Electrochemical and Computational Insights on the Application of Expired Metformin Drug as a Novel Inhibitor for the Sweet Corrosion of C1018 Steel

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ABSTRACT: An expired metformin drug (MET) was used as a corrosion inhibitor for C1018 carbon steel in a CO2-saturated 3.5 wt % NaCl + 340 ppm acetic acid solution under static conditions. The inhibitor was evaluated using electrochemical methods complemented with surface analytical measurements and computational modeling. The drug displayed a high inhibition efficiency of ∼90% at 200 ppm. Impedance analyses revealed a rise in the charge transfer resistance at the steel–solution interface upon the addition of the inhibitor. Polarization measurements suggested that MET acted more like a cathodic-type corrosion inhibitor and significantly reduced the corrosion current density. The adsorption of MET on the steel substrate followed the Langmuir isotherm, showing a mixed type of physical and chemical modes of adsorption. The thermodynamic parameters revealed strong and spontaneous adsorption on the steel surface. The surface analysis using SEM supported the inhibitor adsorption on the steel substrate. Based on the DFT simulation, inhibition by MET is mainly achieved by its protonated form, which leads to the formation of a thin film on the steel surface rather than the modification of the work function of the steel surface. The experimental and theoretical estimations of pKa complemented the DFT results, both agreeing that the monoprotonated form of MET is the dominant form in which the inhibitor adsorbs on the steel surface to form a thin film rather than modify the work function of the steel surface.

1. INTRODUCTION

Steel pipelines find a wide range of applicability in the upstream, midstream, and in the downstream industrial processes dealing with the recovery, transport, and storage of oil.1 Carbon dioxide gas, when dissolved in the aqueous medium, forms carbonic acid, which creates a highly corrosive medium and causes significant damage to the steel structures.2–4 This type of carbon dioxide corrosion taking place in the absence of high levels of hydrogen sulfide gas is termed as the sweet corrosion.5,6 The presence of acetic acid in the corrosive solution makes the corrosive environment more aggressive and has been observed to cause an elevation in the corrosion rate. To counter this issue, a number of organic compounds are introduced as additives in the corrosive solution to minimize the damage caused to the steel structures. Most of the research and development in the area of sweet corrosion inhibitors have been reported on the use of imidazoline-based corrosion inhibitors.7,8 It should be noticed that these molecules require a tedious synthesis procedure, are expensive, and are highly toxic. Therefore, considering the environmental constraints, there is a lot of research work currently undergoing in the area of environment-friendly corrosion inhibitors.9,10

Metformin (N,N-dimethylbiguanide; MET) is the medication administered in cases of type 2 diabetes. It comes under the category of biguanide drugs. Due to their nontoxic properties and environmentally benign nature, pharmaceutical products have risen as ideal candidates to replace the traditionally employed toxic corrosion inhibitors.11 However, there is a major drawback associated with the use of fresh drugs, which restricts their applicability for corrosion inhibition. Fresh drugs are considerably expensive compared to the conventionally used organic compounds for corrosion inhibition, especially considering the requirement of the large-scale supply at a lower price. On the other hand, a lot of tedious and cumbersome procedure is required for the disposal of the expired or leftover drugs.12,13 Considering the activity of the expired drugs, in an earlier report, it has been described that the drug may still retain their potency even after a span of

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>10 years. Therefore, the application of the expired or unused drugs for corrosion inhibition can provide a useful alternative for environmentally benign corrosion inhibitors at a reasonable price. Earlier, we have demonstrated that the application of expired drugs in corrosion inhibition can allow a cost-effective alternative to the otherwise tedious disposal of the leftover drugs. MET contains five nitrogen atoms, which together provide this molecule greater adsorption and film-forming behaviors on the metallic substrate and appreciable anticorrosion behavior. In addition, being a drug molecule, MET is highly soluble in the aqueous environment.

Earlier, the drug MET is reported as an inhibitor for alloy steels in HCl environments. There is an ongoing quest for environmentally benign inhibitors developed from functionalized glucose, chemically modified chitosan, and macrocyclic inhibitors for sweet corrosion. Accordingly, we herein report MET as an inhibitor for C1018 steel in a CO2-saturated 3.5 wt % NaCl, containing acetic acid solution having an exposed area of 3.45 cm². The corrosion testing was undertaken using the Gamry Reference 600 potentiostat. The surface analytical studies were carried out by scanning electron microscopy using a JEOL SEM electron microscope. The metal samples were subjected to SEM analysis. The working electrode was an epoxy-mounted C1018 carbon steel being a drug molecule, MET is highly soluble in the aqueous environment.

2. EXPERIMENTAL SECTION

2.1. Materials and Instrumentation. Metformin hydrochloride (MET) (Figure 1) (500 mg) tablets were procured from the local pharmacy. The precleaned carbon steel specimens were subjected to acetone degreasing and then washed by water and stored in vacuum desiccators. The electrochemical corrosion testing was undertaken using the conventional three-electrode cell assembly connected with a Gamry Reference 600 potentiostat. The surface analytical studies were carried out by scanning electron microscopy using a JEOL SEM electron microscope. The metal samples were immersed in the corrosive electrolytes without and containing the inhibitor for 24 h and recovered, followed by drying, and were subjected to SEM analysis.

2.2. Electrochemical Corrosion Measurements. The working electrode was an epoxy-mounted C1018 carbon steel having an exposed area of 3.45 cm². The corrosion testing was conducted in a corrosion cell completely deaerated and saturated with CO₂ gas. Purging was done for 1 h prior to inhibitor loading and inhibitor injection. A Ag/AgCl reference electrode and a graphite cylinder as the counter electrode were used. Before the incorporation of the RCE into the test solution and administering the corrosion inhibitor, the NaCl electrolyte containing 340 ppm acetic acid was subjected to purging with CO₂ gas at 1 atmospheric pressure, and the CO₂ was bubbled during the experiment in the electrochemical cell.

Before conducting the electrochemical tests, the working electrode potential was measured in the open circuit condition to achieve a stable value upon which the electrochemical measurements were performed. The 3.5 wt % NaCl, containing 340 ppm acetic acid electrolyte was prepared fresh for each of the experiments. Replicated measurements were undertaken to ensure the reproducibility of the results. Impedance analyses were undertaken in the frequency range of 10⁵ to 10⁻² Hz at a 10 mV amplitude. Polarization experiments were undertaken by potential scanning of the working electrode in the range ±250 mV vs the E<sub>corr</sub>. The corrosion inhibition efficiency was evaluated using the data from EIS (η<sub>EIS</sub>%) and the PDP studies (η<sub>PDP</sub>%) as

\[
\eta_{EIS} = \frac{R_{ct} - R_{ct}^{MET}}{R_{ct}} \times 100
\]

\[
\eta_{PDP} = \frac{i_{corr}^{0} - i_{corr}^{MET}}{i_{corr}^{0}} \times 100
\]

where \( R_{ct} \) and \( R_{ct}^{MET} \) symbolize the blank and the inhibited charge transfer resistances, respectively; \( i_{corr}^{0} \) and \( i_{corr}^{MET} \) provide the corresponding corrosion current densities.

