investigations were devoted to reduce aluminum corrosion to some degree (Ono and Habazaki, 2009). EFM is an intermodulation technique that uses a dual frequency potential perturbation to calculate the current density response at sums, disparities, and multiples of the input frequency, with the advantage of minimizing background noise distortion during calculation (Abdel-Rehim et al., 2006). EFM is a non-destructive and quick method with an internal self-check by two causality parameters for determining corrosion rate without using Tafel slopes (Xiong et al., 2021). This system used a limited signal ac method, similar to EIS, in which two ac voltages are summed and worked on an electrode,  $\pm 10 \text{ mV}$  to  $\pm 20 \text{ mV}$  around the E<sub>corr</sub>, is simultaneously applied to the corroding metal, and the alternating current density responses are determined at higher frequencies (known as harmonic and intermodulation frequencies) than the input frequencies (Abdel-Rehim et al., 2006). To serve as a consistency check for the result obtained, the experimental values of causality factors (CF-2 and CF-3) obtained during an EFM calculation are normally compared to certain mathematically-established theoretical values of 2 and3, respectively. The EFM technique has been shown to provide knowledge about corrosion processes such as localized pitting and crevice corrosion, as well as the forming of a passive coating on the corroding metal surface, in addition to calculating instantaneous corrosion intensity (i.e. uniform active corrosion) (Abdel-Azim et al., 2021). The corrosion current density, polarization resistance, Tafel constants, and causality factors are calculated using the current peaks obtained at the harmonic and intermodulation frequencies, giving EFM the advantage of calculating output current more clearly with limited interference from background signals (Shaban et al., 2021). A number of pyrimidine derivatives have been synthesized and their suitability for corrosion inhibition of a variety of metal samples in acidic medium has been investigated (Abdel-Azim et al., 2021; Arrousse et al., 2020; Rasheeda et al., 2018; Xu et al., 2018). The pyrimidine skeleton is found in a wide range of natural products, including nucleic acids, vitamins, enzymes, chlorophyll, hemoglobin, and hormones (Rasheeda et al., 2018). Because of the wide range of biological activities found for these compounds, pyrimidine derivatives have become environmentally friendly compounds. Pyrimidine molecule is a good corrosion inhibitor which can donate electrons to unoccupied orbital of metal surface and can also accept free electrons from the metal surface by using their anti-bonding orbital. So pyrimidine derivatives are likely to be excellent corrosion inhibitors at industrial applications due to their efficiency and their non-toxic nature (Rasheeda et al., 2018). Pyrimidine derivatives can inhibit corrosion by physisorption or chemisorption of the inhibitors to the metal surface. In the present work, the corrosion inhibition of aluminum in 1 M HCl solution was investigated by pyridine-pyrimidine derivatives (PD, PA, ADT and EMMD) using electrochemical frequency modulation (EFM) method at different concentrations and temperatures, Scanning electron microscope (SEM), Energy dispersive X-ray spectroscopy (EDX) and Atomic force microscope (AFM). In addition, density functional theory (DFT) and molecular dynamic simulation (MD) are used to calculate molecular properties are associated to inhibition efficiency (Quadri et al., 2021) using molecular modeling. Adsorption mechanism is investigated, and thermodynamic adsorption parameters of the inhibitors are determined. Finally, the molecular dynamics simulation confirms the results obtained by the DFT and the experimental data.

#### 2. Experimental details

#### 2.1. Materials

Structures of the investigated Pyridine-pyrimidine derivatives are shown in Fig. 1. Inhibitors ADT and EMMD were synthesized in the laboratory following a procedure described elsewhere (Sherif et al., 1993; Taylor and Cheng, 1960). (PD) (CAS No141-86–6) and (PA) (CAS No 109–12-6) are bought from (Sigma-Aldrich) and used without any pretreatments. The investigated pyridine-pyrimidine derivatives are dissolved in ethanol and then added to 1 M HCl solution at concentrations of  $(10^{-7}-10^{-3}M)$ . Solutions were prepared from bidistilled water of resistivity 13 M $\Omega$  before each set of experiments.

### 2.2. Specimen and solution

Aluminum cylindrical rod of chemical composition (wt%), Al (94.62%), Mg (2.9%), Zn (2%) and Cu (0.48%), were mounted in Teflon. An epoxy resin was used to fill the space between Teflon and aluminum electrode. The circular cross sectional area of the aluminum rod was ( $0.28 \text{ cm}^2$ ) which exposed to the corrosive medium and used in electrochemical measurements. The exposed surface was mechanically abraded and polished with emery papers up to 4/0 grit size. These polished samples cleaned with acetone, washed with double-distilled water and finally dried at room temperature. Then these aluminum samples were used as working electrode (WE). The aggressive electrolyte solution 1 Mwas made from hydrochloric acid (37%) and used for all studies.

# 2.3. Electrochemical measurements

Electrochemical frequency modulation, EFM, was carried out using two frequencies 2 Hz and 5 Hz. The base frequency was 1 Hz, so the waveform repeats after 1 s. The higher frequency must be at least two times the lower one. The higher frequency must also be sufficiently slow that the charging of the double layer does not contribute to the current response. Often, 10 Hz is a reasonable limit. Electrochemical frequency modulation, EFM, was performed by a three electrode cell, in addition to the (WE), platinum mesh was used as a counter electrode (CE) and the reference electrode (RE) was a saturated calomel electrode (SCE). The counter electrode was separated from the working electrode compartment by fritted glass. The reference electrode was connected to a Lugging capillary to minimize IR drop. The working electrode was dipped in the test solution for 60 min to establish a steady state open circuit potential (E<sub>ocp</sub>) for 1500 s in 1 M HCl solution without and with the inhibitors. Each experiment was performed 3 times and mean values of the corrosion current density were calculated. Measurements were performed using Gamry Instrument Potentiostat/Galvanostat/ZRA. This includes a Gamry Framework system based on the ESA400, Gamry applications that include EFM 140 for electrochemical frequency modulation measurements along with a computer for collecting data. Echem Analyst 6.33 software was used for plotting, graphing and fitting data.

NH<sub>2</sub>

pyridine-2,6-diamine (PD)

H<sub>2</sub>N





6-amino-3,4-dihydropyrimidine-2(1H)-thione (ADT)



ethyl (R)-6-(4-chlorophenyl)-2-mercapto-4-methyl-1,6-dihydropyrimidine-5-carboxylate (EMMD)

Fig. 1 Chemical structures of the studied compound.

# 2.4. Surface morphology

The adsorption of inhibitors was confirmed by surface characterization of Al samples of size  $2.00 \times 2.50 \times 0.04$  cm before and after corrosion inhibition using Scanning electron microscope (SEM), Energy dispersive X-ray spectroscopy (EDX) and Atomic force microscope (AFM) by immersing in 1 M HCl in the absence and presence of investigated pyridine-pyrimidine inhibitors for 24 h at 298 k.The Al samples were taken out from the test solution, washed with double-distilled water, cleaned in ultrasonic bath containing acetone for 5 min and dried at room temperature. The samples investigated using an Inspect S50 FEI scanning electron microscope with an accelerating voltage of 20 kV at  $1000 \times$ magnification. The surface composition was also recorded using EDX detector model coupled with SEM. Finally, AFM analysis which is used for 3D structure of the metal specimen was evaluated using Flex axiom Nanosurf C3000 controller.

### 2.5. Computational details

The calculations in this study were performed by the Gaussian 09 program package using density functional theory (DFT) by

Becke's three parameters function -Lee-Yang-Parr (B3LYP) with a triple valence baseline group 6-311 + + G (d, p). The Gaussian View 5.0.9 was used to visualize the structural feature as well as the simulation of the available vibrational frequencies. All calculations which were performed on a PC with processor core i7. DFT is applied to determine the theoretical parameters such as the energies of highest occupied and lowest unoccupied molecular orbital (E<sub>HOMO</sub> and E<sub>LUMO</sub>), energy gap ( $\Delta E$ ), dipole moment ( $\mu$ ) (Khaled, 2006; Khaled et al., 2011), ionization energy (I), electron affinity (A), absolute electronegativity ( $\chi$ ), absolute hardness ( $\eta$ ), absolute softness (S), absolute electrophilicity parameter ( $\omega$ ),  $\Delta E_{Back-donation}$  the back donation and the number of transferred electrons ( $\Delta N$ ) (El-Deeb et al., 2018).

The energies of HOMO and LUMO orbitals of the inhibitor molecule are associated to the ionization potential (I) and the electron affinity (A) respectively, by the following relationships (Khaled and Abdelshafi, 2013):

$$I = -E_{HOMO} \tag{1}$$

$$A = -E_{LUMO} \tag{2}$$

The absolute electronegativity ( $\chi$ ) and the absolute hardness ( $\eta$ ) are calculated according to the relations (3 and 4) (Khaled and Abdelshafi, 2013):

$$\chi = \frac{I+A}{2} \tag{3}$$

$$\eta = \frac{I - A}{2} \tag{4}$$

whereas the inverse of the hardness called softness (S) is calculated according to the relation (5) (Khaled, 2009).

$$S = \frac{1}{\eta} \tag{5}$$

The fraction of electron transferred ( $\Delta N$ ) was also determined by employing the equation below:

$$\Delta N = \frac{(\chi_{Al} - \chi_{inh})}{2(\eta_{Al} + \eta_{inh})} \tag{6}$$

where  $\chi_{Al} = 3.23 \text{ eV mol}^{-1}$  and  $\chi_{inh}$  signify the absolute electronegativity of Al and inhibitor molecule, respectively,  $\eta_{Al} = 0 \text{ eV mol}^{-1}$  and  $\eta_{inh}$  signify the absolute hardness of Al and the inhibitor molecule, respectively.

The absolute electrophilicity parameter $\omega$  is given by Eq. (7) (Parr et al., 1999) and  $\Delta E_{Back-donation}$  by Eq. (8) :

$$\omega = \frac{\mu^2}{2\eta} \tag{7}$$

$$\Delta E_{Back-donation} = -\frac{\eta}{4} \tag{8}$$

The first derivative of the electronic density  $p(\vec{r})$  with respect to the number of electrons N, in a constant external potential  $v(\vec{r})$  gives the Fukui function ( $f_k$ ) expressed as follows Eq. (9):

$$f_k = \left(\frac{\partial p(\vec{r})}{\partial N}\right)_{v(\vec{r})} \tag{9}$$

#### 2.6. Molecular dynamics simulation

The molecular dynamics module in Materials Studio 7.0 software from BIOVIA has been used to build corrosion system that composed of aluminum oxide substrate and pyridinepyrimidine adsorbate. DMol<sup>3</sup> codes of Materials Studio was used for geometry optimization of single inhibitor molecules (PD, PA, ADT and EMMD). The most stable aluminum oxide surfaces Al<sub>2</sub>O<sub>3</sub> (111) was selected for this simulation. The molecular simulation task was carried with a slab thickness of 1 nm, a supercell of  $(2.47 \times 4.15 \times 1.70 \text{ nm})$  and a vacuum of 3 nm. The force field that used in the simulations was COM-PASS force field.

