Original Article

Evaluation of corrosion inhibition performance of phosphorus polymer for carbon steel in [1 M] HCl: Computational studies (DFT, MC and MD simulations)

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Pentaglycidyl ether pentabisphenol A of phosphorus (PGEPBAP) phosphorus polymer was investigated as corrosion inhibition for carbon steel in aggressive solution using potentiodynamic polarization (PDP), electrochemical impedance spectroscopy (EIS), weight loss (WL), scanning electron microscope (SEM), density functional theory (DFT), electrostatic potential (ESP), radial distribution function (RDF), molecular dynamics (MD) and Monte Carlo (MC) simulations. The higher inhibition efficiencies for PDP, EIS and WL studies at 10−3 M concentration of PGEPBAP phosphorus polymer are 94.18 %, 91.79 % and 91.3 %, respectively. ΔECorr (23.7 mV) value of PGEPBAP phosphorus polymer is lower than 85 mV has been assigned to mixed type inhibitor. PGEPBAP formed protective film on carbon steel surface by adsorption according to Langmuir adsorption isotherm. SEM morphology suggested that PGEPBAP could effectively block acid attack by chemisorption on metal surface. To evaluate the polymer inhibitor and potential mechanism were especially realized DFT, ESP, RDF, MD and MC simulations.

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1. Introduction

Carbon steel is among the most interesting materials in the industry due to their high availability and physico-chemical...
characteristics and thier relatively low cost [1–3]. These characteristics ensure that carbon steel is extensively utilized in several fields of applications such as chemical treatment, spatial construction, metal processing, seawater and petroleum refining [4–6]. The corrosion of substrates could be prevented or minimized by introducing phosphorus polymers compounds into aggressive environment [7]. Then, the addition of polymers chemicals compounds in corrosive solution (HCl, H2SO4, H3PO4 and HNO3) are designated as corrosion inhibitor by protective layer formation on the steel surface and this form of corrosion protection is referred to as inhibition [8–10]. In addition, phosphorus polymers are adsorbed on the steel surface, whether by physisorption, chemisorption and/or physicochemical adsorption [11–13]. The chemical adsorption distributes or transmits the load from the phosphorus polymers to the metal surface, resulting in the development of a coordinated type covalent bond. However, the physical adsorption is Van der Waals and electrostatic interaction between the loaded phosphorus polymers and the metal surface of the contaminated metal [14]. Phosphorus polymers having active centers (especially heteroatoms such as O, N and S), aromatic rings, epoxide groups, phosphorus atoms and e-electrons can be employed as corrosion inhibitors of steel [15–17]. The objective of this paper is to investigate the phosphorus polymer as corrosion inhibition for carbon steel in aggressive solution ([1 M HCl]). Then, the influence of PGEPBAP phosphorus polymer at various concentrations was evaluated using potentiodynamic polarization (PDP), electrochemical impedance spectroscopy (EIS), weight loss (WL), adsorption isotherms and surface morphological. In addition, density functional theory (DFT) computational, electrostatic potential (ESP), molecular dynamics (MD) and Monte Carlo (MC) simulations was investigated to understand the experiments data.

2. Experimental details

2.1. Material and inhibitor used

During this manuscript, carbon steel samples with following chemical composition (mass percentages %): 0.19 carbon, 0.075 manganese, 0.055 phosphorus, 0.625 iron, 0.047 sulfur and 0.008 other were tested [18]. The solution used ([1 M HCl]) was investigated from the commercially acid 37 % HCl, using dilution with double distilled water. The concentrations range from 10−3 to 10−6 M was realized and the surface of carbon steel employed is of 1 cm². The structure of PGEPBAP phosphorus polymer inhibitor tested is shown in scheme 1. PGEPBAP was characterized and confirmed by Fourier transformed infrared (FTIR) and nuclear magnetic resonance (NMR) spectroscopy (Figures SI 1, SI 2 and SI 3) (Supporting Information) [19].

