A comparative study of two corrosion inhibitors: 1,4-diallyl-6-chloroquinoxaline 2,3-(1*H*,4*H*)-dione (**1a**) and 1,4-diallyl-6-nitroquinoxaline-2,3-(1*H*,4*H*)-dione (**1b**)

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Abstract

Corrosion inhibition by 1,4-diallyl-6-chloroquinoxaline-2,3-(1*H*,4*H*)-dione (**1a**) and 1,4-diallyl-6-nitroquinoxaline-2,3-(1*H*,4*H*)-dione (**1b**) on mild steel was studied in 1.0 M HCl solution by using the electrochemical techniques and the weight loss measurements at temperature 308 K. The results obtained clearly revealed that inhibitors (**1a**) and (**1b**) behave as a mixed type inhibitors and adsorbed onto the mild steel surface by chemisorption. The weight loss results indicate that inhibitors (**1a**) and (**1b**) are good corrosion inhibitors and their optimum inhibition efficiency reaches up to 95% and 89% respectively, at a concentration of 10⁻³ M and a temperature of 308 K. In addition, the potentiodynamic polarization studies indicate that (**1a**) and (**1b**) are mixed-type corrosion inhibitors and EIS show that the transfer resistance increases with the increase in the inhibitor concentration. The adsorption of the molecules of the inhibitors (**1a**) and (**1b**) onto the mild steel surface was found to follow the Langmuir adsorption isotherm. The values of the change in Gibbs free energy of adsorption (ΔG_{ads}) strongly support the chemisorption of the molecules of the studied inhibitors on the mild steel surface. The results obtained from electrochemical and weight loss measurements were in reasonable agreement.

Keywords: adsorption, corrosion, polarization, electrochemical impedance spectroscopy, mild steel, weight loss.

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1. Introduction

The use of acids, salts and alkaline materials in solutions in industrial applications cause extensive severe corrosion of metals, which prompt tremendous financial misfortunes. These issues were taken into consideration by many researchers in this field, in order to minimize and control the corrosion of metals. The utilization of inhibitors is one of the reasonable methods used to control this phenomenon. Inhibitors can act in the protection of metals in several environments [1]. They can adsorb on the metal surface, block the active sites of the metal surface and decrease the corrosion rate [2]. The adsorption of inhibitor on the metal surface depends mainly on the physicochemical adsorption properties of the inhibitor functional groups and the electron density at the donor site [3]. Many researchers studied the corrosion inhibition efficiency of organic compounds and the physicochemical adsorption properties [4]. Quinoxaline derivatives are used as corrosion inhibitors of mild steel in acidic medium [5, 6]. In addition, the structural units containing the quinoxaline nucleus have many biological activities. They are used in the form of antibacterial agents [7], anti-amoebic [8], anti-viral [9], anticancer [10, 11] and anti-tubercular [12, 13].

Quinoxaline derivatives are used in other fields, such as agro-chemistry as antioxidants [14] and as pesticides [15].

In this work, the corrosion inhibition efficiency of 1,4-diallyl-6-chloroquinoxaline-2,3-(1*H*,4*H*)-dione (**1a**) and 1,4-diallyl-6-nitroquinoxaline-2,3-(1*H*,4*H*)-dione (**1b**), has been investigated on mild steel (MS) in 1.0 M HCl solution.

In this study, weight loss measurements and electrochemical techniques were used for the evaluation of the inhibition efficiency of the inhibitors (**1a**) and (**1b**).

2. Experimental part

2.1 Materials and solutions

For reliable and reproducible results, the mild steel (MS) samples were polished with fine-grained abrasive paper (Grade 100-400-800-600-1200) before each test. The (MS) polished samples were rinsed with double distilled water, degreased with acetone, then air-dried and kept in a desiccator [16–18]. The mass percentage composition of the (MS) is specified in Table 1.

Table 1. The mass percentage composition of mild steel (MS).

Element	Fe	C	Si	P	Mn	Al	S
% Mass	99.21	0.21	0.38	0.09	0.05	0.01	0.05

Hydrochloric acid (37%) used in this study was from Merck. The 1.0 M HCl solution was prepared by dilution with doubly distilled water. The concentrations of inhibitors ranging from 10^{-6} M to 10^{-3} M were prepared by dissolving the appropriate amount of the compounds 1,4-diallyl-6-chloroquinoxaline-2,3-(1*H*,4*H*)-dione (**1a**) and 1,4-diallyl-6-nitroquinoxaline-2,3-(1*H*,4*H*)-dione (**1b**) in 1.0 M HCl solution.