# 3. Results and discussions

#### 3.1. Effect of concentration

Fig. 2 displays the EFM spectra of aluminum in 1 M HCl in the absence and presence of  $10^{-3}$ M and  $10^{-7}$ M, as example, of pyridine-pyrimidine derivatives at 298K .Each spectrum is a current response as a function of frequency and the larger peaks have been used to calculate the corrosion current density (i<sub>corr</sub>). Table 1 shows EFM parameters which are calculated using the Eqs. 10 - 14, such as corrosion current density i<sub>corr</sub>, corrosion rate (CR)(Tan et al., 2021a), Tafel constants ( $\beta_a$ ,  $\beta_c$ ), inhibition efficiency  $\eta_{EFM}$ %, and causality factors (CF-2, CF-3) as a function of inhibitor concentrations in the absence and presence of the PD, PA, ADT and EMMD inhibitors (Danaee and Nikparsa, 2020).

$$i_{corr} = \frac{I_{\omega_1,\omega_2}^2}{2\sqrt{8I_{\omega_1,\omega_2}I_{2\omega_2\pm\omega_1} - 3I_{\omega_2\pm\omega_1}^2}}$$
(10)

$$\beta_a = \frac{I_{\omega_1,\omega_2} U_0}{I_{\omega_2 \pm \omega_1} + \sqrt{8I_{\omega_1,\omega_2}I_{2\omega_2 \pm \omega_1} - 3I_{\omega_2 \pm \omega_1}^2}}$$
(11)

$$\beta_{C} = \frac{I_{\omega_{1},\omega_{2}}U_{0}}{-I_{\omega_{2}\pm\omega_{1}} + \sqrt{8I_{\omega_{1},\omega_{2}}I_{2\omega_{2}\pm\omega_{1}} - 3I_{\omega_{2}\pm\omega_{1}}^{2}}}$$
(12)

$$CR = \frac{0.13 \times i_{corr} \times E_w}{\rho} \tag{13}$$

where I is the instantaneous current density at the working electrode at frequency  $\omega$ ,  $U_0$  is amplitude of the sine wave distortion, i<sub>corr</sub>iscorrosion current,  $E_w$  and  $\rho$  are the equivalent weight and density of the corroding metal respectively.

The  $\eta_{EFM}$ % was calculated by the following Eq. (Fouda et al., 2020).

$$\eta_{\rm EFM} \% = \left(\frac{i_{corr}^o - i_{corr}}{i_{corr}^o}\right) \times 100 \tag{14}$$

where  $i_{corr}$  and  $i_{corr}^{o}$  are corrosion current densities with and without inhibitor, respectively. It is obvious from data in Table 1 the corrosion current densities values icorr decrease while efficiency of inhibition values  $\eta_{\text{EFM}}$ %, increase by increasing the concentration of investigated compounds, compared to the existence of 1 M HCl solution alone for Al. indicating the adsorption of the inhibitors on the metal surface (Shalabi et al., 2015). The inhibition efficiency obtained from this technique is as follows: (PD < PA < ADT < EMMD) The causality factors values (CF-2 and CF-3) in Table 1 are very close to theoretical values of 2.0 and 3.0 respectively. Causality factors serve as an internal check on the validity of Tafel slopes and corrosion current densities, suggesting that the obtained results are of good values. Table 1 shows very slight change in the anodic ( $\beta a$ ) and cathodic ( $\beta c$ ) Tafel slopes as revealing that the mechanism of anodic (Al dissolution) and cathodic reaction is not influenced by incremental addition of the pyridine-pyrimidine derivatives.

# 3.2. Effect of temperature

Electrochemical frequency modulation technique is employed to study the effect of temperature on the corrosion behavior of Al in 1 M HCl solution in the absence and presence of  $10^{-3}$ M of the Pyridine-pyrimidine derivatives at the temperature range 298–323 K. Corresponding data are given in Table 2 shows, in the studied temperature range 298–323 K, the corrosion rate of Al increases with increasing temperature both in uninhibited and inhibited solutions. Fig. 3 depicts an intermodulation spectrums for aluminum in 1 M HCl without and with  $10^{-3}$ M EMMD at 303 and 323 K as an example. In the presence of  $10^{-3}$ M Pyridine-pyrimidine derivatives corrosion rate values are always much lower than those without



**Fig. 2** Intermodulation spectrums for aluminum in 1 M HCl without and with  $10^{-3}$  M and  $10^{-7}$  M of PD, PA, ADT and EMMD at 298 K.

inhibitor and increased by increasing the temperature from 298 to 323 K, consequently  $\eta_{EFM}$ % decreased by increasing temperature Fig. 4 indicating that the adsorption of inhibitors species on aluminum surface at these conditions is not merely physical or chemical adsorption but obeying a comprehensive adsorption (physical and chemical adsorption)(Fouda et al., 2016).

Thermodynamic activation parameters like apparent activation energy  $(E_a^*)$ , enthalpy of activation  $(\Delta H^*)$  and entropy of activation  $(\Delta S^*)$  give important information about corrosion inhibition mechanism (Lin et al., 2021). The corrosion process's activation energy  $(E_a^*)$ , was calculated using the Arrhenius equation:

$$\log Rate = -\frac{E_a^*}{2.303RT} + \log A \tag{15}$$

where A is the pre-exponential factor. Fig. 5 depicts Arrhenius plot of  $\log(Rate)$  v/s (1000/T) giving a linear plots with slope

equal to  $(-E_a^*/2.303R)$  Activation energy  $(E_a^*)$ , values determined from the slopes of these linear plots and shown in Table 3. Activation energy values for 1 M HCl solution (10.48 KJmol<sup>-1</sup>) was found to be less when compared to the inhibited solution (28.58, 36.79, 38.81 and 46.85 KJmol<sup>-1</sup>) for (PD, PA, ADT and EMMD) respectively which indicate that, the corrosion development has becomes hard due to demonstrating the process involves establishing of the energy barrier in presence of studied inhibitors (Oguzie, 2006). Order of the  $\eta_{EFM}$ %can also be validated by the values of  $E_a^*$  for these studied inhibitors molecules where, for  $10^{-3}$ M at 298 K, the highest value of  $E_a^*$  for EMMD (46.85 KJmol<sup>-1</sup>) shows that EMMD is the most effective inhibitor (95.68%), while the lowest value of  $E_a^*$  for PD (28.58 KJ/mol) indicates that PD is the least effective corrosion inhibitor (86.72%).

Table 3 summarizes the values of enthalpy and entropy of activation ( $\Delta H^*$ ) and ( $\Delta S^*$ ) respectively of the corrosion pro-

Inhibitor	Conc/M	$i^a_{corr}/\mu A~cm^{-2}$	$\beta_a^b/m V dec^{-1}$	$-\beta_c^c/mVdec^{-1}$	Corrosion Rate <sup>d</sup> /mpy	CF-2 <sup>e</sup>	CF-3 <sup>f</sup>	$\eta_{EFM}\%$	θ
Blank	0.00	951.9 ± 2.52	79.16 ± 2.56	$133.40 \pm 4.02$	$1460 \pm 3.29$	$1.87 \pm 0.39$	$2.47 \pm 1.70$		_
PD	$10^{-7}$	$419.4 \pm 3.11$	$74.22 \pm 3.70$	$144.10 \pm 7.14$	$643.10 \pm 4.11$	$1.85 \pm 3.72$	$2.26~\pm~3.57$	55.94	0.56
	$10^{-6}$	$351.4 \pm 7.95$	$72.36 \pm 6.45$	$128.70 \pm 6.21$	$538.90 \pm 6.24$	$1.98~\pm~2.26$	$2.00~\pm~5.67$	63.08	0.63
	$10^{-5}$	$272.4 \pm 6.21$	$71.51 \pm 4.50$	$145.70 \pm 6.80$	$417.60 \pm 6.39$	$1.85 \pm 2.82$	$1.88~\pm~5.16$	71.38	0.71
	$10^{-4}$	$167.6 \pm 6.53$	$77.97 \pm 2.67$	$153.60 \pm 7.08$	$257.10 \pm 6.42$	$1.77  \pm  0.75$	$1.95~\pm~3.39$	82.39	0.82
	$10^{-3}$	$126.4 \pm 5.50$	$63.07 \pm 6.80$	$125.00 \pm 5.02$	$193.90 \pm 6.23$	$1.89~\pm~1.62$	$2.06~\pm~4.49$	86.72	0.87
PA	$10^{-7}$	$369.3 \pm 2.05$	$78.62 \pm 6.17$	$185.30 \pm 8.90$	$566.20 \pm 4.28$	$1.82~\pm~0.86$	$2.07~\pm~2.59$	61.20	0.61
	$10^{-6}$	$286.5 \pm 5.22$	$62.70 \pm 5.24$	$126.60 \pm 7.46$	$439.30 \pm 6.03$	$1.89~\pm~0.42$	$2.42~\pm~1.64$	69.90	0.70
	$10^{-5}$	$211.6 \pm 5.70$	$68.70 \pm 3.71$	$144.40\pm6.65$	$324.50 \pm 6.69$	$1.85~\pm~5.23$	$2.28~\pm~5.63$	77.77	0.78
	$10^{-4}$	$112.7 \pm 8.17$	$57.68 \pm 8.01$	$111.10 \pm 5.77$	$172.90 \pm 8.48$	$1.79~\pm~1.95$	$2.12~\pm~2.01$	88.16	0.88
	$10^{-3}$	$80.14 \pm 6.87$	$69.17 \pm 5.94$	$138.20 \pm 5.08$	$122.90 \pm 7.15$	$2.11 \pm 2.72$	$2.39~\pm~2.32$	91.58	0.92
ADT	$10^{-7}$	$323.1 \pm 6.34$	$68.13 \pm 8.43$	$113.40 \pm 6.57$	$495.4 \pm 8.39$	$1.86~\pm~1.24$	$2.19~\pm~3.18$	66.06	0.66
	$10^{-6}$	$217.5 \pm 6.65$	$65.62 \pm 5.63$	$137.90 \pm 5.53$	$333.4 \pm 6.59$	$1.80~\pm~1.08$	$2.87~\pm~1.30$	77.15	0.77
	$10^{-5}$	$134.8~\pm~6.38$	$54.51 \pm 6.04$	$99.79 \pm 6.53$	$206.7 \pm 6.88$	$1.84~\pm~0.97$	$2.83~\pm~0.94$	85.84	0.86
	$10^{-4}$	$85.07 \pm 6.60$	$63.88 \pm 5.49$	$118.90\pm0.75$	$130.4 \pm 7.16$	$1.74~\pm~0.62$	$2.21~\pm~2.03$	91.06	0.91
	$10^{-3}$	$41.21 \pm 4.97$	$59.56 \pm 7.12$	$92.58 \pm 6.19$	$63.19 \pm 6.29$	$1.73~\pm~3.32$	$2.07~\pm~3.01$	95.67	0.96
EMMD	$10^{-7}$	$245.6 \pm 5.43$	$69.04 \pm 8.73$	$138.80\ \pm\ 4.81$	$376.6 \pm 5.03$	$1.86~\pm~3.48$	$2.43~\pm~2.74$	74.20	0.74
	$10^{-6}$	$185.3 \pm 4.26$	$64.46 \pm 7.95$	$137.30 \pm 6.56$	$284.1 \pm 5.87$	$1.91 \pm 1.72$	$2.71~\pm~2.48$	80.53	0.81
	$10^{-5}$	$118.6 \pm 4.27$	$69.38 \pm 4.78$	$146.10 \pm 8.24$	$181.8 \pm 3.14$	$1.87~\pm~0.92$	$2.40~\pm~1.93$	87.54	0.88
	$10^{-4}$	$61~\pm~6.76$	$89.19 \pm 7.41$	$167.00 \pm 4.87$	$93.53 \pm 5.39$	$1.99~\pm~2.92$	$1.19~\pm~6.34$	93.59	0.94
	$10^{-3}$	$41.12 \pm 3.83$	$56.72 \pm 5.79$	$94.28~\pm~8.01$	$63.05 \pm 5.83$	$1.69~\pm~1.16$	$1.88~\pm~2.36$	95.68	0.96

 Table 1
 Electrochemical frequency modulation parameters for aluminum in 1 M HCl in the absence and presence of different concentrations of pyridine-pyrimidine derivatives at 298 K.