2.3. Molecular Simulation Details. 2.3.1. Molecular Dynamics (MD) Simulations. All MD simulations were conducted using the GROMACS 18.1 code and OPLS-AA force fields, which are successfully described kinds of systems. Systems were first energy minimized with the steepest descendent method to the convergence on the maximum force of 100 kJ/(mol nm). The particle mesh Ewald (PME) algorithm was applied to treat the electrostatic interactions, and a cutoff of 12 Å was used for van der Waals (VDW) and short-range electrostatic interactions. All bonds involving hydrogen atoms were constrained by the LINCS algorithm. The system was coupled to a thermal bath using a Nosé–Hoover thermostat with a time constant of 0.1 ps for equilibration and 0.5 ps for production. The pressure was controlled with a Parrinello–Rahman barostat with a time constant of 2 and 5 ps for equilibration and production, respectively. A time step of 2 fs was set for the simulations, and the coordinates were saved at 10 ps intervals.

2.3.2. Density Functional Theory Simulations. All density functional theory (DFT) simulations were carried out using the Vienna ab initio simulation package (VASP) version 5.4 with the projector augmented wave pseudopotentials (PAW) and the periodic boundary conditions. The Brillouin zone was sampled using gamma kpoint only as we use a large supercell and the Methfessel– Paxton smearing method with a width of 0.2 eV was used for the occupations of the electronic levels. The Perdew–Burke–Ernzerhof (PBE) functional within the generalized gradient approximation (GGA) was used to describe the electron interaction energy of exchange-correlation. The electronic energies were converged within the limit of 10⁻⁷ eV, and the cutoff of 520 eV was used. All geometries were optimized using the 0.01 eV/Å force criteria. All the calculations are spin-polarized. Through all the calculations, the DFT + D3 approach, developed by Grimme, was used for the long-range dispersion correction.

An iron slab of 16.22 × 12.16 dimension in x–y directions was generated with five layers of thickness, three of them were...
fixed, and two were allowed to relax during the geometric optimization. The Atom-in-Molecules (AIM) approach was used for the atomic charge analysis using Bader code developed by the Henkelman group. Further analysis of the wave function was done using the VASPKIT code. The adsorption energy of the metformin (MET) molecule was calculated as follows:

$$E_{ads} = E_{Fe\ slab@MET} - [E_{Fe\ slab} + E_{MET}]$$  \hspace{1cm} (3)

where $E_{Fe\ slab@MET}$ is the total energy of the Fe slab@MET complex, $E_{Fe\ slab}$ and $E_{MET}$ are the energies of Fe slab and MET, respectively.

### 3. RESULTS AND DISCUSSION

#### 3.1. Impedance Analysis of Corrosion Inhibitor Adsorption

The electrochemical measurement via impedance spectroscopy (EIS) is a nondestructive tool for the analysis of corrosion inhibitor films formed on metal surfaces. The EIS spectra provide an understanding of the charge and mass transfer processes occurring during the electrodissolution of the metal substrate exposed to the corrosive electrolyte. The Nyquist plots obtained for the C1018 steel during sweet corrosion in the CO$_2$-saturated 3.5 wt % NaCl + acetic acid solution without and with different concentrations of the MET inhibitor are depicted in Figure 2a. The steel substrate in the absence of MET shows a single depressed semicircle characteristic of the solid metallic electrolytes undergoing corrosion and is attributable to the charge transfer control of the electrochemical process. In the presence of MET, the depressed semicircle at a high frequency is followed by a Warburg diffusion phenomenon at a low frequency. Larger Nyquist loops are observed in the presence of MET, such that the loop size is directly proportional to the MET concentration. This signifies that MET imparts a significant resistance against the dissolution of the C1018 carbon steel during the sweet corrosion. The low-frequency diffusion phenomenon could be attributed to the movement of the inhibitor species from the bulk of the solution to the electrode surface and/or the movement of corrosion products from the interface to the bulk solution.

The Nyquist plots shown in (a) are identical to those observed in Figure 2d.e. The addition of the corrosion inhibitor enlarges the size of the phase angle and increases the value of absolute impedance. The rise in log $|Z|$ values upon the addition of the corrosion inhibitor to the corrosive solution supports the adsorption and the inhibition behavior of MET. These observations support the improvement in the capacitive performance of the adsorbed inhibitor film at the metal—solution interface. The equivalent circuit diagrams used for fitting the EIS data are displayed in Figure 2b,c for the steel in the blank and inhibited solutions, respectively. In Figure 2b, the circuit diagram consists of $R_{c}$ (the uncompensated resistance of the electrolyte) and $R_{ct}$ (the charge transfer resistance). A constant phase element (CPE) is used in place of an ideal double-layer capacitor to account for the surface inhomogeneity of the corroding metal surface. In such a case, the CPE impedance can be given by the equation.
the oxidation and reduction kinetics occurring at the steel surface during the sweet corrosion was analyzed using the potentiodynamic polarization (PDP) measure. Moreover, the more effective and compact adsorption in the presence of a higher MET concentration increases significantly in the presence of the inhibitor and reached 89% at the 200 ppm dosage. This MET adsorption on the steel surface increases the distance between the steel substrate and the reference electrode, hence the increased $R_i$ values in the presence of MET. The isolation of the steel surface from the corrosion agents also confers lower $Y_0$ values and translates to the reduction of charge and solution percolation at the steel–solution interface. Moreover, the more effective and compact adsorption in the presence of a higher MET concentration must be the reason that the diffusion phenomenon decreases, as seen from the lowering values of $W$ in Table 1.

### 3.2. Polarization Measurements

The effect of MET on the oxidation and reduction kinetics occurring at the steel–solution interface during the sweet corrosion was analyzed using the potentiodynamic polarization (PDP) measurements. The obtained PDP results are depicted in Figure 3 without and with the varying dosage of the inhibitor MET in CO2-saturated 3.5 wt % NaCl + acetic acid. The extrapolated polarization parameters, such as the corrosion potential ($E_{corr}$), corrosion current density ($i_{corr}$), and the anodic ($\beta_a$) and cathodic ($\beta_c$) Tafel constants are presented in Table 2. The values of the inhibition efficiency ($\eta$%), deduced according to eq 2, are also provided in Table 2.

![Potential vs. Ag/AgCl](image)

**Figure 3.** Potentiodynamic polarization curves recorded for the C1018 steel surface in the CO2-saturated 3.5 wt % NaCl + acetic acid solution without and with the different concentrations of the corrosion inhibitor MET.

