

## Study of Some [N-substituted] *p*-aminoazobenzene as Corrosion Inhibitors for Mild-Steel in 1M H<sub>2</sub>SO<sub>4</sub>

Hanan H. Al-Doori<sup>1</sup> and Mehdi S. Shihab

Department of Chemistry, College of Science Al-Nahrain University, Baghdad-Iraq.

<sup>1</sup>E-mail: hanan\_aldoori@yahoo.com.

### Abstract

Azo dye derivatives were prepared as corrosion inhibitors for mild steel in 1M H<sub>2</sub>SO<sub>4</sub> solution by weighting loss measurements as evaluation tools. It has been observed that inhibition efficiency orders are A<sub>1</sub> > A<sub>3</sub> > A<sub>2</sub> with the highest inhibiting efficiency of 82% for 10<sup>-3</sup>M. Increasing in inhibitor concentration accompanies with corrosion rate decreases, inhibition efficiencies increase and surface coverage degree increases. Semi-empirical molecular orbital calculations of prepared compounds A<sub>1</sub>, A<sub>2</sub>, and A<sub>3</sub> as molecular models gave useful information to predict the interaction between the surface of metal and the organic molecules as corrosion inhibitors.

**Keyword:** Azo dyes, Corrosion, Mild steel, Adsorption isotherm.

### 1. Introduction

Corrosion is an afflicting problem associated with every use of metals. The damage by corrosion results in highly cost for maintenance and protection of materials used. Development of methods to control corrosion is a challenge to scientists working in this area<sup>(1)</sup>. Mild steel is widely applied as the constructional materials in many industries due to its excellent mechanical properties and low cost<sup>(2)</sup>. Mild steel is an alloy form of iron, which undergoes corrosion easily in acidic medium. Acidic solutions are extensively used in chemical laboratories and in several industrial processes such as acid pickling, acid cleaning, acid descaling and oil wet cleaning etc.<sup>(3)</sup>. The use of inhibitors is one of the most practical methods for protection against metallic corrosion, especially in acidic media<sup>(4)</sup>. The selection of inhibitor is controlled by its economic availability, its efficiency to inhibit the substrate material and its environmental side effects. So most of the excellent acid inhibitors for corrosion of steel in acidic medium are organic compound containing nitrogen, oxygen and/or sulphur atoms<sup>(5,6)</sup>. The inhibition process has been shown to occur via inhibitor adsorption isotherm and the efficiency of the inhibitors strongly depends on the structure and chemical characteristics of the adsorbed inhibitor layer formed under particular experimental conditions<sup>(7)</sup>. Azo compounds are the most widely used class of dyes due to their

application in various fields, such as the dyeing of textiles, and fibers<sup>(8)</sup>. Some studies have shown that the inhibition of the corrosion by organic dyes is mainly attributed to the formation of complex compounds between the metal-ions and the nitrogen of azo binding at the electrode surface<sup>(9)</sup>. In the present work, some azo dye derivatives as corrosion inhibitor were prepared. The aim of this work is to investigate the efficiency of these organic compounds as corrosion inhibitor for mild steel in solution of 1M sulfuric acid.

### 2. Materials and Methods

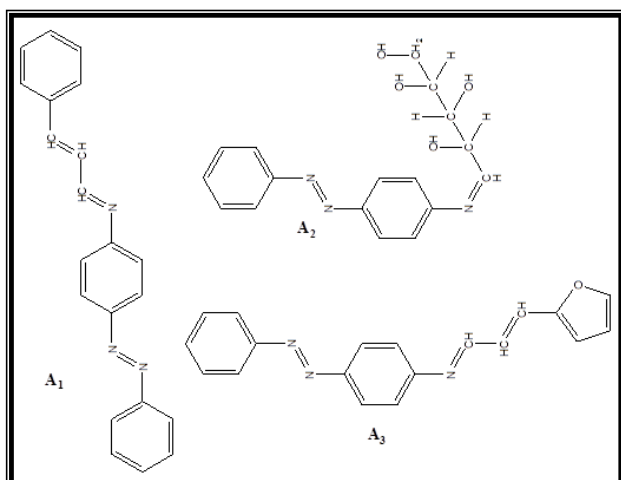
**Materials:** All the chemicals were supplied from Merck, Fluka and Alfa chemicals Co. and used as received.

