Preparation and Investigation of Some New Pyrazole Derivatives as Corrosion Inhibitors for Mild Steel in Acidic Media

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Abstract

Preparation of some new pyrazole derivatives by using a few steps starting from 4-acetylaniline to prepare azo compound (3). Chalcone derivatives (A1-A3) were obtained by reaction compound (3) with a proper aldehyde(benzaldehyde,4-(N,N-dimethylamino) benzaldehyde, terephalaldehyde). Chalcone derivatives (A1-A3) reacted with a proper hydrazine (hydrazine hydrate, phenyl hydrazine) to yield pyrazole derivatives (B1, B2, B3, B4, B5, B6). All prepared structure compounds were confirmed using spectroscopic and^{1}H-NMR techniques. Prepared compounds (B1, B2, B3, B4, B5, B6) were successfully applied as organic corrosion inhibitors for mild steel in 1M H_2SO_4 solution at 30^{o}C by using a weight loss method. The results of weight loss measurements showed that corrosion inhibition efficiency by increasing the concentration of organic inhibitors for mild steel in 1M H_2SO_4 solution at 30^{o}C.

Keywords: pyrazole derivatives, weight loss method, corrosion inhibition efficiency.

1. Introduction

Corrosion is a process of materials defect due to reaction with its environment. Wet, saline, acidic and aerated conditions make iron and its alloys to be exposed to corrosion process on the surface. This kind of harmful attack can cause deterioration in the mechanical, physical and chemical properties of metal. Therefore, many researchers deal with creation and developing protection methods to reduce the damage effects of the metal. Organic inhibitors are very effective way for the reducing of corrosion of metals and alloys due to generate a thin film that controls and prevents access of corrosive agents to the metal surface. The organic inhibitors that used for control corrosion of steel are organic compound containing nitrogen, oxygen and/or sulphur atoms [1-6].

Azo compounds are the most widely used class of dyes due to their application in various fields, such as the dyeing of textiles, and fibbers [7]. Some studies have shown that the inhibition of the corrosion by organic dyes are mainly attributed to the formation of complex compounds between the metal-ions and the nitrogen of azo binding at the electrode surface [8].

The most efficient corrosion inhibitors used in hydrochloric acid contain hetero atoms such as sulfur, nitrogen and oxygen containing compounds [9, 10]. Survey of literature reveals that pyrazole derivatives are effective corrosion inhibitors up to 80^{o}C. The encouraging results obtained by pyrazolic compounds [11,12] have incited us to synthesize other compounds and to test their addition on the corrosion behavior of steel in acidic media.

In the present work, we studied the inhibition properties of some new prepared pyrazole derivatives for the corrosion of mild steel in 1M H_2SO_4 solution. Weight loss measurements were used for investigating the corrosion behavior.

2. Materials and Methods

2.1. Synthesis of the organic inhibitors

a) Azo derivatives (**3**) [13]

4-acetylaniline (0.01 mol) and conc. HCl (10 mL) was taken in 250 mL Erlenmeyer flask containing (40 mL) of water and stirred vigoursly to make a homogeneous solution by adding (25 g) of crushed ice. Place the beaker in ice-water bath at (0-5)$^{\circ}$C for half hr. Then (2.6 g) of sodium nitrite solution in (6 mL) of water was added slowly with constant stirring for 10-15 min. and allowed the flask to stand for 10 min; Aniline(0.01 mole) was added with stirring, Sodium acetate (10.5 g) in (20 mL) of water was added during a period of 5 min. A precipitate of diazoamino benzene derivative (3) was filtered and washed with cold water, the recrystallized from ethanol. Physical properties of the compound (3) is given in Table1.

b) Chalcones (**A1-A3**) [14]: A cooled solution of (25mmol) of NaOH in (100mL) of water and (80 mL) of ethanol was prepared. The solution is kept at about 20–25°C and stirred vigorously while one-half of a mixture of (10 mmole, 2.9g) of 1-(4-acetophenyl)-3-phenyl triazene and (10 mmol) of aproper aldehyde (benzaldehyde, 4-(N,N-dimethylamino) benzaldehyde, terphalaldehyde) is added in about two or three min. a yellow forms which soon becomes a precipitate. After 15 min. the rest of the mixed reagents are added, and the container is rinsed with a little alcohol which is added to the mixture. Vigorous stirring is continued for 1.5 h longer, and the mush is then filtered with suction on a large Buchner funnel. The product is thoroughly washed with distilled water and then dried at room temperature. The physical properties of synthesized compounds (A1-A3) are given in Table (1).