### Table 1. Electrochemical Impedance Parameters Obtained in the Static Condition for the Adsorption of Inhibitor MET on the C1018 Steel Surface

| concn (ppm) | $R_i$ (Ω cm²) | $Y_0 \times 10^{-4}$ (S s⁻¹) | $n$ | $W$ (Ω s⁻¹ cm²) | $R_d$ (Ω cm²) | $\chi^2 \times 10^{-3}$ | $\eta$% |
|------------|----------------|-----------------------------|-----|----------------|----------------|----------------|--------|
| 0          | 2.397          | 1.020                       | 0.807| 11.90          | 149.1          | 0.199       | 68.32 ± 0.14 |
| 50         | 7.287          | 2.121                       | 0.710| 11.64          | 224.1          | 0.258       | 78.92 ± 1.75 |
| 100        | 7.061          | 1.94                         | 0.702| 10.12          | 321.4          | 0.242       | 85.30 ± 1.42 |
| 150        | 7.413          | 1.90                         | 0.609| 8.70           | 448.4          | 0.239       | 89.47 ± 1.42 |
| 200        | 8.200          | 1.55                         | 0.627| 7.87           | 697.2          | 0.216       | 90.72 ± 1.25 |

$Z_{CPE} = Y_0^{-1}(j\omega)^{-n}$

where $Y_0$ is the quantity of the CPE, $j$ is an imaginary unit ($j = -1^{1/2}$), $\omega$ is the angular frequency, and $n$ is the phase shift. However, the diffusion effect in the presence of MET compels the use of equivalence circuit as shown in Figure 2c, whereby a Warburg diffusion element ($W$) is introduced. The EIS parameters derived from the respective equivalent circuits are detailed in Table 1.

Results from Figure 2 suggest that MET adsorbs at the electrochemical interface and forms a protective film that retards the charge and the mass transfer occurring due to electrode dissolution of the steel. The corrosion inhibition efficiency was obtained using the values of the charge transfer resistance ($R_i$), according to eq 1. As can be seen from Table 1, the inhibition efficiency increased significantly in the presence of the inhibitor and reached 89% at the 200 ppm dosage. This MET adsorption on the steel surface increases the distance between the steel substrate and the reference electrode, hence the increased $R_i$ values in the presence of MET. The isolation of the steel surface from the corrosion agents also confers lower $Y_0$ values and translates to the reduction of charge and solution percolation at the steel–solution interface. Moreover, the more effective and compact adsorption in the presence of a higher MET concentration must be the reason that the diffusion phenomenon decreases, as seen from the lowering values of $W$ in Table 1.

### Table 2. Potentiodynamic Polarization Parameters for the Adsorption of MET on the C1018 Steel Surface

| concn (ppm) | $E_{corr}$ (mV/Ag/AgCl) | $i_{corr}$ (µA cm⁻²) | $\beta_a$ (mV/dec) | $\beta_c$ (mV/dec) | $\eta$% |
|------------|-------------------------|----------------------|------------------|------------------|--------|
| Blank      | −649                    | 47.70                | 13               | 17               |        |
| 50         | −687                    | 15.35                | 110              | 152              | 67.82  |
| 100        | −700                    | 10.82                | 121              | 146              | 77.32  |
| 150        | −726                    | 8.14                 | 124              | 121              | 82.94  |
| 200        | −745                    | 6.53                 | 140              | 123              | 86.31  |

The perusal of Figure 3 reveals that MET shifts the $E_{corr}$ values of the steel toward more cathodic potentials, from −649 (without MET) to −746 mV (with 200 ppm MET). There is a resultant decrease in the $i_{corr}$, from 47.70 (without MET) to 4.33 µA cm⁻² (with 200 ppm MET), and this yields an inhibition efficiency as high as 86.31%. Here, it is noteworthy to mention that this inhibition efficiency is considerably higher compared to that noted by earlier authors at higher concentrations. Furthermore, this high inhibition efficiency is remarkable considering that in the present study the investigations have been carried out in the presence of acetic acid, which is known to increase the corrosiveness of 3.5 wt % NaCl in the presence of CO2. Although the MET addition shifts the anodic and cathodic arms of the PDP curves toward lower values, it can be clearly seen that the effect of MET on the cathodic current is more obvious than its effect on the anodic current. MET can, therefore, be regarded as a more cathodic-type inhibitor. The higher $\beta_a$ and $\beta_c$ values, corresponding to lower $i_{corr}$ values, in Table 2 should also translate to a higher corrosion resistance based on the Stern–Geary equation shown as follows:

$$R_p = \frac{1}{i_{corr}} \left( \frac{\beta_a \beta_c}{2.303(\beta_a + \beta_c)} \right)$$

Given the sweet corrosion environment, it is well established that the cathodic and anodic reactions occurring at the steel surface involve hydrogen ion reduction and iron oxidation, respectively. The more significant effect on the cathodic phenomenon by MET indicates that the inhibitor impedes the steel corrosion by competing with the hydrogen ions for adsorption at the cathode. In this way, the inhibitor blocks the sink, which consumes electrons released via iron oxidation at the anode. It can be reasoned, therefore, that MET exists as a protonated species in the solution. This reasoning agrees well with the report of Singh et al., where Raman and NMR
characterizations confirmed that MET existed as a protonated species at very a low pH (<1.5). The effective blockage of cathodic sites on the steel surface by MET suppresses the electron flow from anodic sites where iron oxidation occurs. The overall effect is the reason that $i_{\text{corr}}$ diminishes in the presence of MET and the inhibition efficiency increases with the increasing MET concentration.

3.3. Adsorption Isotherm. The adsorption of an organic inhibitor molecule on the surface of metal can be properly understood using a suitable adsorption isotherm. The structural aspects of the corrosion inhibitor, the metal substrate under study, the temperature of the electrolyte, etc. present the parameters that control the interaction between a corrosion inhibitor and a given metallic substrate. Therefore, the data obtained via the EIS and the PDP studies were fitted to a number of adsorption isotherms. The most suitable fit was obtained in the case of the Langmuir isotherm that can be given as:

$$\frac{C}{\theta} = \frac{1}{K_{\text{ads}}} + C$$  \hfill (6)

where the terms $K_{\text{ads}}$, $C$, and $\theta$ represent the equilibrium constant for adsorption, the inhibitor concentration, and the surface coverage, respectively. The Langmuir isotherm assumes that the adsorbed film on the metallic surface has a thickness equal to one molecule in diameter. In addition, this isotherm assumes that all the equilibrium adsorption sites are similar and have equal affinity for the adsorbate and that there is no interaction between the adsorbed molecules, indicating the existence of homogeneous adsorption. Moreover, each adsorption site holds only one adsorbate molecule. The plots of the Langmuir adsorption isotherm are shown in Figure 4.

The slope and the regression coefficient are both close to unity, which satisfies the assumptions of the Langmuir adsorption isotherm. It can be observed that for both EIS and the PDP data, the slope and the regression coefficient are close to unity, which supports the validity of the Langmuir isotherm. The $K_{\text{ads}}$ was used to calculate the standard free energy of adsorption ($\Delta G_{\text{ads}}^0$):

$$\Delta G_{\text{ads}}^0 = -RT\ln(55.5K_{\text{ads}})$$  \hfill (7)

where the symbols $R$ and $T$ have their usual meaning, and the value 55.5 provides the molar concentration of water. The calculated $\Delta G_{\text{ads}}^0$ values from the EIS and PDP data are $-31.78$ and $-32.06$ kJ mol$^{-1}$, respectively, showing that the adsorption of the inhibitor molecules on the steel substrate obeys a mixed mode of physical and chemical adsorption.

3.4. Surface Analysis. The protective influence of MET on the steel samples was studied using scanning electron microscopy (SEM) investigations. The steel samples were immersed in the corrosive solution without and containing the 150 ppm dose of the inhibitor MET and then analyzed for the surface morphology. The results are displayed in Figure 5a,b. The steel surface without the inhibitor shows considerable surface damage due to the corrosive attack of the electrolyte. A number of cracks and the accumulations attributable to the corrosion products can be visualized in the morphology. Contrariwise, the inhibited sample shows an improved surface smoothness and homogeneity of the steel substrate. This indicates that MET is adsorbed on the metallic substrate and formed a film, which provided protection from the corrosion damage.

