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5-(2-Chlorobenzyl)-2,6-Dimethylpyridazin-3-One: An efficient Inhibitor of C38 Steel Corrosion in Hydrochloric Acid

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ABSTRACT

In the present paper, we report the synthesis of 5-(2-chlorobenzyl)-2,6-dimethylpyridazin-3-one (CBDP) as a potential inhibitor of C38 Steel in aerated 1M HCl solution was studied. For this aim, electrochemical techniques such as potentiodynamic polarization curves, weight loss (WL) and electrochemical impedance spectroscopy (EIS). All the techniques used for the studies shows the increase in inhibition efficiency and decrease in the corrosion rate by increasing the inhibitor concentration. Impedance measurements showed that the double-layer capacitance decreased and charge-transfer resistance increased with increase in the inhibitor concentration and hence increasing in inhibition efficiency. Polarization measurements indicated that, the studied inhibitor acts as mixed type corrosion inhibitor. The adsorption of CBDP molecules on the C38 steel surface obeys Langmuir adsorption isotherm, and the thermodynamic parameters were determined and discussed.

Keywords: Steel, Hydrochloric acid, Inhibitors, Pyridazine, Polarisation curves, Impedance.

INTRODUCTION

Corrosion is a fundamental process playing an important role in economics and safety, particularly for metals and alloys. Steel has found wide application in a broad spectrum of industries and machinery; however its tendency to corrosion. The corrosion of steel is a fundamental academic and industrial concern that has received a considerable amount of attention [1]. Using inhibitors is an important method of protecting materials against deterioration due to corrosion, especially in acidic media [2]. Acid solutions are widely used in industry, some of the important fields of application being acid pickling of iron and steel, chemical cleaning and processing, ore production and oil well acidification. As acidic media, HCl and H_2SO_4 are generally used in the treatment of steel and ferrous alloys. Because of the general aggression of acid solutions, inhibitors are commonly used to reduce the corrosive attack on metallic materials. The review including extensive listing of various types of organic inhibitors has been published [3]. Most well-known acid inhibitors are organic compounds containing nitrogen, sulfur, and oxygen atoms. Among them, nitrogen-containing heterocyclic compounds are considered to be effective corrosion inhibitors on steel in acid media [4]. N-heterocyclic compound inhibitors act by adsorption on the metal surface, and the adsorption of N-heterocyclic inhibitor takes place through nitrogen heteroatom, as well as those with triple or conjugated double bonds or aromatic rings in their molecular structures.

Up to now, many N-heterocyclic compounds, such as imidazoline derivatives [5], 1,2,3-trizaole derivatives [6], 1,2,4-trizaole derivatives [4,7–11], tetrazole derivatives [12,13], pyrrole [14], pyridine derivatives [15–17], pyrazole derivatives [18–21], bipyrazole derivatives [22,23], pyrimidine derivatives [24], pyridazine derivatives [25], indole derivatives [26–28], benzimidazole derivatives [29–33], quinoline derivatives [34] and quinoxaline derivatives [35-40] have been used for the corrosion inhibition of iron or steel in acidic media.
The present work was established to study the corrosion inhibition of C38 steel in 1M HCl solution by new pyridazine derivative as corrosion inhibitor using different techniques: weight loss, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS). The thermodynamic parameters were calculated and discussed. The chemical structure of the studied pyridazine derivative is given in Figure 1.

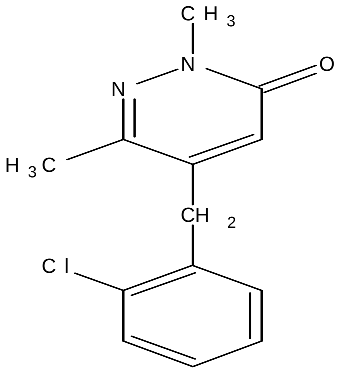

Figure .1 The molecular structure of CBDP.

MATERIALS AND METHODS

2.1. Materials and reagents

C38 Steel strips containing (0.09 % P; 0.38 % Si; 0.01 % Al; 0.05 % Mn; 0.21 % C; 0.05 % S and the remainder iron) were used for electrochemical and gravimetric studies. Prior to all measurements, are abraded with a series of emery paper from 180 to 1200 grade. The specimens are washed thoroughly with bidistilled water degreased and dried with acetone. The aggressive solution (1M HCl) was prepared by dilution of Analytical Grade 37 % HCl with double-distilled water.