<sup>a</sup> The standard deviation range for i<sub>corr</sub> [0.83–3.29].

 $^{\rm b}$  The standard deviation range for  $\beta a$  [1.03–3.51].

<sup>c</sup> The standard deviation range for  $\beta c [0.30-3.58]$ .

<sup>d</sup> The standard deviation range for CR [1.32-3.41].

<sup>e</sup> The standard deviation range for CF-2 [0.47-2.10].

<sup>f</sup> The standard deviation range for CF-3 [0.38–2.55].

cess which calculated using the transition state theory (Fouda et al., 2020). According to Eq. (16) where h is the Plank's constant  $N_A$  is the Avogadro's number. The calculated thermodynamic parameters are tabulated in Table 3.

$$\log \frac{Rate}{T} = \log \frac{R}{N_A h} + \frac{\Delta S^*}{2.303R} - \frac{\Delta H^*}{2.303RT}$$
(16)

The transition plots of  $\log(Rate/T)$  v/s (1000/T) for Al in 1 M HCl at 10<sup>-3</sup>M of inhibitors PD, PA, ADT and EMMD, give straight lines as shown from Fig. 6 with slope of  $(-\Delta H^*/2.303R)$ and an intercept of  $(log R/N_A h + \Delta S^*/2.303 R)$  The positive and increased values of  $\Delta H^*$  for corrosion of Al in the presence of inhibitors reflect the endothermic nature of Al dissolution process and also indicate suggesting that the dissolution of Al is slow in the presence of inhibitors. On the other hand, the values of  $\Delta S^*$  are more positive confirming higher protection behavior of Al after adding of inhibitors (Fouda et al., 2017a). To gain a better understanding of the adsorption mechanism, the heat of adsorption  $(Q_{ads})$  was calculated from the kinetic thermodynamic model by the following equation.

$$\log\left(\frac{\theta}{1-\theta}\right) = \log A + \log C - \left(\frac{Q_{ads}}{2.303RT}\right) \tag{17}$$

where A is a constant, C is the inhibitor concentration,  $\theta$  is the occupied and  $(1 - \theta)$  is the vacant site not occupied by the inhibitor. Fig. 7 shows the plot of  $log(\theta/1 - \theta)$  as a function of 1/T for the PD, PA, ADT and EMMD. The values of heat of

adsorption were evaluated from the slope of the linear plots and are listed in Table 3. The values of  $Q_{ads}$  are negative for all the studied inhibitors and where inhibition efficiencies decrease with increase in temperature, this indicates to the presence of physical-chemical adsorption of Pyridinepyrimidine derivatives on Al surface (Umoren et al., 2014). Finally the trend in  $(E_a^*)$ ,  $(\Delta H^*)$ ,  $(\Delta S^*)$  and  $(Q_{ads})$  consistent with the order of the  $\eta_{EFM}$ % (PD < PA < ADT < EMMD) demonstrating that EMMD exhibited the highest inhibition performance due to the presence of heteroatoms O, S atoms, with N atom.

# 3.3. Adsorption isotherm

The adsorption process of Pyridine-pyrimidine derivatives on Al surface was studied using various isotherms, El Awady, Flory-Huggins and Langmuir adsorption isotherms. Values of the degree of surface coverage  $\theta$  from EFM within the temperature range 298–323 K were used to determine which isotherm best described the adsorption process. The data were tested graphically by fitting to the above listed adsorption isotherms, and the correlation coefficient ( $R^2$ ) was used to determine the best-fit isotherm. A very good fit is observed with a regression coefficient ( $R^2 = 1$ ) for the Langmuir adsorption isotherm (Fig. 8), which confirms the validity of this adsorption of different concentrations of Pyridine-pyrimidine derivatives inhibitors on Al surface in 1 M HCl. The Langmuir adsorption isotherm is based on the view that every adsorption

**Table 2** Electrochemical frequency modulation parameters for aluminum in 1 M HCl in the absence and presence of  $10^{-3}$ M of pyridine-pyrimidine derivatives at different temperatures.

Inhibitor	Temp./K	$i^a_{corr}/\mu A~cm^{-2}$	$\beta_a^b/m V dec^{-1}$	$-\beta_c^c/m \mathrm{Vdec}^{-1}$	Corrosion Rate <sup>d</sup> /mpy	CF-2 <sup>e</sup>	CF-3 <sup>f</sup>	$\eta_{EFM}\%$
Blank	303	999 ± 6.15	$28.44 \pm 5.28$	$45.18 \pm 6.72$	$1532 \pm 6.43$	$1.59 \pm 1.83$	$1.24 \pm 2.41$	
	308	$1098 \pm 7.68$	$35.49 \pm 5.68$	$40.69 \pm 7.71$	$1684 \pm 7.05$	$1.76 \pm 1.10$	$1.62~\pm~1.98$	
	313	$1111 \pm 8.14$	$40.77 \pm 7.54$	$50.38 \pm 6.69$	$1703 \pm 7.77$	$1.93 \pm 2.22$	$1.36 \pm 2.21$	
	318	$1249~\pm~3.88$	$35.39 \pm 5.75$	$47.43 \pm 6.08$	$1915 \pm 5.30$	$1.17 \pm 2.63$	$1.23 \pm 1.77$	
	323	$1315 \pm 5.87$	$39.54 \pm 4.68$	$65.57 \pm 7.04$	$2016 \pm 5.25$	$2.25~\pm~3.48$	$1.10~\pm~2.03$	
PD	303	$169.5 \pm 8.17$	$63.08 \pm 5.73$	$124.2 \pm 7.94$	$260 \pm 7.41$	$1.89\pm0.39$	$1.85 \pm 1.58$	83.04
	308	$203.8 \pm 5.48$	$81.43 \pm 5.61$	$176.5 \pm 6.71$	$312.6 \pm 6.77$	$1.93 \pm 1.62$	$1.79 \pm 0.26$	81.44
	313	$239.5 \pm 6.79$	$67.52 \pm 3.35$	$131.7 \pm 5.21$	$367.3 \pm 5.35$	$1.89~\pm~1.96$	$2.22 \pm 2.26$	78.44
	318	$268.2 \pm 7.43$	$68.86 \pm 3.88$	$156.3 \pm 4.65$	$411.2 \pm 6.84$	$1.94 \pm 2.76$	$1.97 \pm 0.70$	78.53
	323	$323.5 \pm 7.51$	$74.74 \pm 7.12$	$142.6 \pm 5.91$	$496 \pm 8.69$	$1.90 \pm 1.34$	$2.25 \pm 1.15$	75.40
PA	303	$96.96 \pm 6.45$	$57.95 \pm 6.08$	$109.5 \pm 7.48$	$148.7 \pm 7.44$	$1.87 \pm 2.23$	$1.92 \pm 1.23$	90.30
	308	$157~\pm~4.03$	$61.81 \pm 5.42$	$107 \pm 7.65$	$240.8 \pm 5.44$	$1.81 \pm 1.08$	$2.04~\pm~0.76$	85.70
	313	$192.9 \pm 7.86$	$65.18 \pm 6.63$	$143.3 \pm 6.54$	$295.8 \pm 7.46$	$1.88~\pm~0.52$	$2.35\pm0.83$	82.64
	318	$210.5 \pm 5.48$	$65.63 \pm 7.63$	$128.8 \pm 5.95$	$322.8 \pm 6.16$	$1.85 \pm 1.67$	$2.37 \pm 1.85$	83.15
	323	$239.5 \pm 7.39$	$67.52 \pm 5.68$	$131.7 \pm 5.62$	$367.3 \pm 6.62$	$1.89 \pm 2.14$	$2.22 \pm 1.74$	81.79
ADT	303	$64.13 \pm 6.69$	$73.83 \pm 4.19$	$127.6 \pm 5.37$	$98.33 \pm 6.76$	$1.73 \pm 1.84$	$1.86 \pm 2.11$	93.58
	308	$89.13 \pm 7.03$	$60.55 \pm 6.27$	$115.8 \pm 6.38$	$136.7 \pm 6.67$	$1.82 \pm 0.57$	$2.76 \pm 1.15$	91.88
	313	$130.5 \pm 4.65$	$61.72 \pm 6.01$	$115.1 \pm 7.13$	$200.1 \pm 4.03$	$1.80\pm0.49$	$2.23~\pm~0.97$	88.25
	318	$149.3 \pm 4.92$	$72.68 \pm 5.62$	$170.7 \pm 5.82$	$229 \pm 5.42$	$1.85 \pm 0.53$	$2.46 \pm 1.13$	88.05
	323	$176.9 \pm 4.92$	$63.46 \pm 7.60$	$130.3 \pm 5.90$	$271.2 \pm 4.21$	$1.82 \pm 3.24$	$2.31 \pm 1.54$	86.55
EMMD	303	$59.52 \pm 6.88$	$56.49 \pm 6.72$	$94.15 \pm 7.47$	$91.26 \pm 6.03$	$1.83 \pm 2.02$	$2.08 \pm 2.26$	94.04
	308	$78.98 \pm 8.45$	$85.47 \pm 6.19$	$171 \pm 5.78$	$121.1 \pm 8.67$	$1.61 \pm 1.98$	$1.69 \pm 2.92$	92.81
	313	$95.81 \pm 4.71$	$67.41 \pm 5.66$	$146.8 \pm 6.79$	$146.9 \pm 5.88$	$1.87 \pm 0.86$	$2.96 \pm 4.13$	91.38
	318	$125.3 \pm 5.73$	$69.43 \pm 5.85$	$151.7 \pm 5.89$	$192.1 \pm 6.31$	$1.92~\pm~5.08$	$1.85 \pm 2.09$	89.97
	323	$137.3 \pm 4.65$	$66.67 \pm 5.18$	$133.8 \pm 5.40$	$210.6 \pm 5.81$	$1.89\pm0.88$	$2.55 \pm 2.61$	89.56

a The standard deviation range for icorr [1.56-3.40]

b The standard deviation range for  $\beta a$  [1.35–3.06].

c The standard deviation range for  $\beta c$  [1.87–3.20].

d The standard deviation range for CR [1.62-3.50].

e The standard deviation range for CF-2 [0.20-2.04].

f The standard deviation range for CF-3 [0.11-1.66].

f The standard deviation range for IE% [0.15-0.33%].

site is identical and energetically equivalent (Fouda et al., 2017a).