3.5. Computational Studies. Molecular dynamics simulations are conducted in a brine solution of NaCl (3.5 wt %) and at 373 K, which are relevant conditions for the environment in the oil & gas industry. MET is monoprotonated in a neutral aqueous solution and depending on its protonation position can form different tautomers, as shown in Figure 6. The pKa values of the mono- and diprotonated form of MET, which characterize its basicity, are 3.1 and 13.8. Therefore, MET is monoprotonated in a wide range of pH. Herein, we have focused on the dynamics of the monoprotonated forms (MET1, MET2, and MET3, see Figure 6). The molecular mechanic parameters of the OPLS-AA force field for MET are taken from Mondal et al. MD simulations are conducted for 300 ns.

The aim of these simulations is to examine the conformational diversity of MET tautomers, which might affect the adsorption simulations. Results shown in Figure 6, showing the superposition of 300 ns snapshot trajectories indicates that the skeleton of MET is quite rigid, and the three tautomers are planar except MET3 for which we have generated two conformations as explained in the DFT Simulation details section. Therefore, we proceed with our DFT simulations of...
the adsorption of MET tautomers using optimized structures of MET1, MET2, and two conformations of MET3.

Three tautomers of MET (MET1, MET2, and MET3) are considered similar to our MD simulations setup (see Figure 6). We have considered two conformations of MET3 (I and II) because this form is not planar, and we thought that the initial conformation might affect the adsorption simulation results. Therefore, we considered the conformation MET3-I as predicted by DFT optimization and MD simulations and another planar conformation MET3-II (see Figure 7) in which we forced the planarity of the molecular skeleton.

DFT simulation is a valuable tool to study the molecular mechanism of corrosion inhibition. DFT enables access to deeper insights into the adsorption phenomena and the accompanying electronic effects.\(^{78,79}\) Due to the important modifications that the corrosion inhibitor can induce on the metal surface, DFT is considered the best option to examine these aspects. Other empirical potentials used in the literature cannot afford such informational flow because it neglects the electronic effects and considered the atoms as hard spheres carrying fixed charges. Therefore, any changes in the charge density at the interface cannot be captured by these empirical potentials. Nevertheless, these potentials are efficient for large-scale simulations. In contrast, DFT simulations of the inhibitor adsorption on the metal surface can capture the details of many phenomena that take place at the interface metal@molecule. By using DFT, we can have access to more accurate adsorption energies that can be compared with the experimental counterpart, the charge transfer at the interface, detailed molecule interactions, and the work function modification of the metal surface. Having all this in hand assembled with the experimental data, we can explain the mechanism of the inhibition and perform the rational design of more potent inhibitors.\(^{80–82}\)

Periodic DFT simulations are employed in order to examine the adsorption of the MET molecule on the Fe slab (100). First, we have optimized the three tautomers of MET (MET1, MET2, MET3-I, and MET3-II) on the Fe slab, as depicted in Figure 7. We focused on the parallel conformation as the axial conformations do not show a significant adsorption capacity compared to the parallel one. The adsorption energies of MET1, MET2, MET3-I, and MET3-II, are \(-3.91\), \(-4.47\), \(-3.00\), and \(-2.92\) eV, respectively. The adsorption energies indicate a favorable and spontaneous binding between the Fe slab and MET tautomers, whatever its protonation form. This is in agreement with the experimental free energy of adsorption estimated using the Langmuir isotherm. However, the adsorptions of MET1 and MET2 are the dominant adsorbed forms on the steel surface. Concerning MET3, starting with
different conformations are converged to almost the same structure without any considerable difference in the adsorption energies.

The charge density binding analysis depicted in Figure 8 put in evidence of the chemisorption nature of MET tautomers as there is accumulation of electronic density between Fe−C and Fe−N bonds. The Fe−C and Fe−N bond distances in most cases are around 2.0 Å, which supports the covalent nature of MET−Fe interaction (see Figure 8). The strength of the adsorption does not only reflect the origin from a covalent interaction between Fe with C and N atoms but also from the strong electrostatic interactions at their interface. In order to gain deeper insights into the electronic flow along the Fe slab@MET interface, we have calculated the atomic charges using the AIM approach, using the Bader code as detailed in the experimental section. The calculation of atomic charges (see Figure S1 and Table S1) clearly shows a charge transfer. First, the covalent interaction between Fe with C and N atoms of MET resulted from the hybridization of p orbitals of the adsorbate and d orbitals of Fe atoms, and so the electronic donation comes from the adsorbate to the vacant d orbital of Fe atoms.

This electronic transfer is accompanied by a back-donation from the occupied d orbitals of Fe atoms into the vacant orbital of C atoms of the adsorbate. Indeed, the total charge of the adsorbate in all the considered conformations is negative, which highlights that the back-donation dominated the total electronic flow at the metal@adsorbate interface. Actually, in the case of Fe slab@MET1 and Fe slab@MET2, Fe slab has a total charge of 0.74 and 0.77 e, respectively; this indicates that there are 0.74, and 0.77 e transferred from the metal surface to the adsorbate. In the case of MET3-I and MET-II, only 0.25 and 0.24 e are transferred from the slab to the adsorbate. As we can observe, the adsorption strength is correlated well with the amount of charge transfer from the metal surface to the adsorbate, which leads to higher polarization at the slab@adsorbate interface that boosts up the electrostatic interaction between the molecule and the slab. The presence of two NH2 groups (MET3) makes the interaction between MET3 and the slab limited to only Fe−N interactions.

The atomic charges reported in Table S1 and visualized on the molecular models depicted in Figure S1 put in evidence of the effect of MET tautomers adsorption on the polarity of the iron slab. In a clean Fe slab, the surface is highly polarized with the accumulation of the negative charges close to the surface. However, upon adsorption, this polarization almost disappeared and localized at the interface between the metal surface and the MET molecule. Also, in Figure S1, the color of N

![Figure 7. DFT molecular models used in adsorption simulations. (a) Overview of the Fe slab and the adsorbate with 25 Å vacuum to ensure that there is no interaction between the slab and its image along the c-lattice constant. The initial and the optimized structures of MET1 (b & f), MET2 (c & g), MET3-I (d & h), and MET3-II (e & i) complexes. Color-code, C: brown, N: blue, and H: white. Fe: dark golden.](https://dx.doi.org/10.1021/acsomega.0c03364)

![Figure 8. Binding charge densities of (a) MET1, (b) MET2, and (c) MET3-I on the Fe slab (100). The isosurfaces is represented in a resolution of 0.003 electron/Å³. Yellow is rich, and light-blue is the depletion of the electron density. The Fe slab is represented by dark golden spheres, MET tautomers are represented in balls and sticks. Color code, C: brown, N: blue, and H: white.](https://dx.doi.org/10.1021/acsomega.0c03364)
atoms is blue, which indicates that the electron transfer is mainly to C atoms.