2.2. Electrochemical study

The electrochemical measurement apparatus composed of three electrode cell namely counter electrode (platinum), reference electrode (Ag/AgCl) and working electrode (carbon steel), respectively. Electrochemical measuring is connected to the SP-200 biological apparatus having a signal magnitude (10 mV) [20]. Then, the electrochemical measuring was realized after achieving equilibrium state open circuit potential (OCP). Electrochemical impedance spectroscopy (EIS) measuring was employed a frequency interval of 100 KHz to 10 mHz at OCP over. Besides, the potentiodynamic polarization (PDP) measuring was registered by displacing the electrode potential from -900 to 0 mV according to OCP at a sweep rate of 0.3 mV/s [21].

2.3. Scanning electron microscopy

Scanning electron microscopy (SEM) was employed to provide photographs and showed the surface of metal using JEOL-JSM-5500 microscope type. This method is supported by the presence of electron beams accelerated using constant potential that excites the specimen surface. The interactions of these primary electrons with the specimen result to the release of secondary electrons, backscattered electrons, X-rays and Auger electrons.

2.4. Monte Carlo (MC) and molecular (MD) simulations

MC and MD simulations are very effective and important methods for realizing intramolecular interactions, namely metal-inhibitor [22]. The phosphorus polymer has numerous active sites that may interact with iron atoms (110), for this purpose the MC and MD simulations are performed using the Forcite model inserted in the Materials studio17 software [23]. This simulation is done under more suitable operating parameters such as simulation box (39.72° 39.72° 56.08 Å) with periodic boundary conditions, vacuum layer (19 Å) that filled with 500H2O, 50H2O, 50 Cl− and PGEPBAP phosphorus polymer, NVT Ensemble with Andersen thermostat, 1.0 fs time step, 300 ps duration with 298 K and COMPASSII used as Force field [24].

3. Results and discussion

3.1. PDP method

Tafel plots were compiled to acquire a more substantial understanding of the kinetics of cathodic and anodic corrosion reactions. Potentiodynamic polarization plots of carbon steel specimen in aggressive solution ([1 M HCl]) without and with various concentrations of phosphorus polymer after 30 min of submersion at 298 K are displays in Fig. 1. The associated electrochemical corrosion variables such as corrosion current density (icorr), corrosion potential (Ecorr), inhibitory efficiency (nTafel (%)), cathodic (βc) and anodic (βa) Tafel constants are determined by Tafel slope and are shown in Table 1. It is know that the electrochemical reaction of carbon steel in [1 M HCl] solution, without inhibitor, is the cathodic reactions related to the proton reduction (Eq. 1) and anodic dissolution reaction of iron (Eq. 2). The corrosion inhibitory efficiency (nTafel (%)) was calculated according to Eq. 3.

\[2H^+ + 2e^- \leftrightarrow H_2\]  

(1)
Scheme 1 – Synthesis of PGEPBAP phosphorus polymer.

<table>
<thead>
<tr>
<th>Inhibitor</th>
<th>Concentration [M]</th>
<th>$E_{corr}$ (mV)</th>
<th>$i_{corr}$ (µA cm$^{-2}$)</th>
<th>Tafel slopes (mV dec$^{-1}$)</th>
<th>$%$DPD (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl</td>
<td>1</td>
<td>439.7</td>
<td>397.3</td>
<td>193.1</td>
<td>94</td>
</tr>
<tr>
<td></td>
<td>$10^{-6}$</td>
<td>451.7</td>
<td>83.1</td>
<td>68.7</td>
<td>59.2</td>
</tr>
<tr>
<td></td>
<td>$10^{-5}$</td>
<td>412.1</td>
<td>41.5</td>
<td>57.9</td>
<td>41.1</td>
</tr>
<tr>
<td></td>
<td>$10^{-4}$</td>
<td>423.3</td>
<td>31.7</td>
<td>60.3</td>
<td>44.9</td>
</tr>
<tr>
<td></td>
<td>$10^{-3}$</td>
<td>416.2</td>
<td>23.1</td>
<td>69</td>
<td>41.3</td>
</tr>
<tr>
<td>PGEPBAP</td>
<td>$10^{-6}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$10^{-5}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$10^{-4}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$10^{-3}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$Fe \rightarrow Fe^{2+} + 2e^-$

$\eta_{Tafel}(\%) = (1 - \frac{i_{inh}}{i_{0}}) \times 100$ (3)

Where $i_0$ and $i_{inh}$ are corrosion current density uninhibited and corrosion current densities inhibited with different concentrations of PGEPBAP, respectively.