Langmuir isotherm 
$$C/\theta = 1/K_{ads} + C$$
 (18)

El – Awady isotherm  $Log[\theta/(1-\theta)]$ 

$$= LogK + YLogC \tag{19}$$

Flory – Huggins isotherm  $Log[\theta/C]$ 

$$= Log K_{ads} + x Log(1 - \theta) \tag{20}$$

Surface coverage ( $\theta$ ) values will be proportional to inhibitor efficiency and it can be calculated by the following equation (Tan et al., 2021b).

$$\theta = \% IE/100 \tag{21}$$

Adsorption parameters derived from Langmuir adsorption isotherms illustrated in Table 4. The high values of  $K_{ads}$  confirm a strong adsorption of the inhibitors on Al surface in 1 M HCl. This can be related to the existence of heteroatoms, such as N, O and S, and  $\pi$ -electrons in the inhibitor molecules (Ramananda Singh et al., 2019) and the adsorption of the EMMD inhibitor on Al surface is stronger than that of PD, PA and ADT. The calculated values of  $K_{ads}$  was used to evaluate  $\Delta G_{ads}^o$  according to the following equation (Tan et al., 2020).

$$\Delta G_{ads}^{o} = -RTln(55.5K_{ads}) \tag{22}$$

where 55.5 refers to the concentration of water expressed in M, R is the universal gas constant,  $\Delta G_{ads}^{\circ}$  is the standard free energy of adsorption and T is the absolute temperature. Generally, the values of  $\Delta G_{ads}^{\circ}$  up to -20 KJ/mol indicates physical adsorption, while those more negative than -40 KJ/molindicates chemisorption (Xu et al., 2018). Table 4 displays  $\Delta G_{ads}^{\circ}$ values of adsorption and showed that the adsorption of Pyridine-pyrimidine derivatives on Al surface is spontaneous and adsorption mechanism is a comprehensive mainly physical adsorption (Fouda et al., 2016). This is also supported by the EFM results where the inhibition efficiency of the investigated inhibitors decreases at higher temperature. The trend of inhibition efficiency with temperature and High values of K<sub>ads</sub> confirmed that PD < PA < ADT < EMMD.

The thermodynamic parameters  $\Delta H_{ads}$  and  $\Delta S_{ads}$  for the inhibitors adsorption were determined from the slopes and intercepts of logK vs. 1/T plots, Fig. 9, for all samples according to the following Van't Hoff linear equation (Fouda et al., 2016).



Fig. 3 Intermodulation spectrums for aluminum in 1 M HCl without and with  $10^{-3}$  M EMMD at 303 and 323 K.

$$logK = -\frac{\Delta H_{ads}}{2.303RT} + \frac{\Delta S_{ads}}{2.303R}$$
(23)

where  $\Delta H_{ads}$  and  $\Delta S_{ads}$  are the heat of adsorption and the standard entropy of adsorption respectively, T is the absolute temperature and R is the universal gas constant. Generally, an exothermic adsorption process  $\Delta H_{ads}^0 < 0$  is attributed to either



Fig. 5 Arrhenius plots of the log C.R versus 1000/T (K)-1 for aluminum in 1 M HCl in absence and presence of  $10^{-3}$  M PD, PA, ADT and EMMD.

Table 3 Kinetic and thermodynamic parameters for aluminum dissolution in 1 M HCl without and with  $10^{-3}$ M of pyridine-pyrimidine derivatives.

Inhibitor	$E_a^*(\mathrm{KJ/mol})$	$\mathbf{Q}_{ads}(\mathbf{KJ}/\mathbf{mol})$	$\Delta H^*(\mathrm{KJ/mol})$	$\Delta S^*(J/mol \ K)$
Blank	10.48		13.04	-36.57
PD	28.58	-22.25	31.33	-0.43
PA	36.79	-30.20	41.54	19.60
ADT	38.81	-30.49	45.12	31.27
EMMD	46.85	-39.67	49.58	41.30

chemisorption or physisorption or mixture of both processes, while endothermic process  $\Delta H_{ads} > 0$  is due to chemisorption (Fouda et al., 2016). The enthalpies values up to 41.9 KJmol<sup>-1</sup> are related to physisorption, while those around 100 KJmol<sup>-1</sup> or higher are attributed to chemisorption. In this work, the negative values of  $\Delta H_{ads}^{\circ}$ , displayed in Table 4, indicates that the adsorption process of inhibitor molecules is a mixture of both processes and that is in agreement with results obtained by activation parameter  $E_a^*$ . The values of  $\Delta S_{ads}^{\circ}$  are



Fig. 4 Inhibition efficiency and temperature for aluminum in 1 M HCl with 10<sup>-3</sup> M of PD, PA, ADT and EMMD.



**Fig. 6** Transition-state plots of the log C.R/T versus 1000/T (K)-1 for aluminum in 1 M HCl in absence and presence of  $10^{-3}$ M PD, PA, ADT and EMMD.



Fig. 7 Plot of  $\log(\theta/1 - \theta)$  against 1000/T (K)-1 for aluminum in 1 M HCl in absence and presence of  $10^{-3}$  M PD, PA, ADT and EMMD.

large and negative showed that on going from reactants to the metal/solution interface the disordering decreases, that is the main reason responsible for inhibitor adsorption on aluminum surface and that is accompanied with exothermic adsorption process (Fouda et al., 2016).

# 3.4. Quantum chemical studies using density functional theory (DFT)

# 3.4.1. Calculation of the main quantum parameters

The optimized geometries of the compounds are obtained using the B3LYB/6–311 + +G (p,d) level and are presented in Fig. 10. In this study, dihedral angles analysis was applied to determine the flatness of the studied geometrical structures. The analysis showed that; the most stable geometry of the studied compounds is planar structures which are favored in the inhibition reaction (Khaled and El-Maghraby, 2014). The frontier molecular orbital energy of the highest occupied molecular orbital and the lowest unoccupied molecular orbital



Fig. 8 Langmuir, El-Awady and Flory-Huggins adsorption isotherm models of the pyridine-pyrimidine derivatives onto aluminum surface into 1 M HCl.

denoted as  $E_{HOMO}$  and  $E_{LUMO}$ , respectively, energy gap ( $\Delta E$ ), dipole moment ( $\mu$ ), ionization energy (I), electron affinity (A), absolute electronegativity ( $\chi$ ), absolute hardness ( $\eta$ ), absolute softness ( $\sigma$ ), absolute electrophilicity parameter ( $\omega$ ) and fraction of electrons transferred ( $\Delta N$ ) are determined for both neutral and protonated pyridine-pyrimidine derivatives are listed in Tables 5a and 5b. Fig. 11a shows the shape of the HOMO, LUMO orbitals, and electrostatic potential (ESP) distribution of the studied inhibitors. The electron density indicates that a negative charge in red is easily delocalized on the N, S, O and Cl atoms because of the lone pair. thus, we can consider that EMMD would reveal a more suitable affinity to the adsorption onto the aluminum surface through the lone pair electrons located on N, S and O atom to the vacant aluminum P-

**Table 4** Adsorption parameters derived from Langmuiradsorption isotherms for  $10^{-3}$ M pyridine-pyrimidine derivativeson the Al surface in 1 M HCl at different temperatures.

parameters	PD	PA	ADT	EMMD
$K_{ads} (M^{-1}) * 10^3$	452	621	610	1157
$\Delta G_{ads}^{\circ}(KJ \ mol - 1)$	-42.23	-43.01	-42.96	-44.55
$\Delta H_{ads}^{\circ}(KJ \ mol - 1)$	-30.15	-30.44	-30.59	-39.60
$\Delta S_{ads}^{\circ}(Jmol^{-1}K^{-1})$	-24.50	-19.85	-20.04	-50.81



**Fig.9** Plot of logK vs. 1000/T (K)<sup>-1</sup> for aluminum in 1 M HCl in presence of  $10^{-3}$  M PD, PA, ADT and EMMD.

orbital. Generally, a high value of E<sub>HOMO</sub> is often associated with a higher tendency of the molecule to donate electrons to an acceptor metal having an empty or vacant orbital molecular leading to stronger adsorption on the metal surface and better inhibition efficiency (Al-Mobarak et al., 2010). On the other hand, the lower the value of ELUMO, indicates that the molecule would accept electrons easily from the metal surface and thus lead to stronger adsorption and higher inhibition efficiency. Also, the energy difference between the HOMO and the LUMO,  $\Delta E_{gap}$  is the parameter that measures the chemical reactivity of the molecule towards adsorption on the metal surface (Zhang et al., 2021). As the  $\Delta E_{gap}$  decreases, the reactivity of the molecule increases leading to an increase in the inhibition efficiency of the molecule because the energy to remove an electron from the last occupied orbital will be low (Zhang et al., 2021). The calculated ( $\Delta E$ ) values listed in Tables 5a and 5b indicate that the EMMD display the smallest value of  $\Delta E$ , meaning that the inhibitor EMMD molecule represent the highest reactivity, compared to the other molecules and, consequently, the better inhibition efficiency in accordance with the experimental results. The studied compounds are more prone to protonation on the pyridine-pyrimidine derivatives nitrogen (Fig. 11b). The trend for  $\Delta E$  values have the order inhibitor > inhibitor H+ in the aqueous phase. These consequences mean the highest inhibition efficiency and reactivity of studied inhibitors in the protonated form (Fig. 11b). Furthermore, it has also been reported that the values of dipole moment  $(\mu)$  of inhibitors follow the order ofPD < PA < ADT < EMMD which increases the polarizability and facilitate adsorption of EMMD on the aluminum surface. This may regarded to increase the opportunity of inhibitors molecules accumulation on the Al surface, consequently, increase the pyridine-pyrimidine derivatives adsorption on the Al surface and therefore inhibition efficiency enhanced (Mineva et al., 2001). In addition, the global properties as global hardness ( $\eta$ ), global softness ( $\sigma$ ) are important characteristics for measuring the molecular stability and reactivity. A soft molecule has a small energy gap and a hard molecule has a great energy gap (Djenane et al., 2019; Hasanov et al., 2007). Results in Table 5a showed that the value of (S) increases in order, PD < PA < ADT < EMMD, this behaviour is attributed to chemical structure, where existing of the heteroatoms substituents leads to increase the electrons transfer between the studied inhibitors and the Al surface that forming a strong protective film. Furthermore, the global hardness  $(\eta)$  of inhibitor H + species in aqueous solution (Table 5b), is lower than that of inhibitor (Table 5a), which indicates stronger dipoledipole interactions of the protonated form and Al interface in comparison to that of inhibitor. The fraction of electrons transferred ( $\Delta N$ ) between the pyridine-pyrimidine derivatives inhibitors and Al surface atom were listed in Table 5a and showed that  $\Delta N < 3.6$  indicates that the investigated inhibitors contribute electrons to the aluminum interface implies a greater tendency of the inhibitors to adsorb on the metal surface by donor-acceptor interactions of non-bonding electron pairs of the heteroatoms and  $\pi$ -electrons with the vacant Porbitals of the aluminum atom.