We have further calculated the work function of the clean surface and the complex with the three tautomers of MET molecule in order to link its structure with its inhibition efficiency. The work function ($\phi$) is defined as the minimum energy required to extract an electron from the metal surface or the energy required to move an electron from the Fermi level into a vacuum.

$$\Phi = \Phi_{\text{vac}} - E_F$$  \hspace{1cm} (8)

where $\Phi_{\text{vac}}$ is the electrostatic potential in the vacuum region, and $E_F$ is the fermi level. The planar average of the electrostatic potential ($\Phi_{\text{vac}}$) along the Z axis for the three tautomeric forms of MET molecule adsorbed on the Fe slab, and the clean slab is shown in Figure 9. The work function was calculated using 25 Å as a vacuum, and it was found to be 3.52 eV for MET1, 3.40 eV for MET2, 3.30 eV MET3-I, and 3.82 eV for the clean iron slab (Exp. is 4.67 eV).83 First, it is worth noting that the PBE functional is underestimating the work function of the metal surfaces, and it depends on the number of slab layers that increases the cost of the calculations; however, we herein are interested in the relative trend of the work function rather than the absolute values. It is clear that the inhibition efficiency of MET tautomers is not related to its ability to change the level of the valence band and, consequently, its work function. The inhibition capacity of MET is originating from its adsorption on a thin film that prevents the fluid from the corrosion environment to penetrate to the slab. MET is a donor/acceptor of hydrogen bonds, which supports its capacity to also form multilayers adsorbed on the Fe slab.

Altogether, DFT simulations supported that the adsorption of MET tautomers (monoprotonated form) is chemical in nature rather than physical. An accumulation of the electron density at the Fe slab@MET interface along Fe−C and Fe−N bonds evidences the chemisorption of the molecule. Furthermore, the electron transfer from the metal surface to the adsorbate boosted up the electrostatic interaction between the slab and adsorbate, which enhances its stability. The calculation of the work function of the Fe@MET complexes showed that the origin of MET corrosion capacity is due to the formation of an adsorbed thin film that prevents the penetration of the corrosion fluid into the iron surface. Indeed, MET does not lead to change the work function of Fe slab significantly, which rules out that MET modifies the positions of the valence band of the slab.

**3.6. Mechanisms of Corrosion and Inhibition.** During the sweet corrosion of steel, the dissociation of carbon dioxide (CO$_2$) takes place in the aqueous solution to yield carbonic acid (H$_2$CO$_3$). The latter being diprotic undergoes further dissociation in a two-step process to produce HCO$_3^-$, and CO$_2^-$:8,84,85

$$\text{CO}_2(g) + \text{H}_2\text{O}(l) \rightarrow \text{H}_2\text{CO}_3(aq)$$  \hspace{1cm} (9)

$$\text{H}_2\text{CO}_3(aq) \rightarrow \text{H}^+ + \text{HCO}_3^-(aq)$$  \hspace{1cm} (10)

$$\text{HCO}_3^-(aq) \rightarrow \text{H}^+ + \text{CO}_2^-(aq)$$  \hspace{1cm} (11)

A number of mechanisms have been proposed in the literature to explain the mechanism of corrosion and dissolution of steel in aqueous deaerated solutions of CO$_2$.8

The primary cathodic reactions for the corrosion of steel is the hydrogen evolution, which can be represented via three different modes as

$$2\text{H}_2\text{O}(aq) + 2e^- \rightarrow \text{H}_2(g)$$  \hspace{1cm} (12)

$$2\text{H}_2\text{CO}_3(aq) + 2e^- \rightarrow \text{H}_2(g) + 2\text{HCO}_3^-(aq)$$  \hspace{1cm} (13)

$$2\text{HCO}_3^-(aq) + 2e^- \rightarrow \text{H}_2(g) + 2\text{CO}_2^-(aq)$$  \hspace{1cm} (14)

On the other hand, the primary anodic process is the anodic oxidation of the Fe metal, which can be given as

$$\text{Fe}(s) \rightarrow \text{Fe}^{2+}(aq) + 2e^-$$  \hspace{1cm} (15)

The 3.5 wt % NaCl solution containing the acetic acid under the condition of the CO$_2$-saturated environment presents a corrosive acidic medium. The inhibitor molecule when introduced to this acidic medium, can undergo protonation according to the equilibrium shown below:86

$$\text{MET}_{\text{neutral}} \rightleftharpoons \text{MET}_{\text{protonated}}$$  \hspace{1cm} (16)

The organic corrosion inhibitors generally act by adsorbing at the electrochemical interface. The support for this hypothesis in the present case was obtained via the EIS study, which revealed a rise in the charge transfer resistance. The lowering in the corrosion current densities observed in the PDP measurements also supports the inhibitor adsorption at the metal−electrolyte interface. In addition, the spontaneous adsorption of MET is predicted experimentally (Langmuir isotherm) and theoretically using DFT simulations. MET can form a strong multilayer structure on the steel surface; MET itself is carrying a positive charge, which upon its adsorption can attract Cl$^-$ ions that attract other MET molecules in a sandwich manner. The inhibitor molecules adsorb by replacing the water molecules that are already adsorbed at the metal surface which can be shown as:83,87

$$\text{MET} + M\text{H}_2\text{O} \rightleftharpoons M\text{MET} + \text{H}_2\text{O}$$  \hspace{1cm} (17)

The protonated inhibitor can move towards the cathodic corrosion active sites present at the metallic substrate and adsorb via electrostatic attraction. This is revealed in the present case in the form of the cathodic nature of the PDP results. Furthermore, the protonated inhibitor can also interact with the Cl$^-$ ions that are already adsorbing at the positively charged steel surface via a bridge type of Coulombic interaction. This can explain the lowering in the anodic/cathodic corrosion currents in the PDP studies. The adsorption of the corrosion inhibitor at the metallic substrate,
when investigated by the SEM measurements, revealed a smooth surface morphology. This observation supports the efficient metal surface coverage by MET. Based on the above discussion, the adsorption and the inhibition behavior of MET is demonstrated schematically in Figure 10.

Figure 10. Mechanism of adsorption and inhibition of MET on the carbon steel surface.

3.7. Comparison with Earlier Reports. A number of organic corrosion inhibitors have been explored earlier to mitigate and minimize the sweet corrosion of steel. Herein, we have carried out a comparison of the performance of the earlier reported sweet corrosion inhibitors with MET and the data shown in Table 3. It is revealed that the present inhibitor shows significant protection performance at a dose comparatively lower than most reported doses. This observation becomes more important considering the presence of acetic acid in the corrosion solution, which makes the medium more aggressive. Furthermore, the other listed inhibitors are laboratory-synthesized organic compounds that involve skilled organic chemists and organic synthesis setup. Contrariwise, the present corrosion inhibitor is an easily available drug which due to being past its expiry date, is quite cheaply available. Therefore, from the experimentally obtained results and Table 3, it is obvious that MET presents as a novel and effective inhibitor for application in the oil and gas industry.