**Techniques:** The infrared spectra of the prepared compounds were recorded using FTIR 8300 Fourier transform infrared spectrophotometer of SHIMADZU Company as a potassium bromide (KBr) discs in the wave number range of (4000-400) cm<sup>-1</sup>. Melting points were determined by the open capillary method using hot stage Gallenkamp melting point apparatus and were uncorrected. Spectromaxx, 2009, Germany was used to determine the composition of mild steel samples, (State Company for Inspection and Rehabilitation, Ministry of Industry and Materials).

## 2.1. Synthesis of suggested inhibitors

Azo dyes inhibitors, namely: (E)-N-((E)-3-phenylallylidene)-4-((E)-phenyldiazenyl) aniline **A<sub>1</sub>**, (Z)-5-(4-((E)-phenyldiazenyl) phenylimino) pentane-1,2,3,4-tetraol **A<sub>2</sub>**, (E)-N-((E)-3-(furan-2-yl) allylidene)-4-((E)-phenyldiazenyl) aniline **A<sub>3</sub>**, were synthesized as follow:

First, preparation of azo aniline was carried out by coupling reaction between diazonium salt and aniline<sup>(10)</sup>. Then, a mixture of *p*-aminoazobenzene (1g, 0.01mol), abs. ethanol (20ml) and appropriate aromatic or aliphatic aldehydes (0.01mol) with few drops of glacial acetic acid was refluxed for (8-10) hours. After cooling to room temperature the precipitate was filtered and dried. The product was recrystallized from ethanol<sup>(11)</sup>. The molecular formula of suggested inhibitors is shown in Fig.(1).



**Fig.(1) The molecular formula of suggested inhibitors.**

## 2.2. Preparation of aggressive solution

Aggressive solution of 1M H<sub>2</sub>SO<sub>4</sub> was prepared by dilution of analytical grade 98% H<sub>2</sub>SO<sub>4</sub> with distilled water. Inhibitor concentrations of 1x10<sup>-3</sup> to 5x10<sup>-5</sup> M were prepared in 1M H<sub>2</sub>SO<sub>4</sub> solution at 30°C.

## 2.3. Weight loss measurements

The sheet of mild steel used has the composition percentages (0.002% P, 0.288% Mn, 0.03% C, 0.0154% S, 0.0199% Cr, 0.002% Mo, 0.065% Cu, 0.0005% V) and the remainder iron. The mild steel sheet was mechanically press-cut into disc shape with

diameter (2.5 cm). These disc shapes were polished with emery papers ranging from 110 to 410 grades to get very smooth surface.

However, surface treatments of the mild steel involve degreasing in absolute ethanol and drying in acetone. The treated specimens were then stored in a moisture-free desiccator before their use in corrosion studies.

Mild steel specimens were initially weighed in an electronic balance. After that the specimens were suspended and completely immersed in 250 ml beaker containing 1M sulphuric acid in the presence and absence of inhibitors for 8 hrs. The specimens were removed after 8 hours exposure period at 30°C, washed with water to remove any corrosion products and finally washed with acetone. Then they were dried and reweighed. Mass loss measurements were performed as by ASTM method described previously<sup>(12, 13)</sup> the tests were performed in duplicate to guarantee the reliability of the results and the mean value of the weight loss is reported. Weight loss allowed calculation of the mean corrosion rate in (mg cm<sup>-2</sup> h<sup>-1</sup>). The corrosion rate of mild steel was determined using the relation<sup>(14)</sup>:

$$W = \frac{\Delta m}{st} \dots \dots \dots (1)$$

Where  $\Delta m$  is the mass loss (gm),  $s$  the area (cm<sup>2</sup>) and  $t$  is the immersion period (h). The percentage inhibition efficiency ( $E$  (%)) was calculated using the relationship<sup>(15)</sup>:

$$E\% = \frac{W_{\text{corr}} - W_{\text{corr(inh)}}}{W_{\text{corr}}} \times 100 \dots \dots \dots (2)$$

Where  $W_{\text{corr}}$  and  $W_{\text{corr(inh)}}$  are the corrosion rates of mild steel in the absence and presence of inhibitor, respectively.