Furthermore, the highest fraction of electrons transferred is associated with the best inhibitor EMMD, this correlates well with the trend of experimental corrosion inhibition efficiency. On the other hand, it has been found (Awad et al., 2010) that the anticorrosive molecule-metallic surface process is controlled by an electronic back-donation process. According this concept, the change of energy shows a direct proportionality to the global hardness of the molecule, as defined as  $\Delta E_{Back-donation} = -\frac{\eta}{4}$ , if  $\eta > 0$  and  $\Delta E_{Back-donation} < 0$  this suggests that back-donation from the molecule to metal is energetically favored. The results reported in Tables 5a and 5b show that  $\Delta E_{Back-donation} < 0$  for our inhibitors, thus the charge transfer from the pyridine-pyrimidine derivatives inhibitors to Al surface is energetically favorable meaning that the inhibition efficiency increases with inhibitor adsorption on the metallic surface (Abdallah et al., 2021), The estimated  $\Delta E_{Back-donation}$ values are in accordance with the experimental data in the following tendencyPD < PA < ADT < EMMD. Electrophilicity index measures the capacity of molecule to acquire electrons (Parr et al., 1999), the values of electrophilicity( $\omega$ ) are in increasing order; PD < PA < ADT < EMMD, in accordance with experimental techniques. The low ionization energy of studied inhibitors indicates that it is easy for an atom to remove its outer electrons and it is easy for electrons transfer between the metal and inhibitors, and hence, increases the inhibition efficiency of inhibitors. Finally, the quantum parameters presented in Tables 5a and 5b indicate that the studied pyridine-pyrimidine derivatives have excellent corrosion inhibition properties in the protonated form and this obtained quantum parameters agree completely with the experimental results.



Fig. 10 Optimized geometry, numbering system, natural charges, bond lengths, bond angles, dihedral angle and vector of dipole moment for the studied compounds at the B3LYP/6-311 + +G(d,p).

# 3.4.2. Molecular electrostatic potential (MEP)

The electronic density is correlated to electrophilic and nucleophilic attack by the molecular electrostatic potential (MEP) for considerate the sites and the hydrogen-bonding interactions (Politzer and Murray, 2002). MEP is related to electronegativity, dipole moment, and chemical reactivity of molecules so, it is useful for visualizing the variable and defining how molecules interact with each other via charge distributions. Fig. 11a shows the 3D-MEP for studied inhibitors PD, PA, ADT and EMMD using DFT/B3LYP/6–311 + + G (d,p). According to the MEP plots, the distribution of the lone-pair of the electrons of the oxygen and nitrogen atoms in the negative region is mainly above the atomic sites O and N and are represented in red, and thus the resulted in positive sites about hydrogen and carbon atoms (blue). The color diagram in possible rises for the electronegativity in the subsequent order: red < orange < yellow < green < blue for MEP surface was as follows: electron-rich red (partially negative charge); blue for electron affinity, (partially positive charge); light blue for the area of a little electron affinity, yellow for the little electron-rich region; and green represents neutral (zero potential). This elucidates that the EMMD is the most predominant toward electrophilic attack and so it has the highest capability of bonding to the Al sur-

Table 5a The optimized calculations for the studied compounds at B3LYP/6-311++G (d,p).

Parameters	PD	PA	ADT	EMMD
Total Energy, $(E_T)$ (au)	-359.125	-319.789	-719.207	-1660.507
Energy of highest occupied molecular orbital (E <sub>HOMO</sub> ), (eV)	-5.5436	-6.5462	-5.7794	-6.9088
Energy of lowest unoccupied molecular orbital (E <sub>LUMO</sub> ), (eV)	-0.4045	-1.2923	-0.8693	-4.1398
Energy Gap, (Eg), (eV)	5.1391	5.2539	4.9101	2.7690
Dipole moment, (µ), (Debye)	0.5833	1.7026	2.1722	5.4875
I (eV)	5.5436	6.5462	5.7794	6.9088
A(eV)	0.4045	1.2923	0.8693	4.1398
χ (eV)	2.9740	3.9192	3.3243	5.5243
$\eta(eV)$	2.5696	2.6269	2.4550	1.3845
$S(eV)^{-1}$	0.3892	0.3807	0.4073	0.7223
ω (eV)	1.7211	2.9236	2.2507	11.021
$\Delta N,(eV)$	0.0498	-0.1312	-0.0192	-0.8286
$\Delta E_{BD} (eV)$	-0.6424	-0.6567	-0.6137	-0.3461

**Table 5b** The optimized calculations for the protonated form of the studied compounds at B3LYP/6-311 + + G(d,p).

Parameters	PD-H <sup>+</sup>	PA-H <sup>+</sup>	ADT-H <sup>+</sup>	$EMMD-H^+$
Total Energy, (E <sub>T</sub> ) (au)	-359.666	-320.907	-719.743	-1661.100
Energy of highest occupied molecular orbital (E <sub>HOMO</sub> ), (eV)	-6.2302	-4.5106	-3.9584	-3.0361
Energy of lowest unoccupied molecular orbital (E <sub>LUMO</sub> ), (eV)	-1.0923	-0.5201	-0.4640	-0.4643
Energy Gap, (Eg), (eV)	5.1378	3.9905	3.4944	2.5718
Dipole moment, (µ), (Debye)	1.7537	2.2484	2.5476	2.8466
I (eV)	6.2302	4.5106	3.9584	3.0361
A(eV)	1.0923	0.5201	0.4640	0.4643
X(eV)	3.6612	2.5153	2.2112	1.7502
$V(eV^{-1})$	-3.6612	-2.5153	-2.2112	-1.7502
$\eta(eV)$	2.5689	1.9952	1.7472	1.2859
$S(eV^{-1})$	0.1946	0.2506	0.2862	0.3888
ω (eV)	2.6090	1.5854	1.3992	1.1911
$\Delta N,(eV)$	-0.0839	0.1791	0.2916	0.5754
$\Delta E_{BD} (eV)$	-0.6422	-0.4988	-0.4368	-0.3215

face, agreement well with experimental and theoretical investigations.

# 3.4.3. Natural charges and natural population analysis

The natural population analysis (Politzer and Murray, 2002), was performed on the electronic structures of pyridinepyrimidine derivatives, are calculated by DFT/B3LYP method with 6-311 + + G(d, p) basis set in the gaseous phase. The natural population analysis obviously describes the distribution of electrons in various sub-shells of their atomic orbits. Table 6a depicts the natural charge, natural Population, natural population of the total electrons on the sub-shells, and natural electronic configuration of active sites for PD, PA, ADT and EMMD. In this study the most negative centers are N6, N10 and N11atoms in PD, N5, N8 and N12 atoms in PA, N5, N8 and N10 atoms in ADT, finally N17, N18, O22 and O23 atoms in EMMD. The values obtained indicated that the nitrogen atoms in studied compounds have the highest negative atomic charges, indicating that the inhibitors studied can effectively prevent corrosion of the aluminum by adsorption on its surface through its active sites. S19 and Cl16 atoms in EMMD inhibitor act mostly as electrophilic centers since these atoms possess excess of positive charge, which is actually necessary to balance and stabilize the accumulation of negative charges on the aluminum surface (Fouda et al., 2019). Additionally, the natural population analysis showed that 81 electrons in EMMD compound than the others compounds are distributed on the sub-shells as total-Lewis (effective core, core and valence Lewis) and total non-Lewis (valence non-Lewis and Rydberg non-Lewis). The computed values and percentage of each are presented in Table 6b.

# 3.4.4. Calculation of the atomic loads of Mulliken

In order to predict the possible adsorption centers of the pyridine-pyrimidine derivatives, the Mulliken charge can be utilized. It has been found that the more negative the atomic charges of the adsorbed center are, the easier it is for the atom to give up its electrons to the Metal's unoccupied orbital (El-Haddad et al., 2019). The distribution of the Mulliken charges and the orientation of the polar moment are shown schematically in Fig. 10. The values of the charge's distribution are also showed in Tables 7 and 8. The atoms have high charge densities, are the nitrogen, oxygen, and some carbon atoms. As a result, N, O, S, Cl, and some C atoms are the active adsorptive centers with the highest ability to bind to the metal's surface, so, these atoms act as an electronic donor. Some carbon atoms, on the other hand, have positive charges that nucle-ophiles will attack. Therefore, pyridine-pyrimidine derivatives



Fig. 11a HOMO, LUMO maps, ESP and 3D-MEP for the studied compounds PD, PA, ADT and EMMD using B3LYP/6-311 + G (d,p).

can accept aluminum's electrons through these atoms, and these observations can be confirmed by the study of the Fukui indices.

# 3.4.5. Condensed Fukui indices

The Fukui indices evaluate and analyze the inhibitor molecules' local reactivity as well as their corresponding electrophilic and nucleophilic behavior. The electrophilic and nucleophilic attack is presented by the maximum values of  $f_k^$ and  $f_k^+$ , respectively, (Contreras et al., 1999). Fukui functions for nucleophilic and electrophilic attacks of the inhibitor molecules have been determined by taking the finite difference approximations as introduced by Yang and Mortier (Yang and Mortier, 1986) as follows:

$$f_k^+ = q_k(N+1) - q_k(N)$$
 (for nucleophilic attack) (24)

$$f_k^- = q_k(N) - q_k(N-1) \quad \ (\text{for electrophilic attack}) \qquad (25)$$

where  $q_k$  is the gross charge of the k atom in the molecule, i.e., the electronic density at a particular point (r) in space around the molecule. The  $q_k(N)$  corresponds to the number of electrons in the molecule,  $q_k(N+1)$  corresponds to an anion with an electron added to the LUMO of the neutral molecule and  $q_k(N-1)$  corresponds to the cation with an electron removed from the HOMO of the neutral molecule (Damej et al., 2021).  $f_k^-$  Indicate to reactivity with respect to electrophilic attack or when the molecules loss electrons and the  $f_k^+$ , measures the changes of density while the molecules receive electrons and it corresponds to reactivity with respect to nucleophilic attack. Morell et al. (Morell et al., 2005; Morell et al., 2006) have proposed a double descriptor  $\Delta f_k$ , which is defined as the difference between the nucleophilic and electrophilic Fukui functions and is given by the following equation:

$$\Delta f_k = f_k^+ - f_k^- \tag{26}$$



Fig. 11b HOMO and LUMO maps, for the protonated form of the studied compounds using B3LYP/6-311 + G(d,p).