2.2. Synthesis

Recentely, Benchat et al. [41] synthesized a series of products by alkylation of pyridazines, the authors showed that these products are good activity anti-cancerous and have a low toxicity. In our ongoing research the compoud (CBDP) was synthesised like the reference [42].

The product CBDP was prepared from 5-(2-chlorobenzyl)-2,6-dimethylpyridazin-3-one in situ by the solid-liquid PTC conditions without solvent[3]. To pyridazin (1.2 g, 5 mmol) was added (0.769g,5mmole). TBAB (0,3 ; 1mmome) and méthyl iodide (0,73g , 5 mmole) The mixture was placed in a pyrex tube which was then introduced into a Maxidigest MX 350 Prolabo microwave monomode reactor fitted with a rotational system. At the end of the irradiation time (10 min on 90 w as irradiation power), the mixture was cooled to ambient temperature. The precipitate formed was filtered and watched with water yield : 96% of CBDP solid.

Melting point: 85 ° C
IR (KBr, cm^{-1}): 1747 (CO_2Et), 1663 (C=O), 1591 (C = N) , 1430 ; 1490 (C=C).
^{1}H-NMR (300.14 MHz, $CDCl_3$) δ (ppm): 2. 25 (s, 3H, CH_3), 3.70(s, 3H, CH_3) ; 4.82 (s, 2H, CH_2), 6.53(s,1H, H4), 7.20 (m, 5H, protons -ph).
^{13}C-NMR (75 MHz, $CDCl_3$) δ (ppm):19.11 (CH_3), 35.03 (CH_3) ; 40.77 (CH_2), 127.71 (CH-4), 126,54 (CH-ph); 128,22 (CH –ph) ;131,15 (CH -ph); 131,93 (CH -ph), 132,15 (CH -ph); 134,21 ; 141.9; 145.21; 160.52 (C-3).

2.3. Measurements

2.3.1. Weight loss measurements

Gravimetric measurements are carried out in a double walled glass cell equipped with a thermostated cooling condenser. The solution volume is 50 cm^3. The steel specimens used have a rectangular form (1.6cm × 1.6cm × 0.07cm). The immersion time for the weight loss is 6h at 308K.

2.3.2. Electrochemical measurements

- *Electrochemical cell*

The electrolysis cell was Pyrex of cylinder closed by cap containing five openings. Three of them were used for the electrodes. The working electrode was C38 steel with the surface area of 1 cm^2. Before each experiment, the electrode was polished using emery paper until 1200 grade. After this, the electrode was cleaned ultrasonically with distillate water. A saturated calomel electrode (SCE) was used as a reference. All potentials were given with reference to this electrode. The counter electrode was a platinum plate of surface area of 1 cm^2. The aggressive medium used here is 1M HCl solution was prepared with concentrated HCl and distilled water. The organic compound tested is pyridazine derivative. Its molecule formula is shown in Fig. 1. The concentration range of this compound was 10^{-3} to 10^{-6} M.

- *Polarisation measurements*

The working electrode was immersed in test solution during 30 minutes until a steady state open circuit potential (E_{ocp}) was obtained. The polarization curve was recorded by polarization from -800 mV to 0 mV under potentiodynamic conditions corresponding to 1 mV/s (sweep rate) and under air atmosphere, at frequencies between 100 kHz and 10 mHz was superimposed on the rest potential. The potentiodynamic measurements were carried out using Tacussel Radiometer PGZ 100, which was controlled by a personal computer.

RESULTS AND DISCUSSION

3.1. Gravimetric measurements

In the gravimetric experiment, a previously weighed metal (C38 steel) coupon was completely immersed in 50 mL without and with different concentrations of pyridazine derivative in an open beaker. The beaker was inserted into a water bath maintained at 308 K. From the weight loss results, the inhibition efficiency (% IE) of the inhibitor and degree of surface coverage (Θ) were calculated using equations 1 and 2 [43];

$$\%IE = \left(1 - \frac{W_1}{W_2}\right) \times 100 \tag{1}$$

$$\Theta = 1 - \frac{W_1}{W_2} \tag{2}$$

Where W_1 and W_2 are the weight losses for steel in the presence and absence of the inhibitor in HCl solution and Θ is the degree of surface coverage of the inhibitor.