4. CONCLUSIONS

An expired drug metformin (MET) was analyzed as a novel corrosion inhibitor for carbon steel in sweet condition, i.e., 3.5 wt % NaCl saturated with CO₂ containing acetic acid. A detailed investigation was carried out using electrochemical measurements supported by surface analysis. A high inhibition efficiency of ~90% at 200 ppm was obtained. The major conclusions of the study are given below:

1. The EIS data revealed an elevation in the charge transfer resistance with the inhibitor dose, supporting MET adsorption on the carbon steel substrate. PDP studies revealed a cathodic predominance of the inhibitor performance.
2. MET adsorption obeyed the Langmuir isotherm with high values of ΔG_{ads}°, indicating a mixed mode of physical and chemical adsorption.
3. Significantly smooth and uniform surface morphology was revealed with the adsorbed inhibitor, indicating the adsorption and film formation behavior of MET.
4. MD studies revealed planar geometries of the three tautomeric forms of MET.
5. The charged nature of the monoprotonated MET tautomers gave a high possibility of multilayer deposition on the metal surface using Cl⁻ ions to bridge MET layers, which prevented the aggressive attack of the corrosive electrolyte on the steel surface.
6. DFT simulations predicted spontaneous adsorption of MET on the steel surface and indicated a predominance of the chemical adsorption of inhibitor involving C and N atoms. In addition, it was noted that the back-donation of electrons from the Fe surface to the inhibitor enhances the stability of the inhibitor film.
7. MET adsorption does not modify the position of the valence band of the metal surface, supporting the result that the inhibitor functions by forming a protective thin film.

Table 3. Comparison of the Performance of Sweet Corrosion Inhibitors Reported Earlier with the MET

| inhibitor | metal   | I.E. % | inhibitor dose (ppm) | reference |
|-----------|---------|--------|----------------------|-----------|
| hexamethylene-1,6-bis(N-D-glucopyranosylamine) | API X60 steel | 91.8 | 100 | 20 |
| chitosan Schiff base | J55 steel | 95.4 | 150 | 21 |
| 1,2,4,7,9,10-hexazacyclo-pentadeca-10,15-dien-3,5,6,8-tetraone | J55 steel | 93 | 400 | 22 |
| N,N′-(pyridine-2,6-diyl)bis(1-(4-methoxyphenyl)methanimine) | N80 steel | 72.1 | 400 | 88 |
| 2-(4-methoxyphenyl)-4,5-diphenyl-imidazole | J55 steel | 90.0 | 400 | 89 |
| 1,3-bis(4-methoxyphenyl)-2-(4-methoxyphenyl)imidazolidine | J55 steel | 92.0 | 400 | 90 |
| MET | C1018 steel | 89.47 | 200 | Present work |

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c03364.

Molecular models of Fe slab@adsorbate (Figure S1) and atomic charges calculated using the Bader analysis (Table S1) (PDF)

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M.A.Q. and I.B.O. conceptualized the research; I.B.O. and D.S.C. performed the electrochemical and surface characterization experiments; S.A.A. conducted computational modeling. All authors contributed in the writing of the manuscript.

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REFERENCES
(1) Quraishi, M. A.; Chauhan, D. S.; Saji, V. S. Heterocyclic Organic Corrosion Inhibitors: Principles and Applications; Elsevier Inc.: Amsterdam, 2020.
(2) Kermani, M. B.; Morshed, A. Carbon Dioxide Corrosion in Oil and Gas Production—a Compendium. Corrosion 2003, 59, 659−683.
(3) Moseeva, L. S. Carbon Dioxide Corrosion of Oil and Gas Field Equipment. Prot. Met. 2005, 41, 76−83.
(4) Nelisić, S. Key Issues Related to Modelling of Internal Corrosion of Oil and Gas Pipelines—a Review. Corros. Sci. 2007, 49, 4308−4338.
(5) Kahyarian, A.; Brown, B.; Nelisić, S. Electrochemistry of CO2 Corrosion of Mild Steel: Effect of CO2 on Cathodic Currents. Corrosion 2018, 74, 851−859.
(6) Kahyarian, A.; Singer, M.; Nesic, S. Modeling of Uniform CO2 Corrosion of Mild Steel in Gas Transportation Systems: A Review. J. Nat. Gas Sci. Eng. 2016, 29, 530−549.
(7) Guan, X.; Hu, Y. Imidazoline Derivatives: A Patent Review (2006−Present). Expert Opin. Ther. Pat. 2012, 22, 1353−1365.
(8) Usman, B. J.; Ali, S. A. Carbon Dioxide Corrosion Inhibitors: A Review. Arab J. Sci. Eng. 2018, 43, 1−22.
(9) OSPAR Commission. Protocols on Methods for the Testing of Chemicals Used in the Offshore Oil Industry. Offshore Oil Gas Ind. 2005, 237.
(10) OSHA, U. Globally Harmonized System of Classification and Labelling of Chemicals (GHS). U. N. Econ. Comm. Eur. 2013, 224.
(11) Gece, G. Drugs: A Review of Promising Novel Corrosion Inhibitors. Corros. Sci. 2011, 53, 3873−3898.
(12) Vasilicin, N.; Ordrodi, V.; Borna, A. Corrosion Inhibitors from Expired Drugs. Int. J. Pharm. 2012, 431, 241−244.
(13) Singh, P.; Chauhan, D. S.; Chauhan, S. S.; Singh, G.; Quraishi, M. A. Chemically Modified Expired Dapsone Drug as Environmentally Benign Corrosion Inhibitor for Mild Steel in Sulphuric Acid Useful for Industrial Pickling Process. J. Mol. Liq. 2019, 286, 110903.
(14) Chauhan, D. S.; Sorour, A. A.; Quraishi, M. A. An Overview of Expired Drugs as Novel Corrosion Inhibitors for Metals and Alloys. Int. J. Chem. Pharm. Sci. 2016, 4, 680−691.
(15) Singh, P.; Chauhan, D. S.; Srivastava, K.; Srivastava, V.; Quraishi, M. A. Expired Atorvastatin Drug as Corrosion Inhibitor for Mild Steel in Hydrochloric Acid Solution. Int. J. Ind. Chem. 2017, 8, 363−372.
(16) Dohare, P.; Chauhan, D. S.; Quraishi, M. A. Expired Podocip Drug as Potential Corrosion Inhibitor for Carbon Steel in Acid Chloride Solution. Int. J. Corros. Scale Inhib. 2018, 7, 25−37.
(17) Dohare, P.; Chauhan, D. S.; Sorour, A. A.; Quraishi, M. A. DFT and Experimental Studies on the Inhibition Potentials of Expired Tramadol Drug on Mild Steel Corrosion in Hydrochloric Acid. Mater. Discov. 2017, 9, 30−41.
(18) Singh, A.; Ebenso, E. E.; Quraishi, M. A. Theoretical and Electrochemical Studies of Metformin as Corrosion Inhibitor for Mild Steel in Hydrochloric Acid Solution. Int. J. Electrochem. Sci. 2012, 7, 4766−4779.
(19) Haruna, K.; Saleh, T. A.; Quraishi, M. A. Expired Metformin Drug as Green Corrosion Inhibitor for Simulated Oil/Gas Well Acidizing Environment. J. Mol. Liq. 2020, 113716.
(20) Onyeachu, I. B.; Chauhan, D. S.; Ansari, K. R.; Obot, I. B.; Quraishi, M. A.; Alamri, A. H. Hexamethylene-1, 6-Bis (N−D-Gluco pyranosylamine) as a Novel Corrosion Inhibitor for Oil and Gas Industry: Electrochemical and Computational Analysis. New J. Chem. 2019, 43, 7282−7293.
(21) Ansari, K. R.; Chauhan, D. S.; Quraishi, M. A.; Mazumder, M. A. J.; Singh, A. Chitosan Schiff Base: An Environmentally Benign Biological Macromolecule as a New Corrosion Inhibitor for Oil & Gas Industries. Int. J. Biol. Macromol. 2020, 144, 305−315.
(22) Singh, A.; Lin, Y.; Obot, I. B.; Ebenso, E. E.; Ansari, K. R.; Quraishi, M. A. Corrosion Mitigation of J55 Steel in 3.5% NaCl Solution by a Macrocyclic Inhibitor. Appl. Surf. Sci. 2015, 356, 341−347.
(23) Chauhan, D. S.; Mazumder, M. A. J.; Quraishi, M. A.; Ansari, K. R. Chitosan-Cinnamaldehyde Schiff Base: A Bioinspired Macromolecule as Corrosion Inhibitor for Oil and Gas Industry. Int. J. Biol. Macromol. 2020, 158, 127−138.
(24) Chauhan, D. S.; Mazumder, M. A. J.; Quraishi, M. A.; Ansari, K. R.; Suleiman, R. K. Microwave-Assisted Synthesis of a New Piperonal-Chitosan Schiff Base as a Bio-Inspired Corrosion Inhibitor for Oil−Well Acidizing. Int. J. Biol. Macromol. 2020, 158, 231−243.
(25) Chauhan, D. S.; Ansari, K. R.; Sorour, A. A.; Quraishi, M. A.; Lgzaz, H.; Salghi, R. Thiosemicarbazide and Thiocarboxylhydrazone Functionalized Chitosan as Ecofriendly Corrosion Inhibitors for Carbon Steel in Hydrochloric Acid Solution. Int. J. Biol. Macromol. 2018, 107, 1747−1757.
(26) Chauhan, D. S.; Mouaed, K. E.; Quraishi, M. A.; Bazzi, L. Aminotriaezolothio-Fuctionalized Chitosan as a Macromolecule-Based Bioinspired Corrosion Inhibitor for Surface Protection of Stainless Steel in 3.5% NaCl. Int. J. Biol. Macromol. 2020, 152, 234−241.
(27) Hess, B.; Kutzner, C.; Van Der Spoel, D.; Lindahl, E. Gromacs 4: Algorithms for Highly Efficient, Load-Balanced, and Scalable Molecular Simulation. J. Chem. Theory Comput. 2008, 4, 435−447.
(28) Jorgensen, W. L.; Tirado-Rives, J. The Opls [Optimized Potentials for Liquid Simulations] Potential Functions for Proteins, Energy Minimizations for Crystals of Cyclic Peptides and Crambin. J. Am. Chem. Soc. 1988, 110, 1657−1666.
(29) Jorgensen, W. L.; Maxwell, D. S.; Tirado-Rives, J. Development and Testing of the Opls All-Atom Force Field on Conformational Energetics and Properties of Organic Liquids. J. Am. Chem. Soc. 1996, 118, 11225−11236.
(30) Berendsen, H. J. C.; Grigera, J. R.; Straatsma, T. P. The Missing Term in Effective Pair Potentials. J. Phys. Chem. 1987, 91, 6269−6271.
(31) Abdel-Azeim, S.; Kanj, M. Y. Dynamics, Aggregation, and Interfacial Properties of the Partially Hydrolyzed Polyacrylamide
Polymer for Enhanced Oil Recovery Applications: Insights from Molecular Dynamics Simulations. *Energy Fuels* **2018**, *32*, 3335–3343.