If  $\Delta f_k < 0$ , the site may be preferred for an electrophilic attack, whereas, If  $\Delta f_k > 0$  the s may be favored for a nucleophilic attack. The values of the  $f_k^-$ ,  $f_k^+$  and  $\Delta f_k$  for the inhibitors (PD, PA, ADT and EMMD) and protonated form have been determined and tabulated in Tables 7 and 8. The preferred sites for electrophilic attack is preferably occur at N10 and N11 atoms in PD, at C3, C4 and N8 atoms in PA, at N5 and S9 in ADT, and at S19 and O22 atoms in EMMD, where they are shown by the highest value of  $f_k^-$  and the more negative value of  $\Delta f_k$ . The preferred sites for nucleophilic attack would preferably occur at C4, C5 and N6 atoms in PD, at N5 and N12 atoms in PA, at C3, C4 and N8 and N10 atoms in ADT, and at C7, C12, C16, C17, C18 and O23 atoms in EMMD where the highest value of,  $f_k^+$  and the more positive of  $\Delta f_k$ .

# 3.4.6. Thermodynamic properties

The standard thermodynamic functions, the heat capacity  $C_{p,m}^0$ , entropy  $S_m^0$  and enthalpy  $H_m^0$ , for compounds (PD, PA, ADT and EMMD) were obtained at the DFT/B3LYP/6–311 + +G (d,p) level and are listed in Table 9.

Table 9 showed that the standard heat capacities, entropies, and enthalpies increase at all temperatures from 298 to 323 K, because the intensities of the molecular vibration increase with

Inhibitors	Atom No.	Natural charge	Natura	l population			Natural electronic configuration
			Core	Valence	Rydberg	Total	
PD	N6	-0.573	1.999	3.563	0.0247	7.573	[core]2S(1.36)2p(4.19)3S(0.01)3p(0.01)3d(0.01)
	N10	-0.787	1.999	5.771	0.0170	7.787	[core]2S(1.33)2p(4.44)3p(0.01)
	N11	-0.787	1.999	5.771	0.0170	7.787	[core]2S(1.33)2p(4.44)3p(0.01)
PA	N5	-0.530	1.999	5.510	0.0214	7.530	[core]2S(1.38)2p(4.13)3p(0.01)3d(0.01)4p(0.01)
	N8	-0.776	1.999	5.760	0.0168	7.776	[core]2S(1.31)2p(4.45)3p(0.01)
	N12	-0.530	1.999	5.510	0.0214	7.530	[core]2S(1.38)2p(4.13)3p(0.01)3d(0.01)4p(0.01)
ADT	N5	-0.611	1.999	5.593	0.0197	7.612	[core]2S(1.26)2p(4.33)3p(0.01)
	N8	-0.630	1.999	5.607	0.0237	7.630	[core]2S(1.24)2p(4.37)3p(0.01)4p(0.01)
	S9	-0.242	9.999	6.214	0.0294	16.24	[core]3S(1.78)3p(4.44)3d(0.01)5S(0.01)5p(0.01)
	N10	-0.806	1.999	5.790	0.0172	7.806	[core]2S(1.36)2p(4.43)3p(0.01)
EMMD	C116	-0.005	4.999	3.495	0.0106	8.505	[core]3S(0.92)3p(2.58)
	N17	-0.377	0.999	2.861	0.0165	3.878	[core]2S(0.63)2p(2.23)3p(0.01)4p(0.01)
	N18	-0.282	0.999	2.769	0.0135	3.782	[core]2S(0.68)2p(2.09)3p(0.01)
	S19	-0.042	4.999	2.941	0.0169	7.958	[core]3S(0.86)3p(2.08)3d(0.01)4p(0.01)
	O22	-0.295	0.999	3.289	0.0059	4.295	[core]2S(0.85)2p(2.44)
	O23	-0.275	0.999	3.266	0.0098	4.275	[core]2S(0.81)2p(2.45)3p(0.01)

Table 6a	Natural charge,	natural	population,	natural	population	of th	e total	electrons	on	the	sub-shells	and	Natural	electronic
configurati	on of active sites	for the	studied com	pounds a	at B3LYP/6	-311+	+G (	(d,p).						

Table 6b	Total charge analysis of studied compounds at the B3LYP/6–311 $++$ G(d, p).										
Inhibitors	Core	Valence Lewis	Total Lewis	Valence non- Lewis	Rydberg non- Lewis	Total non-Lewis					
PD	15.99 (99.96% of 16)	40.37 (96.13% of 42)	56.36 (97.18% of 58)	1.51 (2.61% of 58)	0.11 (0.19% of 58)	1.63 (2.81% of 58)					
PA	13.99 (99.96% of 14)	34.49 (95.80% of 36)	48.48 (96.97% of 50)	1.40 (2.80% of 50)	0.11 (0.22% of 50)	1.51 (3.02% of 50)					
ADT	23.99 (99.97% of 24)	42.73 (97.12% of 44)	66.73 (98.13% of 68)	1.13 (1.66% of 68)	0.13 (0.20% of 68)	1.26 (1.86% of 68)					
EMMD	27.99 (99.96% of 28)	51.19 (96.59% of 53)	79.18 (97.75% of 81)	1.63 (2.01% of 81)	0.18 (0.22% of 81)	1.81 (2.24% of 81)					

Table 7	Calcula	ited Fuku	i func	tions ar	nd Mullika	an charge	on
the hetero	oatoms i	for the st	udied 1	neutral	inhibitor	molecules	of
pyridine-j	pyrimidi	ne deriva	tives.				

Compounds	atoms	Mulliken	f+	<i>f</i> -	$\Delta f +$
PD	C4	0.309	0.048	0.022	0.026
	C5	0.308	0.048	0.022	0.026
	N6	-0.390	0.107	0.053	0.054
	N10	-0.448	0.039	0.093	-0.054
	N11	-0.448	0.039	0.093	-0.054
PA	C3	0.509	0.037	0.043	-0.006
	C4	0.216	0.024	0.119	-0.095
	N5	-0.370	0.125	0.102	0.023
	N8	-0.725	0.036	0.209	-0.173
	N12	-0.371	0.125	0.102	0.023
ADT	C3	0.368	0.041	0.018	0.023
	C4	0.487	0.080	0.027	0.053
	N5	-0.366	0.006	0.015	-0.009
	N8	-0.366	0.035	0.013	0.022
	S9	-0.589	0.335	0.456	-0.121
	N10	-0.494	0.033	0.031	0.002
EMMD	C7	0.275	0.081	0.009	0.072
	C12	0.404	0.029	0.024	0.005
	C16	-0.042	0.025	0.013	0.012
	N17	-0.355	0.016	-0.009	0.025
	N18	-0.203	0.095	0.076	0.019
	S19	-0.479	0.175	0.491	-0.316
	O22	-0.373	0.070	0.085	-0.015
	O23	-0.136	0.055	0.034	0.021

Tabl	e 8	Calculate	ed Fu	ıkui fi	unctions and	Mullika	an cl	narge on
the	hete	roatoms	for	the	protonated	form	of	studied
com	poun	ds.						

Compounds	atoms	Mulliken	f+	<i>f</i> -	$\Delta f +$
PD-H <sup>+</sup>	C4	0.634	0.113	-0.051	0.164
	C5	-0.598	-0.143	-0.029	-0.114
	N6	-0.238	-0.033	-0.043	0.010
	N10	-0.349	-0.055	-0.007	-0.048
	N11	-0.349	-0.055	-0.060	0.005
$PA-H^+$	C3	-0.391	-0.369	-0.016	-0.353
	C4	-0.227	-0.072	0.137	-0.209
	N5	-0.112	0.080	-0.078	0.158
	N8	-0.359	-0.094	-0.141	0.047
	N12	-0.055	0.137	-0.115	0.252
$ADT-H^+$	C3	-0.236	-0.102	0.001	-0.103
	C4	-0.272	-0.504	0.193	-0.697
	N5	-0.088	0.055	-0.207	0.262
	N8	-0.153	0.090	-0.051	0.141
	S9	-0.025	0.677	-0.332	1.009
	N10	-0.330	0.007	0.011	-0.004
$EMMD-H^+$	C7	0.603	0.689	0.170	0.519
	C12	0.603	0.689	0.170	0.519
	Cl16	0.495	0.017	-0.019	0.036
	N17	-0.156	-0.217	-0.114	-0.103
	N18	-0.027	-0.046	-0.068	0.022
	S19	-0.267	0.019	0.021	-0.002
	O22	-0.250	-0.154	0.020	-0.174
	O23	0.117	-0.106	0.021	-0.127

T(K)	H <sub>m</sub> <sup>0</sup> (kca	$lmol^{-1}$ )			$C_{pn}^{0}(calr$	$nol^{-1}K^{-1}$ )			S <sub>m</sub> <sup>0</sup> (calm	$\operatorname{nol}^{-1}\mathrm{K}^{-1}$ )		
Inhibitor	PD	PA	ADT	EMMD	PD	PA	ADT	EMMD	PD	PA	ADT	EMMD
298	62.10	79.74	80.80	172.02	21.30	28.20	29.19	73.88	75.11	81.21	86.68	153.12
303	62.70	80.60	81.50	172.71	22.90	28.90	30.20	74.53	76.46	82.40	87.31	153.99
308	63.90	81.40	82.20	173.42	23.50	29.60	31.00	76.43	77.12	83.07	88.22	154.53
313	64.70	82.10	82.90	174.51	24.80	30.20	32.80	77.68	78.77	84.75	89.13	155.68
318	65.30	82.90	83.10	175.36	25.60	31.60	33.60	78.64	65.30	83.10	82.90	175.36
323	66.50	83.60	83.70	177.20	26.70	32.40	34.40	79.88	80.78	86.87	91.94	157.26

Table 9 Thermodynamic properties at different temperatures for the studied compounds at the B3LYP/6-311 + + G (d,p).

the increasing temperature and the efficiency of inhibitors increases in the order EMMD > ADT > PA > PD. The correlations between these thermodynamic properties and temperatures T are shown in Fig. 12. The correlation equations will be helpful for the further studies for pyridine-pyrimidine derivatives inhibitors.

# 3.4.7. Natural bond orbital (NBO) analysis

Natural Bond Orbital NBO analysis indicates the strength of the interaction between atoms, which involves the amount of charge transfer and affects molecular stability. Analysis of NBO as the second-order interaction energy  $E^2$  can be used to determine the orbital filled with electrons or empty, which contributes to the delocalization of electrons from bonding (BD) or lone pair (LP) to anti-bonding (BD)\* (Fouda et al., 2017b). Bonding BD shows the condition of the atom that is bonded to other atoms. The Lone Pair symbol LP shows a lone pair on the associated atom, and the Rydberg symbol RY indicates the type of atomic orbital with the highest quantum number and energy (Mert et al., 2014).



Fig. 12 Correlation graphics of thermodynamic properties and temperatures for the studied Inhibitors at the B3LYP/6-311 + G(d,p).