2.2 Synthesis of inhibitors

The synthesis of the compounds 1,4-diallyl-6-chloroquinoxaline-2,3-(1*H*,4*H*)-dione (**1a**) and 1,4-diallyl-6-nitroquinoxaline-2,3-(1*H*,4*H*)-dione (**1b**) were shown in Scheme 1.

Scheme 1. Synthesis of 1,4-diallyl-6-chloroquinoxaline-2,3-(1*H*,4*H*)-dione (**1a**) and 1,4-diallyl-6-nitroquinoxaline-2,3-(1*H*,4*H*)-dione (**1b**).

2.2.1 Synthesis of (**1a**)

A mass of 0.5 g (3.62 mmol) potassium carbonate and 0.10 mmol of tetra-*n*-butyl ammonium were added to a solution containing 0.3 g (1.45 mmol) of 6-chloro-1,4-dihydroquinoxaline-2,3-dione in 20 ml of dimethylformamide (DMF). After 10 min of stirring, 0.440 g (3.64 mmol) of allyl bromide was added. Then, the mixture was stirred for 6 hours at room temperature. The solution was filtered to remove the salts, then DMF solvent was evaporated under reduced pressure and the residue was dissolved in dichloromethane. The organic phase was dried over anhydrous sodium sulfate (Na₂SO₄) and it was concentrated. Finally, the product was separated from the mixture by silica gel column chromatography using a mixture of hexane/ethyl acetate with a ratio of (3/1) by volume as an eluent.

2.2.2 Synthesis of (**1b**)

A mass of 0.530 g (3.84 mmol) potassium carbonate and 0.10 mmol of tetra-*n*-butyl ammonium were added to a solution containing 0.300 g (1.45 mmol) of 6-nitro-1,4-dihydroquinoxaline-2,3-dione in 20 ml of dimethylformamide (DMF). After 10 min of stirring 0.460 g (3.80 mmol) of allyl bromide was added, then the mixture was stirred for 6 hours at room temperature. The solution was filtered to remove the salts, then DMF solvent was evaporated under reduced pressure and the residue was dissolved in dichloromethane. The organic phase was dried over anhydrous sodium sulfate (Na₂SO₄) and it was concentrated. Finally, the product was separated from the mixture by silica gel column

chromatography using a mixture of hexane/ethyl acetate with a ratio of (3/1) by volume as an eluent.

2.2.3 Spectral data measurements

The spectroscopic characterization of the synthesized compounds (**1a**) and (**1b**) is obtained by recording the ^1H and ^{13}C NMR spectra using (Bruker Avance DPX300) instrument.

2.2.3.1 Spectral data of (**1a**)

^1H NMR and ^{13}C NMR spectra of (**1a**) were shown in Figures 1 and 2, respectively.

^1H NMR (300 MHz, DMSO) δ ppm: 4.79 (m, 4H, $2\text{CH}_2\text{-CH}$); 5.22 (m, 4H, $2\text{CH}_2\text{=CH}$); 5.92 (m, 2H, $2\text{CH}_2\text{=CH}$); 7.19–7.36 (m, 3H, 3CH arom.).

^{13}C NMR (75 MHz, DMSO) δ ppm: 154, 05 (C=O); 153, 82 (C=O); 131, 75 (CH=CH_2); 131, 72 (CH=CH_2); 128, 24 (Cq); 128, 14 (Cq); 126, 09 (Cq); 123, 56 (CH arom.); 117, 73 (CH arom.); 117, 54 (CH_2); 117, 44 (CH_2); 115, 82 (CH arom.); 45, 34 (N- CH_2); 45, 21 (N- CH_2).

Figure 1. ^1H NMR spectrum of 1,4-diallyl-6-chloroquinoxaline 2,3-(1H,4H)-dione (**1a**).

Figure 2. ^{13}C NMR spectrum of 1,4-diallyl-6-chloroquinoxaline 2,3-(1*H*,4*H*)-dione (**1a**).

2.2.3.2 Spectral data of (**1b**)

^1H NMR and ^{13}C NMR spectra of (**1a**) were shown in Figures 3 and 4, respectively.

^1H NMR (300 MHz, DMSO) δ ppm: 4.95 (m, 4H, 2 $\text{CH}_2\text{--CH}$); 5.26-5.43 (m, 4H, 2 $\text{CH}_2\text{=CH}$); 5.88-6.03 (m, 2H, 2 $\text{CH}_2\text{=CH}$); 7.38 (d, 1H, 1CH arom.); 8.11-8.19 (m, 2H, 2CH arom.).