(30) Boțan, V.; Ustach, V.; Faller, R.; Leonhard, K. Direct Phase Equilibrium Simulations of Napim Oligomers in Water. *J. Phys. Chem. B* **2016**, *120*, 3434–3440.

(31) Mahi, A.; Hu, D.; Chou, K. C. Complex Formations between Surfactants and Polyelectrolytes of the Same Charge on a Water Surface. *Langmuir* **2017**, *33*, 7940–7946.

(34) Darden, T.; York, D.; Pedersen, L. Particle Mesh Ewald: An N·Log (N) Method for Ewald Sums in Large Systems. *J. Chem. Phys.* **1993**, *98*, 10089–10092.

(35) Hess, B.; Bekker, H.; Berendsen, H. J. C.; Fraaije, J. G. E. M. Lincs: A Linear Constraint Solver for Molecular Simulations. *J. Comput. Chem.* **1997**, *18*, 1463–1472.

(36) Nose, S. A Unified Formulation of the Constant Temperature Molecular Dynamics Methods. *J. Chem. Phys.* **1984**, *81*, 511–519.

(37) Hoover, W. G. Canonical Dynamics: Equilibrium Phase-Space Distributions. *Phys. Rev. A* **1985**, *31*, 1695.

(38) Martoňák, R.; Liao, A.; Parrinello, M. Predicting Crystal Structures: The Parrinello-Rahman Method Revisited. *Phys. Rev. Lett.* **2003**, *90*, No. 075503.

(39) Kresse, G.; Hafner, J. Ab Initio Molecular Dynamics for Liquid Metals. *Phys. Rev. B* **1993**, *47*, 558.

(40) Kresse, G.; Hafner, J. Ab Initio Molecular-Dynamics Simulation of the Liquid-Metal–Amorphous-Semiconductor Transition in Germanium. *Phys. Rev. B* **1994**, *49*, 14251.

(41) Böchli, P. E. Projector Augmented-Wave Method. *Phys. Rev. B* **1994**, *50*, 17953.

(42) Monkhorst, H. J.; Pack, J. D. Special Points for Brillouin-Zone Integrations. *Phys. Rev. B* **1976**, *13*, 5188.

(43) Methfessel, M.; Paxton, A. T. High-Precision Sampling for Brillouin-Zone Integration in Metals. *Phys. Rev. B* **1989**, *40*, 3616.

(44) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77*, 3865.

(45) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. A Consistent and Accurate Ab Initio Parametrization of Density Functional Dispersion Correction (DFT-D) for the 94 Elements H-Pu. *J. Chem. Phys.* **2010**, *132*, 154104.

(46) Tang, W.; Sanville, E.; Henkelman, G. A Grid-Based Bader Analysis Algorithm without Lattice Bias. *J. Phys.: Condens. Matter* **2009**, *21*, No. 084204.

(47) Sanville, E.; Kenny, S. D.; Smith, R.; Henkelman, G. Improved Grid-Based Algorithm for Bader Charge Allocation. *J. Comput. Chem.* **2007**, *28*, 899–908.

(48) Yu, M.; Trinkle, D. R. Accurate and Efficient Algorithm for Bader Charge Integration. *J. Chem. Phys.* **2011**, *134*, No. 064111.

(49) Wang, X.; Xu, N.; Liu, J.-C.; Tang, G.; Geng, W.-T. Vaspkit: A Pre-and Post-Processing Program for Vasp Code. *arXiv preprint arXiv* 2019, 1908.08269.

(50) Marcus, P.; Mansfeld, F. B., *Analytical Methods in Corrosion Science and Engineering*; CRC press, 2005, DOI: 10.1201/9781420028331.