Compound	Donor (i)	Acceptor (j)	$E^{(2)}(kcalmol^{-1})$	NBO	Population
PD	πC1-N6	π*C4-C5	31.68	πC1-N6	1.74117
	πC2-C3	π*C4-C5	30.77	πC2-C3	1.71650
	LP (1) N10	π*C4-C5	32.31	LP (1) N10	1.82225
	LP (1) N11	πC1-N6	35.57	LP (1) N11	1.82233
	π*C1-N6	π*C4-C5	214.89	π*C4-C5	0.41504
PA	πC1-N5	π*C4- N12	33.99	πC1-N5	1.75655
	πC2-C3	π*C1- N5	35.39	πC2-C3	1.64527
	πC4-N12	π*C2-C3	34.37	πC4-N12	1.97994
	LP (1) N8	π*C4-N12	48.07	LP (1) N8	1.77499
	π*C1-N5	π*C2-C3	195.30	π*C4- N12	1.66715
ADT	LP (1) N5	π*C4-S9	57.26	LP (1) N5	1.69390
	LP (1) N8	π*C2-C3	35.78	LP (1) N8	1.68132
	LP (2) S9	π*C4-N8	12.12	LP (2) S9	1.88564
	π*C4-S9	π*C4-S9	16.27	π*C4-S9	0.44422
EMMD	σC1-C2	π*C3-C4	15.56	σC1-C2	0.98391
	σC1-C7	RY*C7	4315.47	σC1-C7	0.98488
	σC1-C7	RY*H34	455.50	σC28-H32	0.98778
	σC28-H32	RY*C9	1069.84	σC6-H14	0.98886
	σC6-H14	RY*H34	334.76	πC3-C4	0.98973
	πC3-C4	RY*N17	77.30	σC4-Cl16	0.99427
	πC3-C4	RY*O22	31.34	σC7-C10	0.98276
	πC3-C4	σ*C8-S19	11.18	σC7-N18	0.98912
	πC3-C4	σ*C20-O23	19.08	σS19-H24	0.99238
	πC3-C4	σ*C28-H34	50.33	σC20-O22	0.99737
	σC4-Cl16	RY*C7	1051.79	σC28-H32	0.99082
	σC4-Cl16	RY*H34	435.87	σC28-H34	0.99016
	σC4-Cl16	RY*N17	56.39	CR*C9	0.99951
	σC4-Cl16	RY*O22	23.54	CR*Cl16	1.00000
	σC4-Cl16	σ*C21-C27	11.69	CR*N18	0.99961
	σC4-Cl16	σ*C28-H34	31.60	CR*O23	0.99985
	σC28- H32	RY* N17	77.66	CR*O22	0.99987
	σC6-H14	σ*C20-O23	11.38	CR*C28	0.99963
	σC6-H14	σC28-H34	43.84	LP (1) Cl16	0.99603
	σS19-H24	RY*C7	2099.69	LP (1) N17	0.90378
	σS19-H24	RY*N17	11.07	LP (1) N18	0.94526
	σS19-H24	RY*H34	230.25	LP (1) S19	0.99312
	σS19-H24	σ*C20-O23	13.20	LP (1) O22	0.98833
	σC20-O22	RY*C9	47.47	σ*C1-C2	0.24826
	σC20-O22	RY*H34	128.40	σ*C/-C10	0.29836
	σC20-O22	σ*C20-O23	18.65	σ*C20-O23	0.11565
	σC28-H32	RY*O22	40.57		
	σC28-H34	RY*S19	10.29		
	σC28-H32	σC8-S19	38.24		
	σC28-H34	σC9-N18	21.01		
	σC28-H34	σC21-C27	25.64		
	CR*C9	RY*U0	2012.82		
	CR*C9	KY*H34 -*C20 O22	1894.86		
	CR*C9	6*C20-O23	17.30		
	CR*CI16	RY*C28	43.21		
	CR*CII0	KY*H32 DV*C0	18.90		
	CR*N18	R1+C9	111.57		
	CR*N18	KY*H34 -*C20 O22	402.28		
	CR*INI8 CP*O22	0°C20-023	13.30		
	CR*023	KI*C0 DV*1124	122.12		
	CR*022	K I *H34	100.87		
	CR*022	GU2/-H31 DV#N117	2192.33		
	CR*C28	KY*INI/	82.45		
	LP(1) C10	ос28-н34 =C7 С10	254.59		
	LP(1) CIU LP(1) CIU	σC <sup>2</sup> N12	89.48 24.60		
	LP(1) CIU	DV*C4	24.09		
	LP(1) C110 LP(1) C116	RT*C4 DV*N17	1120.46		
	LP(1) CH0	NT INT/	11.21		

(continued on next page)

Table 10 (continued)

Compound	Donor (i)	Acceptor (j)	$E^{(2)}(kcalmol^{-1})$	NBO	Population
	LP (1) Cl16	RY*H34	3366.09		
	LP (1) Cl16	σ*C20-O23	16.80		
	LP (1) N17	σ*C8-N18	19.40		
	LP (1) N18	RY*C4	302.85		
	LP (1) N18	RY*H34	14.63		
	LP (1) N18	σ*C20-O23	35.00		
	LP (1) S19	RY*C4	88.65		
	LP (1) S19	RY*H34	86.57		
	LP (1) O22	RY*C7	30.64		
	LP (1) O22	RY*H34	134.12		
	LP (1) O22	σ*C20-O23	27.95		
	σ*C1-C2	RY*C9	30.13		
	σC1-C2	RY*H31	12.01		
	σ*C1-C2	σ*C5-C6	42.97		
	σ*C7-C10	σ*C20-O23	355.95		
	σ*C20-O23	σ*C20-O23	40.11		
	σ*C20-O23	RY*C7	43.13		
	σ*C20-O23	RY* H34	15.90		

 $E^{(2)} = q_i \frac{(Fij)^2}{(zj-ai)}$  Shows the lowering of stabilization energy, where  $q_i$  is the donor orbital occupancy,  $\varepsilon_i$ , and  $\varepsilon_j$  are donor and acceptor orbital energies (diagonal elements), and Fij is the off-diagonal NBO Fock matrix element.

The NBO analysis by using the second-order perturbative energy results has been generally used to estimate the hybridization and non-covalent interactions, which provide information on the contribution to the lowering of the stabilization energy of a particular molecular system, including hyperconjugation, resonance, etc. (Guerrab et al., 2019; Guerrab et al., 2020). In this study, the second order perturbative energy results for PD, PA, ADT and EMMD compounds were determined and presented in Table 10. Accordingly, the highest contribution to the stabilization energy lowering for studied compounds has come from the LP (1) N11  $\rightarrow \pi$ C1-N6, LP (1) N8  $\rightarrow \pi^*$ C4-N12, LP (1) N5  $\rightarrow \pi^*$ C4-S9 and LP (1) C10  $\rightarrow \sigma$ C7-C10 interactions: the resonance energy for this interactions has been calculated as  $35.57 \text{ kcal mol}^{-1}$ ,  $48.07 \text{ kcal mol}^{-1}$ ,  $57.26 \text{ kcal mol}^{-1}$  and  $89.48 \text{ kcal mol}^{-1}$  for PD, PA, ADT and EMMD compounds, respectively. The contribution to the lowering of the stabilization energy for EMMD is calculated for the electron delocalization from the lone pair of the N18 atom to antibonding orbital  $\sigma$ \*C20-O23 is  $35.00 \text{ kcal mol}^{-1}$ . In addition to the stabilization energy of the LP (1) O22  $\rightarrow \sigma^*$ C20-O23 is 27.95 kcal mol<sup>-1</sup>. It is worth to mention that the stabilization energy of the LP (1) Cl16  $\rightarrow \sigma^*$ C20-O23 interaction is calculated in 16.80 kcal mol<sup>-1</sup>. In conclusion EMMD has the greatest effect on increasing corrosion inhibition efficiency compared to other inhibitors because it has the highest  $E^2$ .

# 3.5. Surface morphology

# 3.5.1. Scanning electron microscope (SEM) analysis

SEM is used to study the surface morphology of the aluminum samples of size  $2.00 \times 2.50 \times 0.04$  cm samples immersed in 1 M HCl for 24 h in the absence and presence of  $10^{-3}$ M pyridine-pyrimidine derivatives PD, PA, ADT and EMMD. Fig. 13 shows the scanning electron microphotographs of alu-



**Fig. 13** SEM images of aluminum immersed in 1 M HCl for 24 h at 298 K: (a) polished Al, (b) uninhibited Al, and  $10_{-3}$  M of (c) PD, (d) PA, (e) ADT and (f) EMMD.

minum in HCl in the absence and presence of  $10^{-3}$ M of investigated compounds. The surface of the polished aluminum sample Fig. 13a is very smooth and shows no corrosion. After immersion in uninhibited 1 M HCl solution for 24 h, the aluminum surface is damaged and is very rough as a result of

many cracks and scratches on the Al surface due to metal dissolution Fig. 13b (Zhang et al., 2019). The presence of  $10^{-3}$  M of inhibitors effectively retarded the dissolution of Al in 1 M HCl and surface damage has been reduced significantly Fig. 13(c- f) as compared to the blank solution (Fig. 13b) by adsorption and formation of protective films of PD, PA, ADT and EMMD on the aluminum surface. Fig. 14 shows particle size in  $\mu m$  of PD, PA, ADT, and EMMD, they are 5.94, 5.23, 2.80 and 0.475  $\mu m$  respectively. On comparing these microphotographs and particle size, it appears that smoothing of the surface of test materials has been observed in the following sequence EMMD > ADT > PA > PD The SEM results are in good agreement with the observed inhibition efficiency values from electrochemical and computational methods.

# 3.5.2. Energy dispersive X-ray analysis

Energy dispersive X-ray analysis (EDX) technique was used to get more information about the composition of the surface of the polished, corroded and inhibited aluminum surface in the absence and presence of  $10^{-3}$ M of pyridine-pyrimidine inhibitors in 1 M HCl solution after immersion of 24 h. The results obtained from the EDX spectra are shown in Fig. 15. Fig. 15a shows that the polished aluminum surface contains a large aluminum peak, whereas after immersing in 1 M HCl in the absence of the inhibitors (Fig. 15b), the aluminum peak was suppressed and the oxygen and chloride peaks observed due

to the formation of oxide, hydroxide, and chloride compounds on the aluminum surface (Amin et al., 2009). In the presence of the inhibitors, the intensity of the aluminum peak was improved which indicates the adsorption of inhibitor molecules on the surface of aluminum, as shows in Fig. 15(c-f) which clearly show a decrease in oxygen and chloride contents and the presence of sulfur, carbon and nitrogen signals in the inhibited samples indicates that the inhibitor molecules containing these elements are adsorbed on the aluminum surface.

# 3.5.3. Atomic force microscopy

The surface analysis of aluminum metal dipped in 1 M HCl solution for 24 h at 298 K in the absence and presence of inhibitors were studied using AFM. SEM micrographs only provide qualitative information about metal surfaces. To get some quantitative information about metal surface morphology we need AFM (Sharma and Kumar, 2021). Fig. 16 shows typical AFM images of polished aluminum metal (Fig. 16a), after immersion in 1 M HCl solution without inhibitor (Fig. 16b), and with inhibitors PD (Fig. 16c) and EMMD (Fig. 16d). One of the texture profiles currently defined by the International Organization of Standardization (ISO) is the roughness profile (ISO 4287), which list certain parameters for the evaluation of surface roughness (Umoren et al., 2020) Some of them are Ra Arithmetical mean height indicates, Ra is referred to as the average surface roughness and Sm average



Fig. 14 Particle size distribution of inhibited Al using SEM analysis with 10<sup>-3</sup> M of (a) PD, (b) PA, (c) ADT and (d) EMMD.