Table 1. Gravimetric results of C38 steel in 1M HCl without and with addition of CBDP at 308 K.

Inhibitor	Con (M)	W(mg/cm^2.h)	E_w (%)	Θ
Blank	1	1.07	-	
CBDP	10^{-3}	0.04	**96.1**	0.961
	5×10^{-4}	0.05	95.2	0.952
	10^{-4}	0.06	94.2	0.942
	5×10^{-5}	0.12	88.3	0.883
	10^{-5}	0.17	84.1	0.841
	10^{-6}	0.24	77.2	0.772

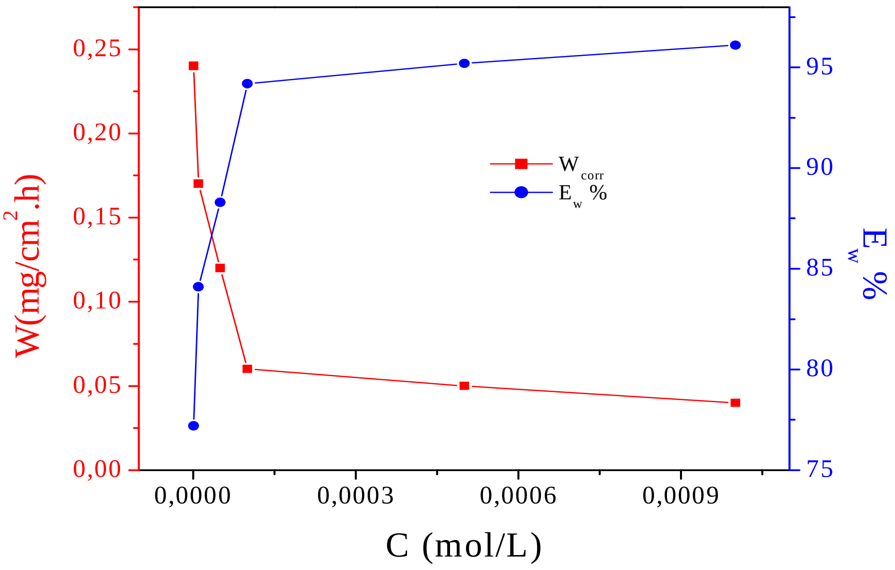

Figure 2. Variation of corrosion rate (W) and inhibition efficiency (E_w) with CBDP concentration for steel in 1M HCl at 308 K.

The values of percentage inhibition efficiency and corrosion rate obtained from weight loss method at different concentrations at 308K are summarized in Table 1. Fig. 2 illustrates the variation of corrosion rate and efficiencies with concentration of inhibitor. It has been found that all of this compound inhibit the corrosion of C38 steel in HCl solution at all concentrations used in this study. It has also been observed that the inhibition efficiency of this compound increases with the increase in concentration. Maximum E_w (%) for each compound was achieved at 10^{-3}M and a further increase in concentration did not cause any appreciable change in the performance of the inhibitor (gravimetric measurement). The corrosion inhibition can be attributed to the adsorption of this compound at the C38 steel / acid solution interface. The corrosion rate decreases with the concentration of inhibitor and in turn the inhibition efficiency evaluated from weight loss measurements for this compound increases to attain 96.1% for 10^{-3}M.

3.2. Potentiodynamic polarization measurements

Fig. 3 show typical Tafel curves obtained for C38 steel in 1M HCl with and without the compound studied. The values of associated electrochemical parameters, i.e., corrosion potential (E_{corr}), corrosion current density (I_{corr}), cathodic Tafel slopes (β_c) and percentage inhibition efficiency (IE (%)) values were calculated from polarization curves and listed in Table 2. The inhibition efficiency IE (%) was calculated from polarization measurements according to the relation given below:

$$E_I(\%) = (\frac{I_{corr} - I'_{corr}}{I_{corr}})\times 100 \qquad (3)$$

Where I_{corr} and I'_{corr} are uninhibited and inhibited corrosion current densities, respectively. They are determined by extrapolation of Tafel lines to the respective corrosion potentials.