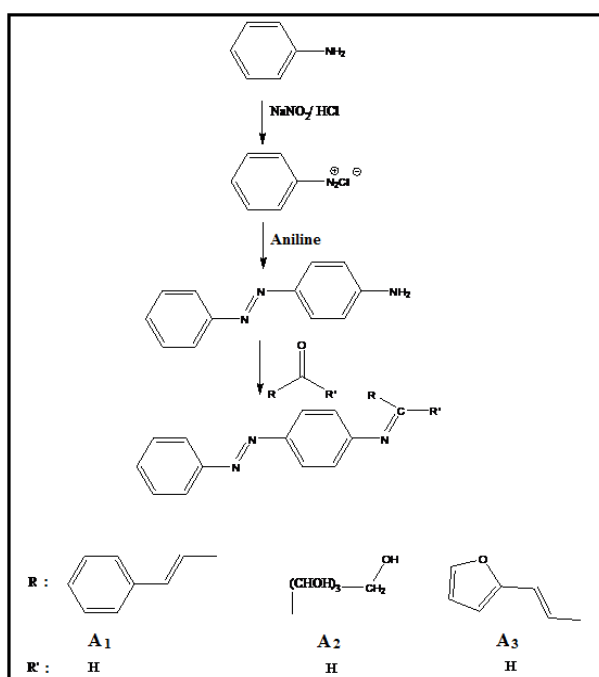
## 2.4. Theoretical calculations

The correlation between theoretically calculated properties and experimentally determined inhibition efficiencies has been studied successfully for uniform corrosion<sup>(16-19)</sup>. The purpose of this work is to provide information about the electron configuration of several organic inhibitors by quantum chemical calculations and to investigate the relationship between molecular structure and inhibition efficiency. All the calculations were performed using the semiempirical calculations

with PM3 method<sup>(20)</sup>. For this purpose the Hyperchem Program<sup>(21)</sup> with complete geometry optimization was used. This computational method has been proven to yield satisfactory results<sup>(18, 19)</sup>. The easiest way to compare the inhibition efficiency of ( $A_1$ ,  $A_2$ , and  $A_3$ ) is to analyze the energies of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). The optimized molecular structures resulted calculated energies  $E_{\text{HOMO}}$ ,  $E_{\text{LUMO}}$ , energy gap ( $\Delta E = E_{\text{LUMO}} - E_{\text{HOMO}}$ ) and other indices are given in Table (2).

### 3. Results and Discussion

Scheme (1) shows the preparation of some azo derivatives of this present work:



*Scheme (1) preparation of azo derivatives ( $A_1$ ,  $A_2$ ,  $A_3$ ).*

The reactions above are included preparation azo aniline compound through usual preparation by using aniline, and followed by adding some derivatives of Schiff's bases moities using different aldehydes. Table (1) shows physical and analytical data of the synthesized compounds ( $A_1$ ,  $A_2$ ,  $A_3$ ).

**Table (1)**  
**Physical and analytical data of the synthesized compounds.**

Comp. no	Mol. formula	Yield (%)	M.W.	M.P. (C°)	appearance	FT-IR data $\nu$ , $cm^{-1}$
Azo aniline	C <sub>12</sub> H <sub>11</sub> N <sub>3</sub>	80	197.24	100-103	Orange to brown	(N=N)1415, aromatic(C-H) 3059, NH <sub>2</sub> (N-H) 3475 and 3379
A <sub>1</sub>	C <sub>21</sub> H <sub>17</sub> N <sub>3</sub>	55	311.14	140-144	Brown	(C=N) 1627, (N=N) 1438, aromatic(C-H) 3035, aliphatic (C-H) 2877, aliphatic (C=C) 1674
A <sub>2</sub>	C <sub>17</sub> H <sub>19</sub> N <sub>3</sub> O <sub>4</sub>	50	329.35	133-132	Brown	(C=N) 1537, (N=N) 1435, aromatic(C-H) 3078, aliphatic (C-H) 2835, (O-H) 3342
A <sub>3</sub>	C <sub>19</sub> H <sub>15</sub> N <sub>3</sub> O	60	301.34	180-183	Brown	(C=N) 1698, (N=N) 1411, aromatic(C-H) 3095, aliphatic (C-H) 2873, (C-O) 1072

The FT-IR spectrum of azo aniline compound showed appearing of  $\nu(N=N)$  band at  $(1415\text{ cm}^{-1})^{(22)}$ , (see Table (1)). The FT-IR spectra of A<sub>1</sub>, A<sub>2</sub>, and A<sub>3</sub> showed disappearing of  $\nu(C=O)$  band of in all products that indicated formation of the suggested inhibitors. Table (1) listed major stretching bands of FT-IR spectra of products <sup>(22)</sup>.