^{13}C NMR (75 MHz, DMSO) δ ppm: 153.47 (C=O); 153, 16 (C=O); 143, 59 (Cq); 131, 63 (Cq); 130, 15 (2CH=CH₂); 126, 98 (Cq); 119, 54 (CH₂); 119, 40 (CH arom.); 119, 14 (CH₂); 115, 95 (CH arom.); 111, 40 (CH arom.); 46, 15 (N-CH₂); 46, 04 (N-CH₂).

Figure 3. ^1H NMR spectrum of 1,4-diallyl-6-nitroquinoxaline-2,3-(1*H*,4*H*)-dione (**1b**).

2.3 Weight loss measurements

Gravimetric measurements are carried out in a double walled glass cell equipped with a thermostatic cooling condenser. The effect of addition of (**1a**) and (**1b**) inhibitors to 1.0 M HCl solutions on the corrosion of MS was determined after 6 h of immersion at (308 ± 1) K using weight loss measurements. The experiments were carried out in duplicate to check reproducibility. The average weight loss of the two runs was calculated. The corrosion rate (v) and the inhibition efficiency (E_w %) were calculated according to the following equations:

$$v = \frac{w}{S \cdot t} \quad (1)$$

$$E_w \% = \left(1 - \frac{v}{v_0} \right) * 100 \quad (2)$$

Where:

w : The average weight loss in (g)

S : The total area in (cm^2)

t : The immersion time in (h)

v and v_0 are the values of corrosion rate with and without the inhibitor, respectively.

2.4 Electrochemical techniques

The electrochemical impedance spectroscopy (EIS) measurements were carried out using Voltalab (Tacussel-Radiometer PGZ 100) potentiostat controlled by Tacussel corrosion analysis software model (Voltamaster4) at static condition. The corrosion cell used has three electrodes. The reference electrode was a saturated calomel electrode (SCE). A platinum electrode with a surface area of 1 cm^2 was used as an auxiliary electrode. The working electrode was a carbon steel of 1 cm^2 surface area. All potentials given in this study were referred to this reference electrode. The working electrode was immersed in the test solution for 1 h to establish a steady state open circuit potential (E_{ocp}).

After measuring the E_{ocp} , the electrochemical measurements were performed. All electrochemical tests were performed in de-aerated solutions at 308 K. After the determination of steady-state current at a corrosion potential, sine wave voltage (10 mV) peak to peak, at frequencies between 100 kHz and 10 mHz are superimposed on the rest potential.

Nyquist plots from these measurements were obtained. The best semicircle fit through the data points in the Nyquist plot was obtained using a non-linear least square fit which gives the intersections with the x -axis.

3. Results and discussion

3.1 Gravimetric measurements

The corrosion inhibition efficiency of the inhibitors (**1a**) and (**1b**) on (MS) in various concentrations in 1.0 M HCl solution was studied. The immersion time was 6 hours and the temperature at 308 K. The range of the concentration of these inhibitors was between 1.0×10^{-6} and 1.0×10^{-3} M. The corrosion rate (v), the inhibition efficiency ($E_w\%$) and the surface coverage (θ) were calculated using equations (1) and (2). The results are listed in Table 2.

Table 2. The corrosion rate, inhibition efficiency and the surface coverage of (MS) in the absence and presence of various concentrations of the inhibitors (**1a**) and (**1b**) in 1.0 M HCl solution at 308 K.

Inhibitor in 1.0 M HCl	C (mol/l)	v (mg·cm ⁻² ·h ⁻¹)	E_w (%)	θ
–	–	0.82	–	–
(1a)	10^{-6}	0.19	77	0.77
	10^{-5}	0.11	87	0.87
	10^{-4}	0.07	91	0.91
	10^{-3}	0.04	95	0.95
(1b)	10^{-6}	0.25	70	0.70
	10^{-5}	0.2	76	0.76
	10^{-4}	0.12	85	0.85
	10^{-3}	0.09	89	0.89

It is clearly noticed that the inhibition efficiency ($E_w\%$) increases with an increase in the concentration of inhibitors (**1a**) and (**1b**), Table 2. The surface coverage (θ) values of MS indicate that the molecules of the inhibitors (**1a**) and (**1b**) are adsorbed on its surface.