c) Pyrazole derivatives (**B1-B6**) [15]: A mixture solution of a chalcone (A1, A2 or A3) (0.01 mol) and hydrazine hydrate (0.01 mol 85%) or phenyl hydrazine (0.01 mol, 99%) in absolute ethanol (50mL) to this add aqueous sodium hydroxide (10%, 6 mL). The reaction mixture was refluxed for 24h and pour into cold water. The obtained product was filtered, washed with water and recrystallized from ethanol. The physical properties of prepared compounds (B1-B6) are given in Table (1).

2.2. Preparation of aggressive solution

Aggressive solution of 1M $H_2SO_4$was prepared by dilution of analytical grade 98% H_2SO_4 with distilled water. Inhibitor concentrations of $1x10^{-2}$ to $5x10^{-4}$ M were prepared in 1M H_2SO_4 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 500 to 1500 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 desiccators 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. The specimens were removed after 8 hours exposure period at 30ºC, 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 per ASTM method described previously [16,17] 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^{-2} h^{-1}). The corrosion rate of mild steel was determined using the relation [18]:

$$W = \frac{\Delta m}{st} \quad \text{...} \ (1)$$

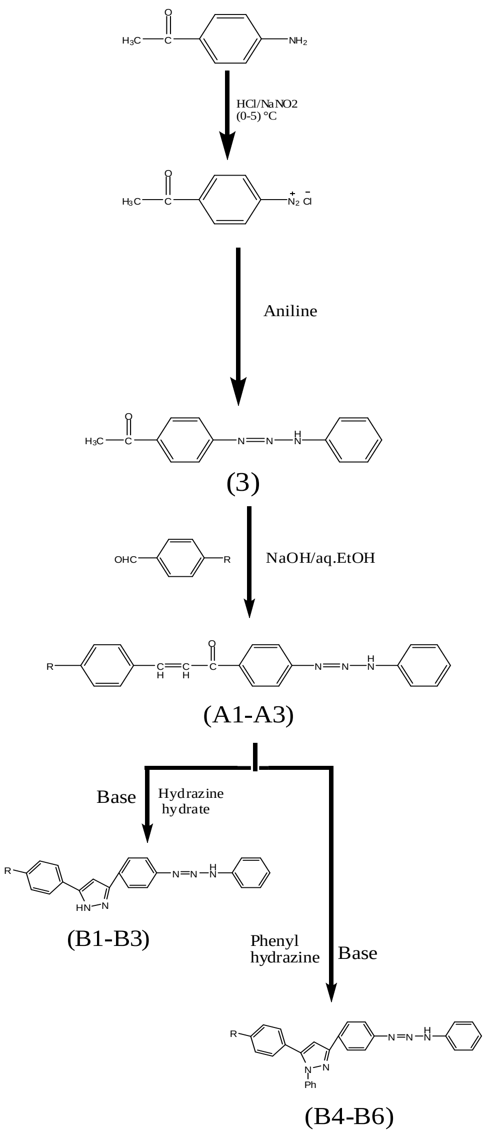
Where Δm is the mass loss, s the area and t is the immersion period. The percentage inhibition efficiency (IE (%)) was calculated using the relationship [19]:

$$IE\% = \left(\frac{W_{corr} - W_{corr(inh)}}{W_{corr}}\right) \times 100 \quad \text{...........} \ (2)$$

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

3. Results and Discussion

Fig.(1) shows the scheme of the present work that included preparation of some new pyrazole derivatives (B1-B6):



R = H, CHO, $(CH_3)_2N$

Fig.(1): The scheme plan of reparation of new pyrazole derivatives (B1-B6).

The reactions above are included new pyrazole derivatives (B1-B6) through usual preparation mehodes by converting 4-acetyl aniline into azo compound (3), and followed to prepare some chalcone derivatives (A1-A3) using different aldehydes in the persence of base. Finelly, pyrazole derivatives (B1-B6) were synthesized by reaction a chalcone derivative (A1-A3) with a hydrazine compound. Table (1) shows Physical properties of the synthesized compounds.