The results of corrosion rate and inhibition efficiency that obtained from weight loss measurements at different concentrations of suggested inhibitors A<sub>1</sub>, A<sub>2</sub>, and A<sub>3</sub> after 8 hours immersion at 30°C are depicted in Figure 6 and summarized in Table (2). These values indicate that the mild steel corrosion is reduced by the presence of suggested inhibitors in 1M H<sub>2</sub>SO<sub>4</sub> at all concentrations that used in the present study. However, there is remarkable decreasing in the weight of mild

steel specimen after 8 hours without using an inhibitor. That's could be explain by adsorption of organic compounds on the mild steel surface which makes impediment towards corrosion environment.

The increase in efficiency of inhibition with concentration indicates that more inhibitor molecules are adsorbed on the metal surface at higher concentration, leading to greater surface coverage.

Table (2)

Corrosion rate, inhibition efficiency, surface coverage ( $\theta$ ) and standard free energy of adsorption for mild steel in 1M  $H_2SO_4$  by using weight loss measurements.

Inhibitor concentration (M)	1M $H_2SO_4$				
	$\Delta M(g)$	Corrosion rate ( $mg\ cm^{-2}\ h^{-1}$ )	E%	$\theta$	$\Delta G^o_{ads}$ (kJ/mol)
Uninhibited	0.113	2.8790	-	-	-34.39 ( $R^2=0.9999$ )
A <sub>1</sub>					
0.001	0.0198	0.5045	82.48	0.8248	
0.0005	0.0235	0.5987	79.20	0.7920	
0.0001	0.053	1.3503	53.10	0.5310	
0.00005	0.0688	1.7529	39.11	0.3911	-36.77 ( $R^2=0.9980$ )
A <sub>2</sub>					
0.001	0.0691	1.7605	38.85	0.3885	
0.0005	0.0731	1.8624	35.31	0.3531	
0.0001	0.0738	1.8803	34.69	0.3469	
0.00005	0.0811	2.0662	28.23	0.2823	-37.59 ( $R^2=0.9998$ )
A <sub>3</sub>					
0.001	0.0611	1.5567	45.93	0.4593	
0.0005	0.0629	1.6025	44.34	0.4434	
0.0001	0.0666	1.6968	41.06	0.4106	
0.00005	0.0741	1.8879	34.43	0.3443	