Maximum inhibition efficiencies, 95% and 89% were obtained by the inhibitors (**1a**) and (**1b**), respectively at an optimum concentration of 1.0×10^{-3} M in 1.0 M HCl solutions at 308 K. Such behavior can be explained by adsorption of the molecules of the inhibitors (**1a**) and (**1b**) on the mild steel surface, which increases with the increase of inhibitor concentration [19, 20]. This suggests that the corrosion inhibition is due to the adsorption of the molecules on the surface of MS and cover its active sites [21, 22].

3.2 Adsorption isotherm

Adsorption isotherm are very important for suggesting the type of adsorption on the metal surface. The adsorption process is a process in which the inhibitor molecules are adsorbed on the metal surface replacing the adsorbed water molecules [23, 24].

Many adsorption isotherms were tried to obtain the best fit of the experimental data of the adsorption of **(1a)** and **(1b)** molecules on a MS surface in 1.0 M HCl solution. The best fit was obtained with the adsorption isotherm of Langmuir, in which the surface coverage values (θ) are plotted against the concentration (C) of the inhibitors **(1a)** and **(1b)**, as shown in Figure 5.

The surface coverage values for the inhibitors were calculated from weight loss measurements at various concentrations of the inhibitors **(1a)** and **(1b)** in 1.0 M HCl solutions at temperature 308 K and listed in Table 2. The correlation between the surface coverage (θ) and the inhibitor concentration (C) is represented by Langmuir adsorption isotherm [25]:

$$\frac{C}{\theta} = \frac{1}{K_{\text{ads}}} + C \quad (3)$$

Where (θ) is the surface coverage, K_{ads} is the adsorption equilibrium constant and C is the concentration of equilibrium inhibitor. The K values were calculated from the intersections of the lines of the (C/θ) axis and are given in Table 3.

The relationship between the adsorption constant K and the change in the free energy of adsorption (ΔG_{ads}) is given in equation (4) and corresponding results are listed in Table 3 [26]:

$$\Delta G_{\text{ads}} = -RT \ln(K_{\text{ads}} \cdot 55.5) \quad (4)$$

Where R is the gas constant, T is the temperature, 55.5 is the molar concentration of water in solution and K is the adsorption equilibrium constant. The K_{ads} values show the strength of the interaction between the adsorbed molecules of the inhibitor and the MS surface. Higher values of K_{ads} indicate stronger adsorption of inhibitor molecules on the metal surface and high inhibition efficiency.

The values of the change in the free energy of adsorption (ΔG_{ads}) are negative for both inhibitors **(1a)** and **(1b)**. Negative values mean spontaneous process of the adsorption of inhibitor molecules on the MS surface and the formation of a stable layer of the inhibitor molecules on the MS surface. Generally, ΔG_{ads} values below $-20 \text{ kJ}\cdot\text{mol}^{-1}$ are consistent with an electrostatic interaction between charged molecules and a charged metal surface, indicating physical adsorption (physisorption). The chemisorption observed when the values of ΔG_{ads} are more negative than $40 \text{ kJ}\cdot\text{mol}^{-1}$ involves the sharing or the transfer of charge of the inhibitor molecules on the metal surface to form a bond [27–28]. The values of ΔG_{ads} presented in Table 3 are more negative than $40 \text{ kJ}\cdot\text{mol}^{-1}$, indicating a chemical adsorption of the inhibitor molecules **(1a)** and **(1b)** on the mild steel surface [29–30].

Table 3. The K_{ads} and ΔG_{ads} values of **(1a)** and **(1b)** inhibitors for MS in 1.0 M HCl solution at 308 K.

Inhibitor	K_{ads} (1 M)	$-\Delta G_{\text{ads}}$ (kJ/mol)	R^2
(1a)	522084.16	43.02	0.99998
(1b)	401955.11	42.37	0.99998

Figure 5. Langmuir isotherm of inhibitors **(1a)** and **(1b)** on MS in 1.0 M HCl solution.

3.3 Electrochemical polarization measurements

The corrosion inhibition mechanism of **(1a)** and **(1b)** on MS specimens was investigated by electrochemical polarization technique.

Figure 6 and Table 4 represent the electrochemical polarization plots. By using the linear Tafel extrapolation method, the current density (i_{corr}), corrosion potential (E_{corr}), cathodic Tafel slopes (β_c) are calculated. It can be figured out from Figure 6 that in the presence of the inhibitors **(1a)** and **(1b)**, especially **(1a)**, the E_{corr} value is more positive than that of the absence of them in 1.0 M HCl solution.