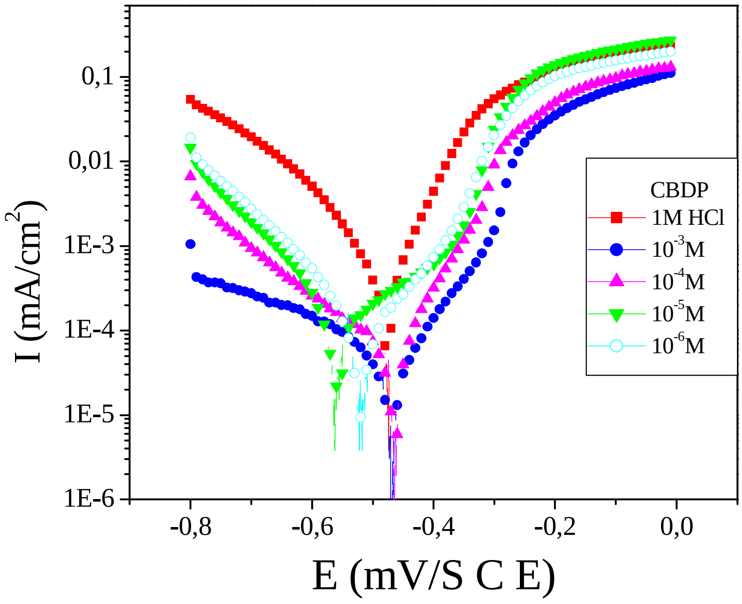

Figure 3. Polarization curves for Steel in 1M HCl in the absence and presence of different concentrations of CBDP at 308K.

The cathodic polarization curves give rise to parallel Tafel lines with the nearly constant cathodic Tafel slopes (β_c) indicate that the addition of inhibitor to the aggressive solution does not modify the proton reduction mechanism and this reaction is activation control. The inhibitor is first adsorbed onto steel surface and then impedes by merely blocking the active sites of steel surface. In this way, the surface area available for H^+ ions is decreased, while the actual reaction mechanism remains unaffected [44].

In the anodic part of polarization curves, a significant inhibition was observed, which may suggest formation of a protective layer of adsorbed species at the metal surface [45]. More increase of potential indicated that the protective layer of inhibitor persisted. This means that the inhibition mode of inhibitor do not depend on the electrode potential. Although, increasing current density at higher over potentials the adsorption phenomenon is more significant against the dissolution of steel. The shape of anodic branch revealed the organic compound may act by the formation of iron-complex as discussed widely in the literature [46]. Pyridazine compound is an efficient inhibitor of steel in HCl solution.

Table 2 indicates clearly a decrease in the corrosion rate in the presence of CBDP. This effect is hugely marked at higher concentration of inhibitor. The inhibitive action is more explicit by E_I % data which increases with inhibitor concentration to reach 95.5 % at 10^{-3}M.

Table 2. Polarisation data of Steel in 1M HCl without and with addition of inhibitors at 308 K

Inhibitors	Conc (M)	$-E_{corr}$ (mV/SCE)	$-\beta_c$ (mV/dec)	I_{corr} ($\mu A/cm^2$)	E_I (%)
Blank	1	475.9	175.6	1077.8	-
CBDP	10^{-3}	469.8	199.4	48.8	**95.5**
	10^{-4}	465.5	158.3	52.9	95.1
	10^{-5}	563.7	132.6	170.0	84.2
	10^{-6}	524.2	147.7	176.6	83.6

3.3. Electrochemical impedance spectroscopic studies

The corrosion behavior of steel, in 1M HCl solution with and without inhibitor, was also investigated by electrochemical impedance spectroscopy (EIS) measurements. Fig. 4 showed impedance behavior of steel corrosion in the form of Nyquist plots. The impedance parameters derived from these plots are given in Table 3. Double layer capacitance values (C_{dl}) and charge-transfer resistance values (R_t) were obtained from impedance measurements. In the case of the electrochemical impedance spectroscopy, E_{Rt} (%) is calculated by charge transfer resistance according to the relation:

$$E_{R_t}\,\% = \frac{R_{t(inh)} - R_t}{R_{t(inh)}} \times 100 \qquad (4)$$

Where $R_{t(inh)}$ and R_t are the charge transfer resistance in the presence and absence of pyridazine, respectively.