Electrochemical parameters could be calculated based on the Tafel plots [25,26]. Cathodic and anodic corrosion current densities diminished considerably with increase in concentration of PGEPBAP in [1 M] HCl, indicating that the phosphorus polymer inhibitor can also affect cathodic and anodic reactions (Eqs 1 and 2) [27]. As shown in Table 1, the corrosion current densities indicate a considerable abatement with increasing of PGEPBAP concentration. As a result, it is proposed that the elevation of PGEPBAP minimizes the dissolution of iron [28]. The corrosion potential displacement ($\Delta E_{corr}$) was evaluated according to Eq. 4 [29]. $\Delta E_{corr}$ values are roughly negligible or nil. Further, the corrosion potential is caused by geometrical obstruction using phosphorus polymer on carbon steel surface. If $\Delta E_{corr}$ values are lower than 85 mV, the inhibitor could be considered as a mixed type inhibitor [30]. In the case, where the $\Delta E_{corr}$ value was negative below -85 mV,
the phosphorus polymer can be assigned as cathodic inhibitor type, whereas the positive value above +85 mV can be suggested as anodic inhibitor type [31]. In this paper, \( \Delta E_{\text{corr}} \) value of polymer was 23.7 mV, therefore classed as a mixed inhibitor type. Addition of PGEPBAP phosphorus polymer to [1 M] HCl solution substantially influenced the cathodic bough slope, the decline in the corrosion current densities of the cathodic bough can indicate that the hydrogen development mechanism was changed by adsorbing the PGEPBAP on metal surface [32].

\[
\Delta E_{\text{corr}} = E_{\text{corr}} - E_0
\]

Where \( E_0 \) and \( E_{\text{inh}} \) denote corrosion potential uninhibited and corrosion potential inhibited with different concentrations of PGEPBAP, respectively.

### 3.2. EIS method

Electrochemical impedance spectroscopy (EIS) is very effective instrument employed to evaluate the corrosion resistance of materials in uninhibited and inhibited solutions and/or coating. Fig. 2 shows the Nyquist curves of carbon steel in aggressive solution ([1 M] HCl) in the absence and in presence of different concentrations of PGEPBAP phosphorus polymer after 30 min immersion at 298 K. EIS spectrums in [1 M] HCl solution with various concentrations of PGEPBAP show an increase in capacitive loops compared to the capacitive loop of blank [33]. Further, in the presence of various concentrations of phosphorus polymer investigated, the diameters of the Nyquist semicircles are generally higher than those of the uninhibited (blank). This suggests that the protective coating is very well adsorbed on the metal surface and that aggressive attack by \( \text{Cl}^- \) ions was efficiently stopped [34]. Then, this indicates that the carbon steel in aggressive solution exhibits more elevated resistance in the presence of different concentration of PGEPBAP and the corrosion inhibition efficiency increase with increasing in the concentration of PGEPBAP [35,36]. Bode curves for carbon steel in aggressive solution [1 M] HCl in the absence and with different concentrations of phosphorus polymer at 298 K are given in Fig. 2. Then, \( \text{log}(Z) \) values of carbon steel increased progressively indicate the improving in corrosion performance. This can be assigned to the formation of a layer protective on metal due to the adhesion of PGEPBAP that resists corrosion mediums in the carbon steel [37]. Nyquist curves are equipped with the equivalent electrical circuit (EEC) as illustrated in Fig. 3 without and with various concentrations of PGEPBAP phosphorus polymer employed, respectively. The EEC is composed of the solution resistance
(R	extsubscript{s}), polarization resistance (R	extsubscript{p}) and constant phase element (CPE). Then, the double layer capacity (C	extsubscript{dl}) and the corrosion inhibition efficiency (\(\eta_{\text{EIS}}(\%)\)) were measured according to Eq.s 5 and 6. The different electrochemical parameters are shown in Table 2. These results are in good agreement with the results obtained by different researchers [15–17,25,38–41]. Finally, the results obtained by the electrochemical impedance spectroscopy method confirm that of the potentiodynamic impedance method.