Table (1)
Physical properties of all prepared compounds.

Name of compound	*Chemical formula*	*Color*	*Molecular weight*	*M. P. ˚C*	*Yield %*
1-(4-acetophenyl)-3-phenyl triazene [**3**].	$C_{14}H_{13}N_3O$	Orange	239.27	107-110	87
3-phenyl-(1-(4-acetophenyl)-3-phenyltriazene)prop-2-en-1-one (**A1**)	$C_{21}H_{17}N_3O$	Brown	327.38	159-161	85
3-(4-benzaldehyde)-(1-(4-acetophenyl)-3-phenyltriazene)prop-2-en-1-one (**A2**)	$C_{22}H_{17}N_3O_2$	Yellow	355.39	153-155	71
3-(4-dimethylamino)phenyl)-(1-(4-acetophenyl)-3-phenyltriazene)prop-2-en-1-one **(A3)**	$C_{23}H_{22}N_4O$	Deep brown	370.45	55-57	91
5-phenyl)-3-[(1,3-triazobenzene)-4-yl]-1H-pyrazole (**B1**)	$C_{21}H_{17}N_5$	Brown	339.39	171-173	72
5-(4-benzaldehyde)-3-[(1,3-triazobenzene)-4-yl]-1H-pyrazole (**B2**)	$C_{22}H_{17}N_5O$	Yellow	367.40	150-152	83
5-(4-dimethylamino)phenyl) - 3-[(1,3-triazobenzene)-4-yl]-1H-pyrazole (**B3**)	$C_{23}H_{22}N_6$	Light brown	382.46	198-200	82
5-phenyl)-3-[(1,3-triazobenzene)-4-yl]-1-phenyl-pyrazole (**B4**)	$C_{27}H_{21}N_5$	Brown	415.49	205-207	71
5-(4-benzaldehyde) -3-[(1,3-triazobenzene)-4-yl]-1-phenyl-pyrazole (**B5**)	$C_{28}H_{21}N_5O$	Brown	443.50	220-222	66
5-(4-dimethylamino)phenyl) - 3-[(1,3-triazobenzene)-4-yl]-1-phenyl-pyrazole (**B6**)	$C_{29}H_{26}N_6$	Dark brown	458.56	83-85	85

The FT-IR spectrum of azo compound (3) showed appearing of ν(N=N) band at about (1597 cm^{-1}), see Table (2) and. The FT-IR spectra of A1, A2 and A3 showed ν(C=O) band at (1658-1655 cm^{-1}) in all products that indicated formation of the chalcone derivatives, see Table (2). The FT-IR spectra of pyrazole derivatives (B1-B6) showed disappearing of ν(C=O) band, respectively. In addition, Table (2) listed major stretching bands of FT-IR spectra of products [20].

Table (2)

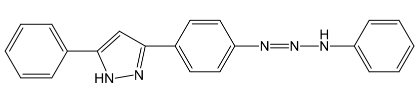
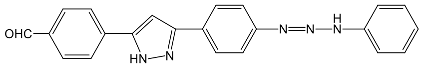
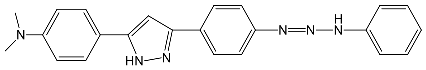
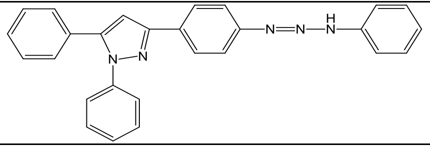
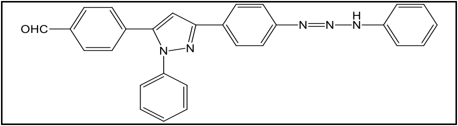
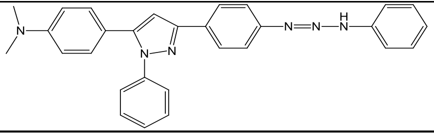
FTIR Spectral data of prepared compounds in cm^{-1}.