The double layer capacitance (C_{dl}) and the frequency at which the imaginary component of the impedance is maximal ($-Z_{max}$) are found as represented in equation 5:

$$C_{dl} = \left(\frac{1}{\omega R_t}\right) \qquad \text{where } \omega = 2\pi f_{\max} \qquad (5)$$

For Nyquist plots (Fig 4) it is clear that the impedance diagrams in most cases does not show perfect semicircle. This behavior can be attributed to the frequency dispersion [47] as a result of roughness and in homogenates of the electrode surface. The impedance response consisted of characteristic semicircles for solutions examined indicating that the dissolutions of steel process occurs under charge transfer control in other words under activation control and the presence of the inhibitor does not change the mechanism of the acid dissolution. These semicircles are of a capacitive type whose diameters increase with increasing inhibitor concentration.

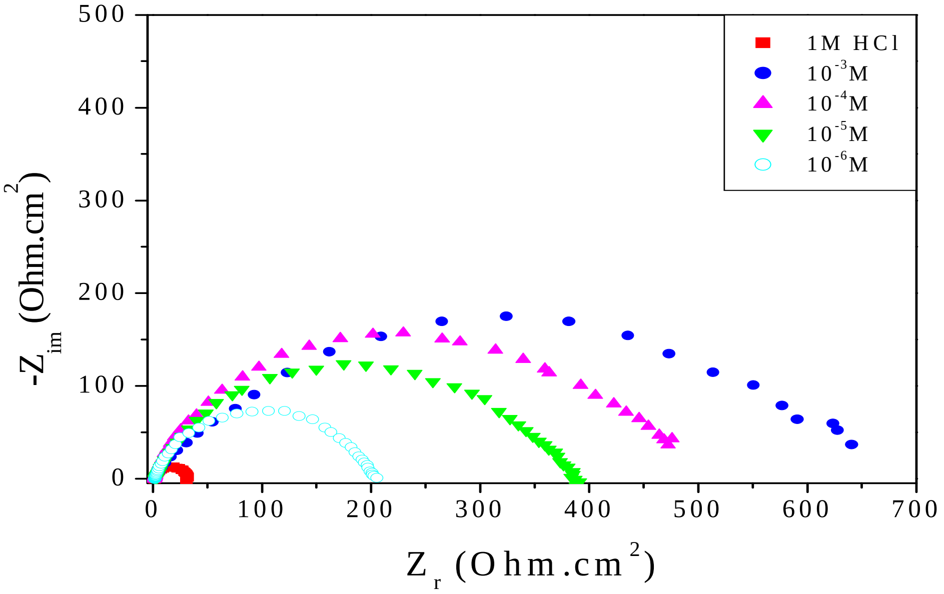

Figure 4. Nyquist diagrams Steel in 1M HCl without and with different concentrations of CBDP.

The values of R_t increases with increasing inhibitor concentration which indicates that the adsorption of inhibitor molecules occurs on the metal surface (Fig 5). The data (Table 3) indicate that increasing charge transfer resistance is associated with a decrease in the double layer capacitance and increase in the percentage inhibition efficiency. The decrease in C_{dl} values could be attributed to the adsorption of the inhibitor molecules at the metal surface. It has been reported that the adsorption of organic inhibitor on the metal surface is characterized by a decrease in C_{dl} [48].

Furthermore the decreased values of C_{dl} (Fig 5) may be due to the replacement of water molecules at the electrode interface by organic inhibitor of lower dielectric constant through adsorption. This phenomenon is generally related to the adsorption of organic molecules on the metal surface and then leads to a decrease in the local dielectric constant and/or an increase in the thickness of the electrical double layer [49].

$$C_{dl} = \frac{\varepsilon_o \varepsilon}{\delta} S \qquad (6)$$

Where δ is the thickness of the protective layer, S is the electrode area, ε_o the vacuum permittivity of vide and ε is dielectric constant of the medium.