\[
C_{\text{dl}} = \frac{\xi}{\omega_{\text{om}}} n^{-1} \tag{5}
\]

\[
\eta_{\text{EIS}}(\%) = \left( 1 - \frac{R_p^0}{R_p} \right) \times 100 \tag{6}
\]

Where \(\xi\), \(\omega_{\text{om}}\), \(n\), \(R_p^0\) and \(R_p\) denotes the angular frequency, the magnitude of CPE, the exponent, the polarization resistance uninhibited and the polarization resistance inhibited with various concentrations of PGEPBAP, respectively.

### 3.3. Adsorption isotherm

Phosphorus polymeric matrixes reduce the corrosion rate of steel in various aggressive media by adsorption on the steel surface [42]. Different models of adsorption isotherms (Langmuir, Frumkin, Temkin and Freundlich) are employed to investigate the type of polymer adsorption on metal surface in [1 M] HCl solution and to determine the free energy adsorption and the recovery rate of the surface, respectively (Fig. 4 and Table 3) [43]. The adsorption coefficient \(K_{\text{ads}}\) is reveals to the standard free energy of adsorption according to Eq. 7. Langmuir adsorption isotherm presents a higher value of the linear regression coefficient (\(R^2 = 1\)) and the free energy adsorption less than ~40 kJ/mol, suggest that the polymer is highly bound to the iron surface by covalent bonds between the phosphorus polymer and the carbon steel surface (chemisorption) [44]. Then, the highest \(K_{\text{ads}}\) value of Langmuir adsorption isotherm indicates the formation of a film protective based on phosphorus polymer on the carbon steel surface [45].

\[
\Delta G_{\text{ads}}^c = -RT \ln(55.5K_{\text{ads}}) \tag{7}
\]

Where \(K_{\text{ads}}\), \(R\) and \(T\) are adsorption coefficient, constant of perfect gases and temperature, respectively.

### 3.4. WL and statistical study

Weight loss method is employed by using carbon steel immersed in [1 M] HCl medium in the absence and with various concentrations of phosphorus polymer for 24 h at 298 K. Further, the corrosion rate (\(W_{\text{corr}}\)) and the inhibitory efficiency (IE %) are calculated according to Eq.s 8 and 9, respectively. From Table 4, we observed that the corrosion rate values decrease versus concentration of phosphorus polymer employed and that its inhibitory efficiency is increased. This result can be explained by the phosphorus polymer with large surface area, the aromatic cycles and the presence of oxygen and phosphorus heteroatoms [46]. To ensure reproducibility, all experiments were repeated three times.

\[
W_{\text{corr}} = \frac{(m_i - m_f)}{S \cdot t} \tag{8}
\]

\[
\text{IE}(\%) = \left( \frac{W_{\text{corr}} - W_{\text{corr}}^i}{W_{\text{corr}}} \right) \times 100 \tag{9}
\]

\(m_i\), \(m_f\), \(S\), \(t\), \(W_{\text{corr}}^i\) and \(W_{\text{corr}}\) are the mass of substrate of metal before the corrosion, the mass of the substrate of metal after the corrosion, total surface area of metal, the corrosion time, the corrosion rate uninhibited and the corrosion rate inhibited by various concentration of PGEPBAP, respectively.