The percentage inhibition efficiency ($E_p\%$) values were calculated using the following equation (5):

$$E_p \% = (i_{\text{corr}(0)} - i_{\text{(inh)}} / i_{\text{corr}(0)}) * 100 \quad (5)$$

Where $i_{\text{corr}(0)}$ and $i_{\text{(inh)}}$ represent the corrosion current density values without and with inhibitor, respectively.

According to Figure 6, the addition of the inhibitors **(1a)** and **(1b)** to 1.0 M HCl solution, led to a large decrease in current densities of the both of anodic and cathodic currents. However, the depression of the cathodic current is more significant compared to the anodic one, suggesting that inhibitors **(1a)** and **(1b)** act as cathodic type inhibitors.

Both inhibitors **(1a)** and **(1b)** provide better corrosion inhibition on the MS due to the presence of hetero atoms (N and O) they have the capability to adsorb on the surface of MS.

It is clearly noticed from Table 3 that, the corrosion current density decreases, while the values of ($E_p\%$) increases, which is due to the interaction of the inhibitors **(1a)** and **(1b)** with the metal surface resulted in formation of an inhibiting layer on the MS surface.

Figure 6. Polarization plots after 1 h immersion of MS in 1.0 M HCl in the absence and presence of various concentrations of **(1a)** and **(1b)** inhibitors.

Table 4. Tafel polarization parameters obtained at different concentrations of inhibitors **(1a)** and **(1b)** in 1.0 M HCl solution.

Inhibitor in 1.0 M HCl	Concentration of inhibitor (M)	$-E_{\text{corr}}$ (mV/SCE)	i_{corr} ($\mu\text{A}/\text{cm}^2$)	E_p (%)
—	—	465	1386	—
(1a)	1.0×10^{-6}	471	309	78
	1.0×10^{-5}	483	257	81
	1.0×10^{-4}	486	123	91
	1.0×10^{-3}	485	101	93
(1b)	1.0×10^{-6}	450	391	72
	1.0×10^{-5}	451	318	77
	1.0×10^{-4}	452	253	82
	1.0×10^{-3}	450	171	88

3.4 Electrochemical impedance spectroscopic (EIS) technique

The corrosion behavior of MS in 1.0 M HCl without and with various concentrations of **(1a)** and **(1b)** inhibitors was examined using electrochemical impedance spectroscopic (EIS) technique at 308 K. Figure 7 (a), (b) represent the Nyquist plots of the inhibitors **(1a)** and **(1b)**, respectively. The impedance parameters including double layer capacitance (C_{dl}), transfer resistance (R_t) and percentage of inhibition efficiency ($E_{\text{EIS}}\%$) were evaluated from the values of charge transfer resistance (R_t) and tabulated in Table 5.

At both higher and lower frequencies the capacitance loop intercepts the real axis. The intercept at the high frequency end represents the solution resistance (R_s), while the intercept

at the lower frequency end represents the total resistance (R_t). The difference between these intercepts is equal to the R_{ct} that represents the measurement of the electron transfer that takes place on the exposed metallic surface under analysis and is inversely proportional to the corrosion rate of the MS surface.

Figure 7. Nyquist plots of MS corrosion in 1.0 M HCl solution without and with various concentrations of inhibitors (**1a**) and (**1b**).

The study of impedance behavior was carried out to evaluate the chemical and physical properties of the corresponding electrochemical system under investigation. The equivalent circuit that exactly fit to the EIS curves generally consisted of a double solution resistance R_s , charge transfer resistance R_{ct} and double layer capacitance C_{dl} (Figure 7). Generally, all the Nyquist plots were observed in semicircles and showed some irregularities which can be ascribed to the non-homogeneous nature or roughness of the MS surface. From the Table 5, it was observed that as the concentration of the inhibitors (**1a**) and (**1b**) increases, the C_{dl} values decrease and the R_t values increase. The variation in R_t values can be explained by the adsorption process by which the inhibition mechanism takes place. As the inhibitors (**1a**) and (**1b**) concentration increases there would be a considerable increase in the amount of adsorption process. It is due to the prevention of the charge transfer of the metal atoms on the metallic surface and solution by adsorbed molecules resulting in raising the charge transfer resistance with the increase in inhibitor concentration of (**1a**) and (**1b**). The lowering of C_{dl} values with the increase in the concentrations of inhibitors (**1a**) and (**1b**) can be associated with the reduction of the local dielectric constant values and rise in the thickness of electrical double layer. These observations testify the inhibitors (**1a**) and (**1b**) action at the solution-metal interface.