Table 3. Data obtained from EIS measurements for C38 steel in 1M HCl in presence of different concentrations of this inhibitor

Inhibitor	Conc (M)	R_t (Ω.cm^2)	f_{max} (Hz)	C_{dl} (μF/cm^2)	E_{Rt} (%)
Blank	1M HCl	31.04	63.34	80.99	-
CBDP	10^{-3}	654.70	15.83	15.36	95.3
	10^{-4}	483.90	15.83	20.79	93.6
	10^{-5}	376.18	20.00	21.16	91.5
	10^{-6}	200.20	20.00	39.77	84.5

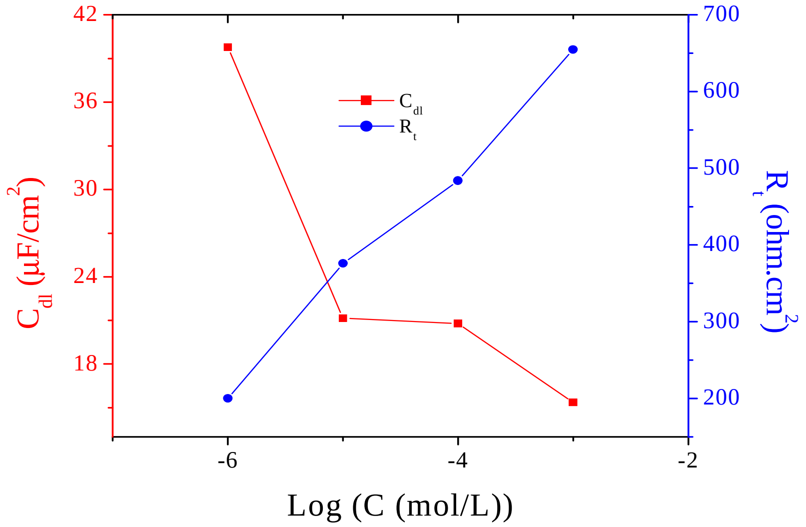

Figure 5. Evolution of transfer resistance and capacitance as function of logarithm of CBDP concentration

A low capacitance may result if water molecules at the electrode interface are largely replaced by organic inhibitor molecules through adsorption [50].The larger inhibitor molecules also reduce the capacitance through the increase in the double layer thickness [51].

The inhibition efficiencies, determined from electrochemical impedance measurements, show the same trend as those obtained from polarization and weight loss measurements. Comparison of the E% values (Tables 1, 2 and 3), obtained using these three methods, show acceptable agreement.

3.4. Adsorption isotherm and thermodynamic parameters

It is well recognised that the first step in inhibition of metallic corrosion is the adsorption of organic inhibitor molecules at the metal/solution interface and that the adsorption depends on the molecule's chemical composition, the temperature and the electrochemical potential at the metal/solution interface. In fact, the solvent H_2O molecules could also adsorb at metal/solution interface. So the adsorption of organic inhibitor molecules from the aqueous solution can be regarded as a quasi-substitution process between the organic compounds in the aqueous phase [Org(sol)] and water molecules at the electrode surface [H_2O(ads)] [52]:

$$\mathrm{Org_{(sol)}} + \mathrm{nH_2O_{(ads)}} \rightarrow \mathrm{Org_{(ads)}} + \mathrm{nH_2O_{(sol)}}$$

Where (n) is the size ratio, that is, the number of water molecules replaced by one organic inhibitor. Basic information on the interaction between the inhibitor and the steel surface can be provided by the adsorption isotherm. In order to obtain the isotherm, the linear relation between degree of surface coverage (Θ) values (Θ = E%/100; Table 1) and inhibitor concentration (C_{inh}) must be found. Attempts were made to fit the Θ values to various isotherms including Langmuir, Temkin, Frumkin and Flory–Huggins. By far the best fit is obtained with the Langmuir isotherm. This model has also been used for other inhibitor systems [53,54]. According to this isotherm, Θ is related to C_{inh} by:

$$\frac{C_{inh}}{\Theta} = \frac{1}{K_{ads}} + C_{inh} \qquad (5)$$

Where K_{ads} denotes the equilibrium constant for the adsorption process.

Fig. 6 shows the plots of C_{inh}/Θ versus C_{inh} and the expected linear relationship is obtained for this compound. The strong correlation (R^2 = 0.99999 for the compound CBDP) confirm the validity of this approach.