Various experimental procedures can be utilized to investigate the characteristics and inhibitory efficiency of the phosphorus polymer by using the WL, PDP and EIS techniques. The WL method is one of the easiest and most widely used methods. In addition, the evaluation and statistical investigation of weight loss data is a very significant step to determine the precision corrosion rate [47]. The arithmetic mean, the average deviation and the standard deviation are calculated according to Eq.s 10,11 and 12. The accuracy of the corrosion rate is measured by using three tests (in our case, \(n = 3\)). Further, in this manuscript, the precision corrosion rate tests show good consistency between all the mass loss tests (Table 4). Then, the results of the mean \(E_X\) are close, which means that the measures of weight loss are in good agreement. Also, the standard deviation (\(\sigma\)) of the inhibitory efficiency measured using WL method means that the results of corrosion rate measured are in good agreement.

\[
X = \frac{1}{n} \sum_{i} x_i \tag{10}
\]

\[
\sigma^2 = \frac{\sum (X - \bar{X})^2}{n} \tag{11}
\]

\[
\sigma = \sqrt{\frac{\sum (X - \bar{X})^2}{n}} \tag{12}
\]
Carbon immersed steel is tested by using [1 M] HCl at 298 K.

3.5. SEM characterization

Carbon steel samples after 24 h of submersion in hydrochloric acid at 298 K uninhibited and inhibited by $10^{-3}$ M of PGEPBAP are shown in Fig. 5. Then, the performance of PGEPBAP phosphorus polymer tested on the carbon steel surface immersed in aggressive solution was analyzed using SEM [40]. In addition, carbon steel surface immersed in the uninhibited solution was extensively affected and corroded by an acid attack. Otherwise, the morphology of carbon steel surface

![Graph](image)

**Fig. 4 – Adsorption isotherms models (Langmuir, Temkin, Frumkin and Freundlich) of PGEPBAP on carbon steel in [1 M] HCl at 298 K.**

<table>
<thead>
<tr>
<th>Models</th>
<th>Linear forms</th>
<th>Curves</th>
<th>Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td>$C_{in} = \frac{1}{K_{ads}} + C_{inh}$</td>
<td>$C_{in} = f(C_{inh})$</td>
<td>$R^2$</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Slope</td>
<td>1.06</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$K_{ads}$ (M$^{-1}$)</td>
<td>9.38 $10^5$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$\Delta G_{ads}$ (kJ mol$^{-1}$)</td>
<td>44.02</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$R^2$</td>
<td>0.922</td>
</tr>
<tr>
<td>Temkin</td>
<td>$\theta = \frac{1}{2} \ln K_{ads} + \frac{1}{2} \ln C_{inh}$</td>
<td>$\theta = f(lnC_{inh})$</td>
<td>Slope</td>
<td>0.04</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$K_{ads}$ (M$^{-1}$)</td>
<td>4.72 $10^7$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$\Delta G_{ads}$ (kJ mol$^{-1}$)</td>
<td>53.72</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$R^2$</td>
<td>0.922</td>
</tr>
<tr>
<td>Frumkin</td>
<td>$\ln(C_{inh} \times \frac{1}{T}) = -L\ln K_{ads} - 2 \times f \times \theta$</td>
<td>$\ln(C_{inh} \times \frac{1}{T}) = f(\theta)$</td>
<td>Slope</td>
<td>13.79</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$K_{ads}$ (M$^{-1}$)</td>
<td>2.87</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$\Delta G_{ads}$ (kJ mol$^{-1}$)</td>
<td>12.56</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$R^2$</td>
<td>0.914</td>
</tr>
<tr>
<td>Freundlich</td>
<td>$\ln\theta = \ln K + \ln C_{inh}$</td>
<td>$\ln(\theta) = f(\ln(C_{inh})$</td>
<td>Slope</td>
<td>0.914</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$K_{ads}$ (M$^{-1}$)</td>
<td>1.056</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$\Delta G_{ads}$ (kJ mol$^{-1}$)</td>
<td>10.008</td>
</tr>
</tbody>
</table>

3.6. DFT and ESP calculations

Frontier molecular orbitals (FMO) distribution density of the energy of highest occupied molecular orbital (E$_{HOMO}$) and the
Table 4 – Values of statistical evaluation and mass loss results obtained for carbon steel/[1 M] HCl/PGEPBAP polymer phosphorus system.