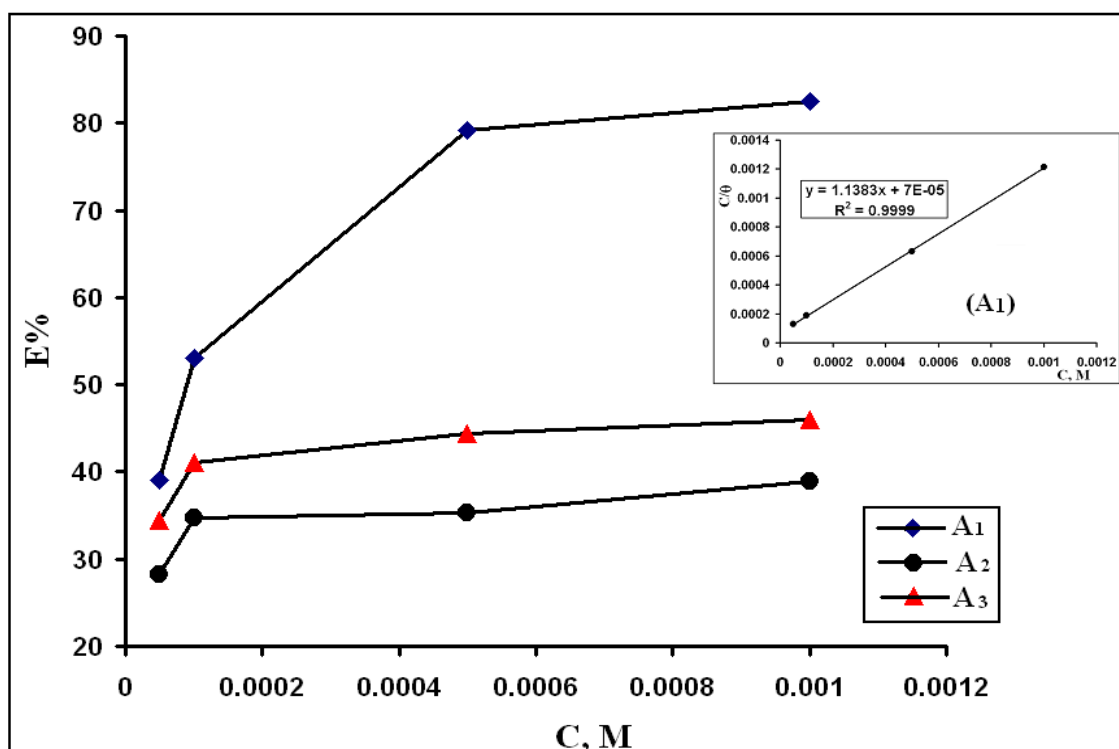


Fig.(2) Effect of inhibitor concentrations on the inhibition efficiency for mild steel 1M  $H_2SO_4$  at 30°C for suggested inhibitors A<sub>1</sub>, A<sub>2</sub>, A<sub>3</sub>). Upper the linear relationship between C/θ versus C for A<sub>1</sub>.

From Table (2) indicates that the protection efficiency increases with increasing the concentration of suggested inhibitors with the maximum inhibition efficiencies were achieved at  $10^{-3}$  M. Thus, the comparative study reveals that order of maximum inhibition efficiency as follow:  $A_1 > A_3 > A_2$ . That order could be explain by the effect of molecular structure of organic inhibitors on inhibition efficiency, as well as adsorption process.

Basic information can be provided from the adsorption isotherms to explain the interaction between the organic compounds and metal surfaces. So that, the degree of surface coverage values ( $\theta$ ) at different inhibitor concentrations in 1M  $H_2SO_4$  was achieved from weight loss measurements ( $\theta = E (\%)/100$ ) (see Table (2)) at  $30^\circ C$  and tested with Langmuir isotherm relationship <sup>(23)</sup>:

$$C/\theta = 1/K_{ads} + C \dots\dots\dots (3)$$

Where C is concentration in M,  $K_{ads}$  is the equilibrium constant of the adsorption process.

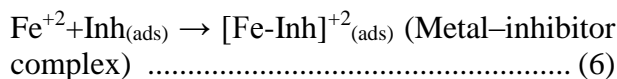
According to the Langmuir isotherm,  $K_{ads}$  values can be calculated from the intercepts of the straight line of plotting  $C/\theta$  versus C (see Fig.(6)).  $K_{ads}$  is related to the standard free energy of adsorption,  $\Delta G^{\circ}_{ads}$ , with the following equation: (The value 55.5 is the molar concentration of water in the solution in M).

$$K_{ads} = \frac{1}{55.5} \exp\left(\frac{-\Delta G^{\circ}_{ads}}{RT}\right) \dots\dots\dots (4)$$

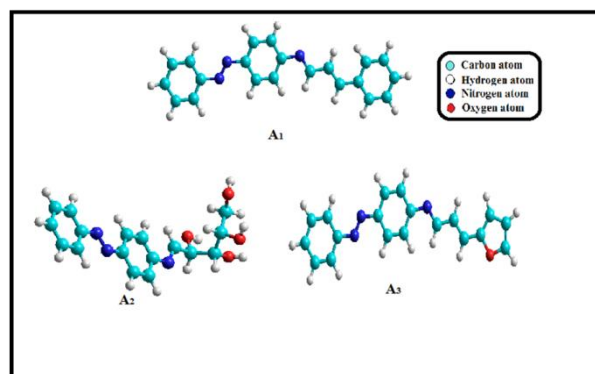
From Table 2, the values of standard free energy of adsorption are negative to indicate that the processes of adsorption of all suggested inhibitors  $A_1$ ,  $A_2$ , and  $A_3$  were spontaneous processes on the mild steel surface after 8 h immersion at  $30^\circ C$  and that's given sense for remarkable interaction between suggested inhibitors and metal surface. Here, adsorbed molecule moves closer to the surface of metal making electrons start to overlap with that of the surface atoms which causes physisorption for suggested inhibitors <sup>(24-27)</sup>.