Table 5. Electrochemical impedance parameters of MS corrosion without and with various concentrations of inhibitors (**1a**) and (**1b**) in 1.0 M HCl solution.

Inhibitor	Concentration of inhibitor (M)	$R_{x_t} (\Omega \cdot \text{cm}^2)$	$C_{dl} (\mu\text{F}/\text{cm}^2)$	$E_{\text{EIS}} \%$
–	–	14.57	200	–
(1a)	1.0×10^{-6}	70	94	79
	1.0×10^{-5}	100	79	85
	1.0×10^{-4}	180	49	92
	1.0×10^{-3}	350	35	96
(1b)	1.0×10^{-6}	49	150	70
	1.0×10^{-5}	83	111	82
	1.0×10^{-4}	118	72	88
	1.0×10^{-3}	155	55	91

From the data in Table 5, it is obvious that both inhibitors (**1a**) and (**1b**) act as potential corrosion inhibitors in 1.0 M HCl solution. Both of them exhibited an inhibition efficiency above 70%, and it reaches 96% and 92% for (**1a**) and (**1b**) at a concentration of 1.0×10^{-3} M, respectively.

Figure 8. Equivalent circuit for EIS measurements.

4. Mechanism of inhibition

The adsorption of inhibitor molecules on metal surface cannot be considered to be only a purely chemical or physical adsorption phenomenon. Chemical adsorption arises from the donor-acceptor interactions between free electron pairs of the heteroatom's (N, O, and S) and π -electrons of multiple bonds and vacant d-orbital's of iron. While in physical adsorption, the inhibitor molecules can be adsorbed on the mild steel surface via electrostatic interaction between the charged inhibitor molecules and charged metal surface [31–35].

Various researches suggest that the presence of chloride ions in the acidic medium stabilizes the adsorption of inhibitor molecules by the formation of a highly stabilized

coordination inter-medium on the metal surface. The chloride ion acts as a ligand, which makes a bridge between the inhibitor molecule and metal surface [36, 37].

The inhibitor molecules function through adsorption on the metal surface, blocking the active sites by displacing water molecules and forming a stable protective layer to decrease the corrosion rate. The adsorption of inhibitor molecules on metal/solution interface influenced by:

1. Chemical structure of inhibitor molecules.
2. Type of destructive electrolyte.
3. Nature and charge of metal surface.

Inhibitor molecules adsorbed on the metal surface by one or more of the following mechanisms:

1. Interaction of unshared electron pairs in the inhibitor molecules with the metal surface.
2. Electrostatic interaction between the charged metal and the charged molecules.
3. Interaction of filled p-orbital electrons with vacant d-orbital of the metal.
4. A combination of all of these.

The high inhibition efficiency of the inhibitors (**1a**) and (**1b**) can be attributed to the presence of large molecules containing heteroatoms such as (N and O, *p* electrons, and aromatic rings), thus inhibiting corrosion by covering large areas on the MS surface.

The inhibitors molecules (**1a**) and (**1b**) are present as either neutral or protonated molecules (cations) in acidic solutions [38]. The change in the free energy of adsorption (ΔG_{ads}) values were around $-40 \text{ kJ}\cdot\text{mol}^{-1}$, indicating the chemical adsorption of the inhibitors (**1a**) and (**1b**) on the MS surface [39].

Figure 9 shows a skeletal representation of adsorption of the inhibitors molecules (**1a**) and (**1b**) on the MS surface [40].

Figure 9. Proposed schematic diagram for the adsorption mechanism of inhibitors (**1a**) and (**1b**) on MS surface in 1.0 M HCl solution.

5. Conclusions

Both of the studied inhibitors (**1a**) and (**1b**) displayed predominant corrosion inhibition efficiency on mild steel in 1.0 M HCl solution. According to the gravimetric and electrochemical analysis, the corrosion inhibition efficiency of the inhibitor (**1a**) is more than (**1b**). The high efficiency of the inhibitors (**1a**) and (**1b**) may be attributed to the presence of two aromatic rings and the presence of Cl and NO₂ groups.

Both compounds obeyed Langmuir adsorption isotherm on MS surface. Surface morphological analysis revealed that the studied compounds form a protective barrier on MS surface and resist the metallic disintegration appreciably.

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