<table>
<thead>
<tr>
<th>Concentration[M]</th>
<th>Corrosion rate (mg cm⁻² h⁻¹)</th>
<th>Statistical evaluation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1st test</td>
<td>2nd test</td>
</tr>
<tr>
<td>[1 M] HCl</td>
<td>3.89</td>
<td>3.64</td>
</tr>
<tr>
<td>10⁻⁶</td>
<td>0.68</td>
<td>0.61</td>
</tr>
<tr>
<td>10⁻⁵</td>
<td>0.61</td>
<td>0.58</td>
</tr>
<tr>
<td>10⁻⁴</td>
<td>0.51</td>
<td>0.48</td>
</tr>
<tr>
<td>10⁻³</td>
<td>0.35</td>
<td>0.31</td>
</tr>
</tbody>
</table>

Fig. 5 – SEM images of carbon steel immersed for 24 h in [1 M] HCl uninhibited and inhibited with 10⁻³ M of PGEPBAP.

Table 5 – Various descriptors quantum chemical for PGEPBAP.

<table>
<thead>
<tr>
<th>Quantum chemical descriptors</th>
<th>E_HOMO (eV)</th>
<th>E_LUMO (eV)</th>
<th>ΔE_gap (eV)</th>
<th>η(eV)</th>
<th>σ(eV⁻¹)</th>
<th>ΔN(eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Values</td>
<td>–4.936</td>
<td>–1.294</td>
<td>3.642</td>
<td>1.821</td>
<td>0.549</td>
<td>0.468</td>
</tr>
</tbody>
</table>

The energy of the lowest unoccupied molecular orbital (E_LUMO) are shown in Fig. 6. Then, we observed that the density distribution HOMO is localized on the aromatic rings, on the phosphorus atom and the glycidyl group bonds oxygen heteroatoms, respectively [48]. However, the electron density distribution LUMO is distributed on the surface of the aromatic rings. Therefore, the high inhibitory power of the inhibitory phosphorus polymer can be explained by the presence of aromatic substituents possessing electrons “π”, the free doublets of oxygen heteroatoms (-O-) and the epoxy groups favoring the sharing of electrons between the PGEPBAP phosphorus macromolecular matrix and the carbon steel surface [49]. Various descriptors quantum chemistry of PGEPBAP, namely energy of the highest occupied molecular orbital (E_HOMO), energy of the lowest unoccupied molecular orbital (E_LUMO), gap energy (ΔE_gap), chemical hardness (η), chemical softness (σ) and altitude of transferred electrons (ΔN₁₁₀) are determined using Gaussian 03 W (Eq.s 13,14,15 and 16) [50]. The various parameters of PGEPBAP are grouped in Table 5. Furthermore, the higher value of the gap energy ΔE_gap (3.642 eV) suggests that the polymer inhibition performance is higher, reflecting the higher protection effectiveness [51]. Moreover, we noticed that the value of η is high, which suggests the existence of an aromatic and epoxy group, respectively. Besides, the number of transferred electrons ΔN < 3.6 reports that the macromolecular to be given electrons on the metal surface and the inhibition efficiency increases [52]. This result suggests that PGEPBAP phosphorus polymer is very well adsorbed by the active centers on the carbon steel surface. Moreover, to investigate the active sites of the inhibiting phosphorus polymer, the molecular electrostatic potential (ESP) was realized. In general, negative charged atomic sites act as nucleophilic centers when they are in contact with the iron surface through a donor-acceptor electron reaction to form a coordination bond [17]. The ESP representation is located at the epoxy groups, the oxygen and phosphorus atoms, respectively. Besides, the epoxy groups, the oxygen and phosphorus atoms are the active centers that present the largest ability to associate to the iron surface.