The thermodynamic parameters from the Langmuir adsorption isotherm are listed in Table 4, together with the value of the Gibbs free energy of adsorption ΔG°_{ads} calculated from the equation:

$$\Delta G^{\circ}_{ads} = -RTLn(55.5K_{ads}) \qquad (6)$$

Where R is the universal gas constant, T the thermodynamic temperature and the value of 55.5 is the concentration of water in the solution [55].

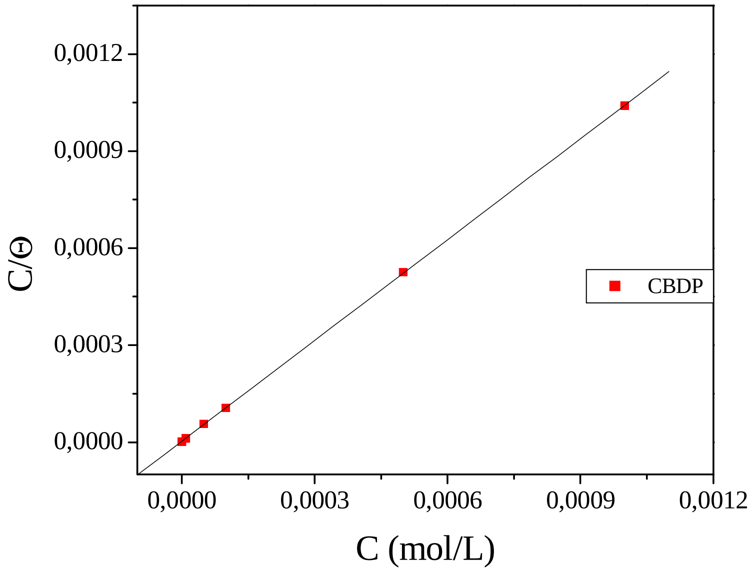

Figure 6 . Langmuir isotherm for the adsorption of pyridazine on the surface of steel in 1M HCl

The thermodynamic parameters for adsorption process obtained from Langmuir adsorption isotherm for the studied pyridazine molecule is given in Table 4. The negative value of ΔG°_{ads} and the higher value of K_{ads} reveal the spontaneity of adsorption process and they are characteristic of strong interaction and stability of the adsorbed layer with the steel surface.

Table 4. Thermodynamic parameters for the adsorption of CBDP in 1M HCl on the C38 steel at 308K

Inhibitor	Slope	K_{ads} (M^{-1})	R^2	ΔG°_{ads} (KJ/mol)
P1	1.03	402107.04	0.99999	-43.329

Generally, the energy values of -20 kJ mol^{-1} or less negative are associated with an electrostatic interaction between charged molecules and charged metal surface, physisorption; those of -40 kJ mol^{-1} or more negative involve charge sharing or transfer from the inhibitor molecules to the metal surface to form a coordinate covalent bond, chemisorption [56, 57]. The calculated

ΔG°_{ads} value of slightly more negative than −40 kJ mol^{-1} indicates, therefore, that the adsorption mechanism of the investigated pyridazine (CBDP) on steel in 1M HCl solution is typical of chemisorption (Table 4).

CONCLUSION

In this work, Chemical (weight loss) and Electrochemical (Galvanostatic and Impedance measurement) methods were used to study the ability of CBDP compound to inhibit the corrosion of C38 steel in aerated 1M HCl solution. The principal conclusions are:

- CBDP acts as an effective inhibitor of C38 steel corrosion in hydrochloric acid.
- The inhibition efficiency increases with inhibitor concentration to attain a value of 96.1% (10^{-3}M) at 303 K
- The Langmuir adsorption isotherm provides a formal description of the adsorptive behaviour of the electron-releasing pyridazine on C38 steel. The value of ΔG°_{ads} indicates that the corrosion inhibition by this compound is due to the formation of a chemisorbed film on the metal surface.
- Polarisation study shows that pyridazine act as mixed-type inhibitor.
- Impedance method indicates that CBDP adsorbs on the C38 steel surface with increasing transfer resistance and decreasing of the double-layer capacitance.
- The data obtained from the three different methods: potentiodynamic polarisation, EIS and weight loss, are in good agreements.

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