(51) Khadiri, A.; Saddik, R.; Bekkouche, K.; Aouniti, A.; Hammouri, B.; Benchat, N.; Bouchachrie, M.; Solmaz, R. Gravimetric, Electrochemical and Quantum Chemical Studies of Some Pyridazine Derivatives as Corrosion Inhibitors for Mild Steel in 1 M HCl Solution. *J. Taiwan Inst. Chem. Eng.* **2019**, *59*, 108140.

(52) Obot, I. B.; Onyechu, I. B.; Umoren, S. A. Alternative Corrosion Inhibitor Formulation for Carbon Steel in CO2-Saturated Brine Solution under High Turbulent Flow Condition for Use in Oil and Gas Transportation Pipelines. *Corros. Sci.* **2019**, *159*, 108140.

(53) Yadav, D. K.; Chauhan, D. S.; Ahmad, I.; Quraishi, M. A. Electrochemical Behavior of Steel/Acid Interface: Adsorption and Inhibition Effect of Oligomeric Aniline. *RSC Adv.* **2013**, *3*, 632–646.

(54) Yadav, D. K.; Quraishi, M. A. Electrochemical Investigation of Substituted Pyranopyrazoles Adsorption on Mild Steel in Acid Solution. *Ind. Eng. Chem. Res.* **2012**, *51*, 8194–8210.

(55) Singh, P.; Chauhan, D. S.; Chauhan, S. S.; Singh, G.; Quraishi, M. A. Bioinspired Synergistic Formulation from Dihydropropyridi-...
(73) Baig, N.; Chauhan, D. S.; Saleh, T. A.; Quraishi, M. A. Diethylenetriamine Functionalized Graphene Oxide as a Novel Corrosion Inhibitor for Mild Steel in Hydrochloric Acid Solutions. *New J. Chem.* 2019, 43, 2328–2337.

(74) Haque, J.; Srivastava, V.; Chauhan, D. S.; Quraishi, M. A.; Kumar, A. M.; Lgaz, H. Electrochemical and Surface Studies on Chemically Modified Glucose Derivatives as Environmentally Benign Corrosion Inhibitors. *Sustainable Chem. Pharm.* 2020, 16, 100260.

(75) Orgován, G.; Noszály, B. Electrodeless, Accurate Ph Determination in Highly Basic Media Using a New Set of 1H Nmr Ph Indicators. *J. Pharm. Biomed. Anal.* 2011, 54, 958–964.

(76) Langmaier, J.; Pišl, M.; Samec, Z.; Zálší, S. Extreme Basicity of Biguanide Drugs in Aqueous Solutions: Ion Transfer Voltammetry and DFT Calculations. *J. Phys. Chem. A* 2016, 120, 7344–7350.

(77) Mondal, S.; Samajdar, R. N.; Mukherjee, S.; Bhattacharyya, A. J.; Bagchi, B. Unique Features of Metformin: A Combined Experimental, Theoretical, and Simulation Study of Its Structure, Dynamics, and Interaction Energies with DNA Grooves. *J. Phys. Chem. B* 2018, 122, 2227–2242.

(78) Kokalj, A. Formation and Structure of Inhibitive Molecular Film of Imidazole on Iron Surface. *Corros. Sci.* 2013, 68, 195–203.

(79) Gustinc, D.; Kokalj, A. A DFT Study of Adsorption of Imidazole, Triazole, and Tetrazole on Oxidized Copper Surfaces: Cu2O(111) and Cu2O(111)-w/o-CuCl. *Phys. Chem. Chem. Phys.* 2015, 17, 28602–28615.

(80) Abdulazeez, I.; Zeino, A.; Kee, C. W.; Al-Saadi, A. A.; Khaleed, M.; Wong, M. W.; Al-Sunaidi, A. A. Mechanistic Studies of the Influence of Halogen Substituents on the Corrosion Inhibitive Efficiency of Selected Imidazole Molecules: A Synergistic Computational and Experimental Approach. *Appl. Surf. Sci.* 2019, 471, 494–505.

(81) Radilla, J.; Negrón-Silva, G. E.; Palomar-Pardavé, M.; Romero-Romo, M.; Galván, M. Dft Study of the Adsorption of the Corrosion Inhibitor 2-Mercaptimidazole onto Fe (1 0 0) Surface. *Electrochim. Acta* 2013, 112, 577–586.

(82) Guo, L.; Qi, C.; Zheng, X.; Zhang, R.; Shen, X.; Kaya, S. Toward Understanding the Adsorption Mechanism of Large Size Organic Corrosion Inhibitors on an Fe (110) Surface Using the Dftb Method. *RSC Adv.* 2017, 7, 29042–29050.

(83) Hökel, J.; Schulte, F. K., Work Function of Metals. In *Solid Surface Physics*, Springer: 1979; pp 1–150.

(84) Mazumder, M. A. J.; Al-Muallem, H. A.; Ali, S. A. The Effects of N-Pendants and Electron-Rich Amidine Motifs in 2-(P-Alkoxophenyl)-2-Imidazolines on Mild Steel Corrosion in CO2-Saturated 0.5 M NaCl. *Corros. Sci.* 2015, 90, 54–68.

(85) Mazumder, M. A. J.; Al-Muallem, H. A.; Faiz, M.; Ali, S. A. Design and Synthesis of a Novel Class of Inhibitors for Mild Steel Corrosion in Acidic Carbon Dioxide-Saturated Saline Media. *Corros. Sci.* 2014, 87, 187–198.

(86) Haque, J.; Srivastava, V.; Chauhan, D. S.; Lgaz, H.; Quraishi, M. A. Microwave-Induced Synthesis of Chitosan Schiff Bases and Their Application as Novel and Green Corrosion Inhibitors: Experimental and Theoretical Approach. *ACS Omega* 2018, 3, 5654–5668.

(87) Solmaz, R.; Kardag, G.; Cahla, M.; Yazici, B.; Erbil, M. Investigation of Adsorption and Inhibitive Effect of 2-Mercaptotiazoline on Corrosion of Mild Steel in Hydrochloric Acid Media. *Electrochim. Acta* 2008, 53, 5941–5952.

(88) Singh, A.; Ansari, K. R.; Xu, X.; Sun, Z.; Kumar, A.; Lin, Y. An Impending Inhibitor Useful for the Oil and Gas Production Industry: Weight Loss, Electrochemical, Surface and Quantum Chemical Calculation. *Scientific reports* 2017, 7, 14904.

(89) Singh, A.; Ansari, K. R.; Liu, W.; Songsong, C.; Lin, Y. Electrochemical, Surface and Quantum Chemical Studies of Novel Imidazole Derivatives as Corrosion Inhibitors for J55 Steel in Sweet Corrosive Environment. *J. Alloys Compd.* 2017, 712, 121–133.

(90) Singh, A.; Ansari, K. R.; Lin, Y.; Quraishi, M. A.; Lgaz, H.; Chung, I.-M. Corrosion Inhibition Performance of Imidazolinederivatives for J55 Pipeline Steel in Acidic Oilfield Formation Water: Electrochemical, Surface and Theoretical Studies. *J. Taiwan Inst. Chem. Eng.* 2019, 95, 341–356.