\[ ΔE_{gap} = E_{LUMO} - E_{HOMO} \]  

\[ η = \frac{ΔE_{gap}}{2} = \frac{E_{LUMO} - E_{HOMO}}{2} \]  

\[ σ = \frac{1}{η} = \frac{2}{E_{LUMO} - E_{HOMO}} \]
3.7. Molecular dynamics simulations

To understand the behavior of the adsorption configuration and the interaction between the PGEPBAP phosphorus polymer tested and the carbon steel surface in [1 M] HCl solution, we realized MD simulations. The energy fluctuation (potential energy, kinetic energy, non-bond energy and total energy) and temperature curves after 500 ps of MD simulations for Fe(110)/PGEPBAP/50HCl/500H2O system are shown in Figures SI 3 and SI 5 (Supporting Information) [17]. Besides, the energy fluctuation and temperature reaches equilibrium by the end of the simulation process. Fig. 7 present the side and top views of the most stable adsorption configuration when the system under study was at equilibrium for the phosphorus polymer adsorbed on the Fe (110) surface at 302 K. Moreover, we observed that the inhibiting phosphorus polymer studied is positioned exactly above the first layer of iron. Thus, the macromolecular structure of PGEPBAP causes coverage of the entire iron surface [53]. In addition, we concluded that our phosphorus polymer contains more active sites. This confirms that the PGEPBAP is very effective against the corrosion of carbon steel. The side and top view of PGEPBAP investigate the molecular chain was adsorbed parallel on the carbon steel surface and their heteroatoms (P and O) were oriented to the metal surface of iron Fe (110).

Radial distribution function (RDF) was used to calculate the bond length between the atoms of PGEPBAP phosphorus polymer and iron. Estimating bond length values allowed us to conclude the types of bonds formed [16]. Then, the bond length values varying from 1 Å to 3.5 Å are associated to chemisorption. Besides, the physisorption interactions are correlated to bond length values greater than 3.5 Å. Fig. 8 shows the variation of RDF versus bond length (r) for the atoms of PGEPBAP compared to surface of iron Fe (110). Furthermore, the result present that the bond length of Fe-PGEPBAP (2.4 Å) is less than 3.5 Å indicating that the most interaction between PGEPBAP and surface of iron Fe (110) is chemisorption type [54]. This confirms the greater ability of PGEPBAP to adsorb on the carbon steel surface.
3.8. Monte carlo simulations

Fig. 9 illustrated the adsorption energy distributions for Fe(110)/PGEPBAP/50HCl/500H₂O system realized by adsorption locator module. From Fig. 9, the adsorption energy distributions of PGEPBAP phosphorus polymer affected -1478 kcal/mol affect the presence of an intense adsorption between the PGEPBAP phosphorus macromolecular matrix and the surface of iron Fe (110) [17]. The energy distribution such as total energy, average total energy, van der Waals energy, electrostatic energy, and intermolecular energy plot after 30,000 steps per cycle of adsorption locator module for Fe (110)/PGEPBAP/50HCl/500 H₂O system is presented in Figure SI 6 (Supporting Information). Fig. 10 present the side and top views of the equilibrium adsorption configuration for Fe(110)/PGEPBAP/50HCl/500H₂O system obtained using adsorption locator module. Furthermore, the structure of phosphorus polymer inhibitory adsorbed on the surface clean of iron Fe (110) is in the flat mode, thus providing the maximum interactions between the heteroatoms (P and O) of macromolecular matrix and the substrate surface [55]. Besides, the outputs descriptors evaluated for Fe(110)/PGEPBAP/50HCl/500H₂O system using MC simulations are grouped in Table 6. From Table 6, the results obtained show that predicts adsorption energies for all types (total energy, adsorption energy, rigid adsorption energy, deformation energy) are negative values suggesting the adsorption ability of PGEPBAP phosphorus polymer on the surface of iron Fe(110) [56].

4. Conclusion

Corrosion inhibition performance of pentaglycidyl ether pentabisphenol A of phosphorus (PGEPBAP) on carbon steel was investigated in aggressive solution by using potentiodynamic polarization (PDP), electrochemical impedance spectroscopy (EIS), weight loss (WL), scanning electron micro-
Fig. 9 – Adsorption energy distributions for Fe (110)/PGEPBAP/50HCl/500 H₂O system using adsorption locator module.