It is generally accepted that the adsorption of an organic inhibitor on a metal surface in acidic media usually involves formation of a metal–inhibitor complex by combining an

inhibitor with freshly generated  $Fe^{2+}$  ions on the steel surface <sup>(28)</sup>:



Therefore, formation of a metal–inhibitor complex could work as protective layer for anodic cell to reduce formation of  $Fe^{+2}$  sites. Thus it could be suggested that at low concentrations of suggested inhibitors probability of formation a compact metal–inhibitor complex is low. The adsorption mechanism for given inhibitors depends on adsorption behavior of organic molecules containing N, O atom. The presence of more than one functional group has been reported to often lead to changes in the electron density of a molecule, which could influence its adsorption behavior<sup>(29)</sup>. The suggested inhibitors could adsorb with the corroding steel surface via the compact metal–inhibitor complex on anodic sites and reduces Fe electro-dissolution. To study the relationship between molecular structure and inhibitive effect of the suggested inhibitors, we used molecular orbitals of semi-empirical calculations with PM3 method. All the theoretical quantum calculations were performed for suggested inhibitors  $A_1$ ,  $A_2$ , and  $A_3$  using more energetically stable conformations in gas phase at  $25^\circ C$  (see Fig.(3)).



**Fig.(3) More energetically stable conformations of prepared inhibitors  $A_1$ ,  $A_2$ , and  $A_3$  with PM3 method.**

The calculated quantum chemical parameters of suggested inhibitor forms are reported in (Table (3)).

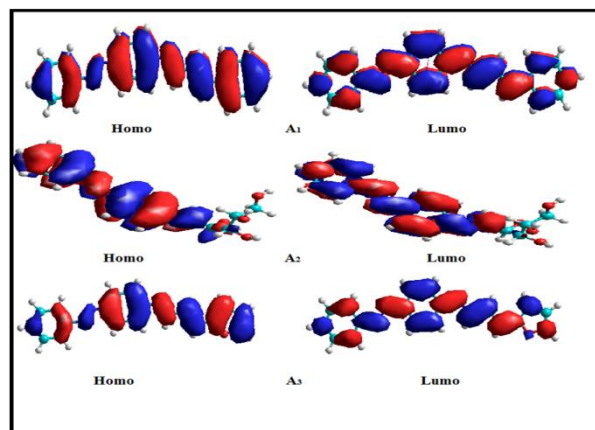
**Table (3)**  
*Calculated quantum chemical parameters of suggested inhibitors by using PM3 method.*

<i>inhibitor</i>	<i>HOMO (eV)</i>	<i>LUMO (eV)</i>	$\Delta E^a$ (eV)	$\mu$ (Debye)	<i>Charge of N atom (-N=C-) (e/atom)</i>	<i>Planarity</i>
A <sub>1</sub>	-8.7493	-1.2083	-7.5089	1.584	-0.0567	Planar
A <sub>2</sub>	-9.0132	-0.9283	-8.0849	3.653	-0.0460	Semi-Planar
A <sub>3</sub>	-8.6245	-1.2346	-7.3899	1.349	-0.0514	Planar

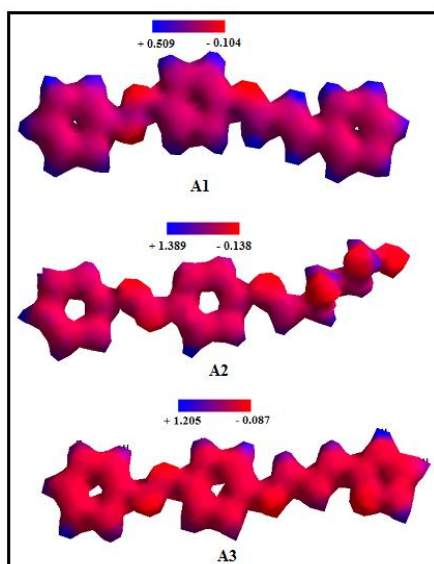
$$^a\Delta E \text{ (energy gap)} = (E_{\text{HOMO}} - E_{\text{LUMO}})$$