**Fig. 15** EDX images of polished aluminum (a) immersed in 1 M HCl (b) and in 1 M HCl with  $10_{-3}$  M of PD (c), PA (d), ADT (e) and EMMD (f) for 24 h at 298 K.

peak spacing. Rp Maximum profile peak height, Rv Maximum profile valley depth, Ry The maximum height of the profile Ry = Rp + Rv, Rq root-mean-square roughness and Rm average peak spacing profile irregularities. The numerical values of these parameters for the studied aluminum metal surfaces are given in the introduced tables in Fig. 16. After polishing the metal, a relatively smooth surface was obtained (Fig. 16a), and the values of all the roughness profile parameters are less than unity. When the Al surface sample was exposed to 1 M HCl solution in the absence of inhibitors, the surface was damaged and corroded as can be seen form (Fig. 16b), because of the corrosive attack by acid solution.

The calculated average surface roughness for uninhibited corroding surface was 105.16 nm.

However, the AFM images in the presence of PD and EMMD Fig. 16 (c and d) showed that the surface becomes smoother and the average roughness was reduced 28.28 and 22.78 nm in the existence of inhibitors PD and EMMD, respectively. Increased surface smoothness in the presence of the inhibitors indicates the adsorption of the inhibitors on the surface of Al. In fact, all parameters are almost smaller than those in (Fig. 16b) justified the development of a consistent inhibitor protective layer on the aluminum surface. The lower values of parameters roughness for EMMD than PD reveals that EMMD protects the Al surface more efficiently

than PD in 1 M HCl solution. These roughness values confirm the inhibition efficiency data observed in the EFM measurements. The AFM results were in good agreement with SEM and EDX results.

# 3.6. Molecular dynamic simulations

### 3.6.1. Binding energy

Molecular dynamics simulations is a useful and new tool to investigate the interaction between inhibitors and metal surface. The adsorption progress of pyridine-pyrimidine derivatives on aluminum surface was investigated by performing molecular dynamics simulations, Fig. 17. In this study, (MD) simulation studies are performed to predict the binding energies  $E_{bind}$  of these pyridine-pyrimidine inhibitors on aluminum surface and to display whether there is a significant correlation between experimental inhibition efficiencies and binding energies for inhibitors included in this study. Interaction energies between Al surface and inhibitor molecules was estimated using molecular dynamic simulation as follows (Madkour et al., 2018; Zuo et al., 2021):

$$E_{ads} = E_{total} - (E_{surface} + E_{inhibitor})$$
(27)

$$E_{bind} = -E_{ads} \tag{28}$$



Fig. 16 Three dimension AFM images of polished Al, uninhibited Al and with  $10^{-3}$ M PD and EMMD.



**Fig. 17** Top views of the most stable low energy configurations for the adsorption of pyridine-pyrimidine inhibitors on Al (111) surface obtained using molecular dynamic (MD) simulations.

where  $E_{ads}$  is the adsorption energy,  $E_{inhibitor}$  is the total energy of the inhibitor compound and  $E_{surface}$  is the total energy of the aluminum surface. When the adsorption occurs between the compound and the Al surface, the energy of the new system is expressed as  $E_{total}$ .

Table 11 shows that EMMD has the highest adsorption energy on Al (111) surface, suggesting that EMMD is the best inhibitor between the investigated compounds which agrees well with the experimental results. The values of binding energy was calculated using Eq. (28). The values indicating that the interactions between pyridine-pyrimidine inhibitors and aluminum surface are very high. It is important to note that, the higher the value of binding energy, the easier the inhibitor adsorbs on the metal surface and the higher the inhibition efficiency. The binding energies obtained are observed to increase in the order: PD < PA < ADT < EMMD, this is

investigated i	minonors on AI (111) surfa	ce.
Inhibitor	$E_{ads}(\text{Kcal mol}^{-1})$	$E_{bind}(\mathrm{Kcal}\ \mathrm{mol}^{-1})$
PD	- 48.71	48.71
PA	-58.26	58.26
ADT	-75.51	75.51
EMMD	-100.92	100.92

 Table 11
 The adsorption and binding energies for the investigated inhibitors on Al (111) surface.

in good accordance with the experimental data and DFT calculations.

# 3.6.2. Radial distribution function

For determining the type of pyridine-pyrimidine derivatives – Al interaction, radial distribution functions (RDFs) (or pair correlation function)  $g_{(r)}$  were used as a useful method to evaluate the bond lengths. The lowest bond length from 1 Å up to 3.5 Å, indicates that the adsorption is chemisorption (Hsissou et al., 2019). While the highest bond length (greater than 3.5 Å) reflects that the adsorption is physisorption (Chafiq et al., 2021). RDFs were calculated using Molecular dynamics simulation. It is known that, there is a relationship during the mechanism of corrosion inhibition between the adsorption potential and bonding length (Chugh et al., 2020). Hansen and McDonald proposed and explained RDFs as the following (Chugh et al., 2020).

$$g_{AB}(r) = \frac{1}{\langle \rho_B \rangle} \times \frac{1}{N_A} \sum_{i \in A}^{N_A} \sum_{j \in B}^{N_B} \frac{\delta(r_{ij} - r)}{4\pi r^2}$$
(29)

where  $\rho_B$  is the particle density of B averaged over all shells around particle A. Here, RDF is defined as the probability of finding particle B within the range around particle A. The RDFs of the Pyridine-pyrimidine derivatives atoms are displayed in Fig. 18 with the help of RDFs graphs, we can judge the interaction type occur onto the surface, by interpreting the first prominent peaks obtained. In present RDF results (via Fig. 18), the first prominent peak is located at smaller than 3.5 Å, which suggests a chemical bonds formation between the Pyridine-pyrimidine derivatives molecules and Al atoms, indicating the synergistic effect of  $\pi$ -electrons and heteroatoms of molecules to increase the adsorption ability of inhibitors on the Al interface. Moreover, other peaks located outside 3.5 Å for EMMD is attributed to physical interactions. The results obtained confirm the comprehensive adsorption of the Pyridine-pyrimidine derivatives inhibitors tested and, consequently, the protection of the metal against dissolution, because of their greater ability to give and to accept electrons on the surface of the metal through these active sites. Finally, MD and RDF results are strongly in line with the experimental, theoretical and surface analysis results.



**Fig. 18** RDFs analysis of the pyridine-pyrimidine derivatives adsorbed on the  $Al_2O_3$  surface.



Fig. 19 Scheme of mechanism of pyridine-pyrimidine derivatives adsorption on Al.

### 3.7. Inhibition mechanism

The pyridine-pyrimidine derivatives in HCl solution, may found in their neutral form or in the form of protonated cations. Furthermore, it is well known that the inhibitors which contain vacant orbitals have a tendency to gain electrons from p-orbital of Al to form stable compounds Therefore, according to the results discussed above, the adsorption of pyridine-pyrimidine derivatives on the Al surface may involve at least one of the following interactions (1) In 1 M HCl solution the aluminum oxide film has a positive surface charge, so it attracts Cl<sup>-</sup> ions. The electronegative donor atoms N, O, S or  $\pi$  electrons aromatic ring, or both in Pyridine-pyrimidine derivatives induce effective inhibitor adsorption on the aluminum surface. As a result, protonated inhibitors have a propensity to adsorb onto the aluminum surface through electrostatic interaction between positively charged molecules inhibitors and negatively charged metal surfaces, facilitating physical adsorption of the inhibitor (Abdelshafi, 2020; Li et al., 2009).

Inhibitor + 
$$XH^+ \leftrightarrow [InhibitorH_X]^X$$

$$Al - OH + H^+ \leftrightarrow Al - OH^2$$

 $Al - OH + OH^- \leftrightarrow Al - O^- + H_2O$ 

$$Al - OH \leftrightarrow Al - O^- + H^+$$

This surface adsorption results in the creation of a protective layer, which displaces water from the metal surface and protects it from corrosion (Bashir et al., 2020). (2) The pyridine-pyrimidine derivatives can be adsorbed on the surface of the aluminum based on electron transfer between electron pairs of heteroatoms and  $\pi$ -electrons of benzene and vacant P-orbital of Al (this is responsible for chemisorption mechanism) and (3) donor–acceptor type interactions Taking into account all these possibilities, we have constructed a schematic representation of the adsorption process of the pyridinepyrimidine derivatives molecules on the aluminum surface (Fig. 19). When the concentrations of pyridine-pyrimidine derivatives increased, the aluminum corrosion resistance in acid solutions increased. Increasing the number of adsorbed inhibitor molecules, increase the surface coverage, creating a barrier for mass and charge transfer. Electrochemical frequency modulation (EFM), quantum chemical calculations, molecular dynamics simulation showed that the %IE of the pyridine-pyrimidine derivatives follow the order: PD > PA > ADT > EMMD.

# 4. Conclusions

Pyridine-pyrimidine derivatives exhibited excellent inhibition behavior for Al corrosion in an aggressive solution, 1 M HCl, solution. Corrosion inhibition performance of pyridine-pyrimidine derivatives was significantly investigated by using electrochemical frequency modulation (EFM) technique, scanning electron microscope (SEM), Atomic force microscopy (AFM), density functional theory (DFT) calculations and molecular dynamics (MD) simulations. EFM results show the inhibition efficiencies of studied inhibitors increase as their concentration increase and decreased by increasing temperature. The maximum efficiency is obtained for a concentration of 10<sup>-3</sup>M at 298 K with a percentage of 86.72%, 91.58%, 95.67% and 95.68% .for PD, PA, ADT and EMMD respectively Further, The inhibition efficiency of the four compounds is given in the following order of PD > PA > ADT > EMMD and EMMD is the most effective inhibitor. CF-2 and CF-3 are very close to theoretical values of 2.0 and 3.0 respectively indicating the validity of Tafel slopes and corrosion current densities, confirming that the obtained results are of good values. Adsorption is the main reason for the inhibition mechanism of the studied inhibitors on the aluminum surface and follows the Langmuir isotherm.  $\Delta G^{\circ}_{ads}$  and  $\Delta H^{\circ}_{ads}$  values indicate the adsorption process is comprehensive adsorption mainly physical adsorption. The results of the molecular dynamic (MD) simulations revealed that, the studied inhibitors are strongly adsorbed on the surface of Al (111) and the trend of the predicted binding energies are in good agreement with the experimental inhibition efficiency. Pyridine-pyrimidine derivatives are likely to inhibit aluminum corrosion in the protonated form than in the neural forms. Quantum chemical computations (DFT) is in good agreement with Molecular dynamics simulations (MD, RDF) and experimental measurements, where they show the presence of good relationship between the molecular structure of the Pyridine-pyrimidine derivatives and its inhibition efficiency.

#### **Declaration of Competing Interest**

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.

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