Fig. 10 – Top, side and density field of iso-surface of the equilibrium adsorption configuration for Fe (110)/PGEPBAP/50HCl/500 H₂O system using adsorption locator module.
scope (SEM), density functional of theory (DFT), molecular dynamics (MD) and Monte Carlo (MC) simulations. In addition, PDP, EIS and WL measurements at 10−3 M of PGEPBAP phosphorus polymer in [1 M] HCl have significantly higher inhibition efficiency equal to 94.18 %, 91.79 % and 91.3 %, respectively. Then, inhibitory efficiencies of PBEPBAP phosphorus polymer elevate with concentrations inhibitor increases. SEM photograph inhibited with 10−3 M of PBEPBAP in [1 M] HCl protects the surface of carbon steel compared with the uninhibited solution (blank). Free energy adsorption ∆G_ads value indicate that PGEPBAP phosphorus polymer obeys the Langmuir adsorption isotherm (chemisorption). Further, DFT calculation, ESP, RDF, MD and MC simulations allow a better comprehension of the experimental findings.

Table 6 – Descriptors calculated using an adsorption locator module for the most stable configurations for Fe(110)/PGEPBAP/50HCl/500H2O system (all values are in Kcal/mol).

<table>
<thead>
<tr>
<th>Structure</th>
<th>PGEPBAP</th>
<th>Total energy (10−3)</th>
<th>Adsorption energy (10−3)</th>
<th>Rigid Adsorption energy (10−3)</th>
<th>Deformation energy (10−3)</th>
<th>dE_adj/dN_adj (10−3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe (110) - 1</td>
<td>−1.08</td>
<td>−1.76</td>
<td>−1.16</td>
<td>−5.98</td>
<td>−1.47</td>
<td></td>
</tr>
<tr>
<td>Fe (110) - 2</td>
<td>−1.08</td>
<td>−1.75</td>
<td>−1.15</td>
<td>−5.97</td>
<td>−1.46</td>
<td></td>
</tr>
<tr>
<td>Fe (110) - 3</td>
<td>−1.07</td>
<td>−1.74</td>
<td>−1.15</td>
<td>−5.97</td>
<td>−1.46</td>
<td></td>
</tr>
<tr>
<td>Fe (110) - 4</td>
<td>−1.07</td>
<td>−1.74</td>
<td>−1.14</td>
<td>−5.97</td>
<td>−1.46</td>
<td></td>
</tr>
<tr>
<td>Fe (110) - 5</td>
<td>−1.06</td>
<td>−1.73</td>
<td>−1.13</td>
<td>−5.97</td>
<td>−1.45</td>
<td></td>
</tr>
<tr>
<td>Fe (110) - 6</td>
<td>−1.06</td>
<td>−1.73</td>
<td>−1.13</td>
<td>−5.98</td>
<td>−1.46</td>
<td></td>
</tr>
<tr>
<td>Fe (110) - 7</td>
<td>−1.06</td>
<td>−1.73</td>
<td>−1.13</td>
<td>−5.98</td>
<td>−1.45</td>
<td></td>
</tr>
<tr>
<td>Fe (110) - 8</td>
<td>−1.06</td>
<td>−1.73</td>
<td>−1.13</td>
<td>−5.99</td>
<td>−1.45</td>
<td></td>
</tr>
<tr>
<td>Fe (110) - 9</td>
<td>−1.06</td>
<td>−1.73</td>
<td>−1.13</td>
<td>−5.98</td>
<td>−1.47</td>
<td></td>
</tr>
<tr>
<td>Fe (110) - 10</td>
<td>−1.06</td>
<td>−1.73</td>
<td>−1.13</td>
<td>−5.98</td>
<td>−1.47</td>
<td></td>
</tr>
</tbody>
</table>

Conflicts of interest

No conflicts of interest to declare.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.jmrt.2020.01.002.

References