A typical electron density distribution of HOMO and LUMO for suggested inhibitors A<sub>1</sub>, A<sub>2</sub>, and A<sub>3</sub> are shown in Fig.(8). Depending on the presence of N, O atom in suggested inhibitors, the repartition density of the HOMO and LUMO is preferentially localized on N of (C=N) and (N=N) groups for all molecules. Moreover, the gap between the LUMO and HOMO energy levels of the molecules was another important factor that should be considered. As the LUMO–HOMO energy gap decreased and the efficiency of inhibitor improved<sup>(30)</sup>. Quantum chemical parameters listed in Table 3 reveal that A<sub>3</sub> and A<sub>1</sub> have lower energy gap comparing with A<sub>2</sub>. That's comes from resonance contribution of electron pairs of oxygen atom and carbon-carbon double bonds. Table (3) shows also different dipole moments for suggested inhibitors A<sub>1</sub>, A<sub>2</sub>, and A<sub>3</sub>. The values of dipole moment can explain due to non-uniform distributions of positive and negative charges on the various atoms, which could be related to improvement the dipole–dipole interaction of organic molecules and mild steel surface. Electrostatic potential maps for suggested inhibitors A<sub>1</sub>, A<sub>2</sub>, and A<sub>3</sub> are depicted in Fig (4). Non uniform distribution of electronic density (see Fig.(4)) and concentration of negative charges on N (C=N), (N=N) for all molecules, which are reflected the different values of calculated dipole moment (see Table (3)). From all above, we obtained different experimental and theoretical results due to different molecular structures, which effected on inhibitive effect of the suggested inhibitors. There are steric and electronic effects to understand the role of molecular

structure on inhibitive effect. Inhibitive effect of the suggested inhibitors depends on N (C=N), (N=N) for all molecules. The planar molecules still prefer for improving the inhibitive effect<sup>(30)</sup> (A<sub>1</sub> and A<sub>2</sub> are planar, see Table (2)). According to values of E% (see Table (2))



**Fig.(4) The frontier molecular orbital density distributions (HOMO and LUMO) for prepared inhibitors A<sub>1</sub>, A<sub>2</sub>, and A<sub>3</sub> by using PM3 method.**



**Fig.(5) Electrostatic potential maps for prepared inhibitors A1, A2, and A3 by using PM3 method.**

Finally, the suggested inhibitor A<sub>1</sub> showed physisorption with  $\Delta G_{\text{ads}}^{\circ} = -34.39 \text{ kJ/mol}$ , it's confirmed with the values of E% (40-83 for different concentrations, see Table (2)) comparing with the others. In spite of low concentration ( $10^{-5} \text{ M}$ ) of A<sub>1</sub> but still E% is higher comparing with the E% values of A<sub>2</sub> and A<sub>3</sub>. We believed that A<sub>1</sub> has planarity and higher electronic density around the  $-\text{N}=\text{CH}$  group comparing with A<sub>2</sub> and A<sub>3</sub> (see Table (2)). In addition, planarity and the regular distribution of the electronic density on the surface of organic molecule A<sub>1</sub> improves the interaction between the organic molecule and metal surface.

#### 4. Conclusion

The prepared azo dyes compound A<sub>1</sub>, A<sub>2</sub>, and A<sub>3</sub> were used successfully as corrosion inhibitors on the mild steel surface in 1M H<sub>2</sub>SO<sub>4</sub> solution at 30°C. The results of inhibitive efficiency (E %) showed interesting inhibitive effects of suggested inhibitors. The values free energy of adsorption revealed physisorption effect for A<sub>1</sub>, A<sub>2</sub>, and A<sub>3</sub>. Molecular models for prepared compounds A<sub>1</sub>, A<sub>2</sub>, and A<sub>3</sub> were achieved by using semi-empirical molecular orbital calculations gave useful information to explain the interaction between the surface of metal and the organic molecules.

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#### الخلاصة

تم تحضير المركبات الازو دايزالتي تم الرمز اليها بالرموز ( $A_1, A_2, A_3$ ) كمثبطات لتآكل معدن الحديد المعامل في الحامض الكبريتيك بتركيز 1 مولاري بواسطة قياسات الفقدان بالوزن حيث تم ملاحظه كفاءه التثبيط لهذه المركبات كالاتي:  $A_2 < A_3 < A_1$  علما ان التآكل على سطح المعدن تقل بزيادة كفاءة المثبط وذلك لان نسبة التغطية ( $A_1, A_2, A_3$ ) على سطح المعدن تزداد بزيادة تركيز مثبط التآكل. الحسابات الجزيئية للمركبات ( $A_1, A_2, A_3$ ) اعطت معلومات مفيدة لتوضيح التأثير بين السطح المعدن والجزيئات العضوية كمثبط للتآكل.