Comp. No.	***νC-H Aromatic***	***νC-H aliphatic***	***νN=N***	***νC=O***	***νN-H***	***νC=C Aromatic***
(3)	3086	2897	1523	1662	3194	1597
A1	3086	-	1527	1658	3190	1585
A2	3039	-	1523	1658	3228	1600
A3	3033	2904	1550	1655	3190	1597
B1	3032	-	1546	-	3182	1604
B2	3032	-	1504	-	3213	1600
B3	3032	2997	1519	-	3197	1600
B4	3055	-	1558	-	3268	1600
B5	3035	-	1550	-	3197	1597
B6	3035	2889	1523	-	3290	1600

The results of corrosion rate and inhibition efficiency that obtained from weight loss measurements at different concentrations of suggested inhibitors (B1-B6) after 24 hours immersion at 30^{o}C are depicted in Fig.(3) and summarized in Table (4). These values indicate that the mild steel corrosion is reduced by the presence of suggested inhibitors in 1M H_2SO_4 at all concentrations that used in the present study. However, there is remarkable decreasing in the weight of mild steel specimen after 24 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.

Table (3)

^{1}H-NMR data of compounds (B1 –B6) in ppm.

Comp. No.	***Compound structure***	***^{1}H-NMR data of (δ-H) in ppm***
B1		1H of –NH-N=N- group (3.3); 14H of aromatic ring and 1H of alkene moiety(7.1-7.9) ; 1H of –NH- pyrazole ring (12.6).
B2		1H of –NH-N=N- group (3.3); 13H of aromatic ring and 1H of alkene moiety (6.5-7.8);1H of carbonyl group(10.3);1H of –NH- pyrazole ring (12.9).
B3		6H of $-CH_3$ group (2.8); 1H of –NH-N=N-group (3.3); 13H of aromatic ring and 1H of alkene moiety (6.8-7.8);1H of –NH- pyrazole ring (13.).
B4		1H of –NH-N=N- group (3.3); 19H of aromatic ring and 1H of alkene moiety (6.8-8.0).
B5		1H of –NH-N=N- group (3.3); 18H of aromatic ring and 1H of alkene moiety (6.6-8.0); 1H of carbonyl group(10.3).
B6		6H of $-CH_3$ group (2.8); 1H of –NH-N=N-group (3.3); 18H of aromatic ring and 1H of alkene moiety (6.4-8.1).

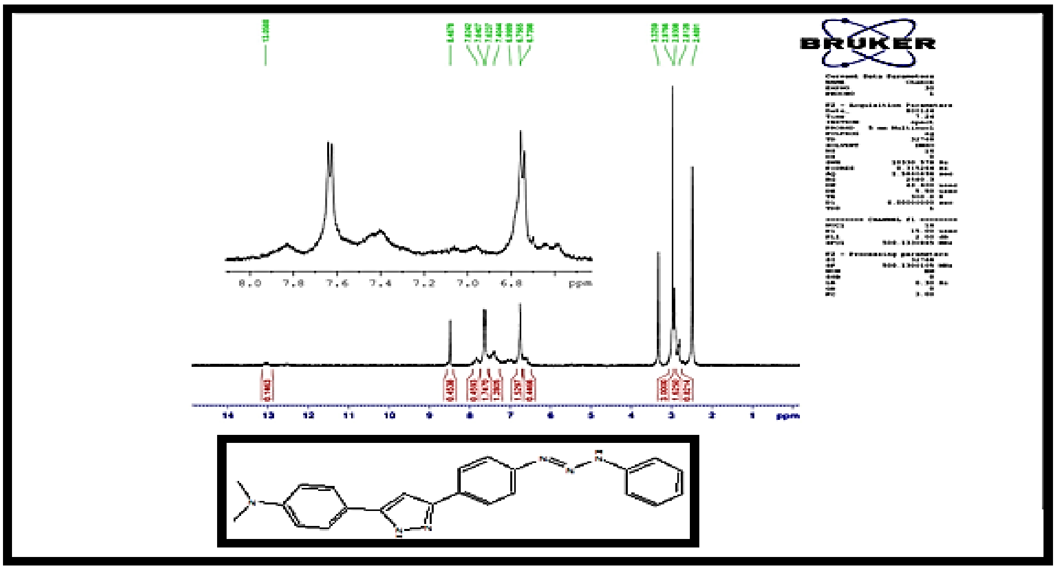


Fig.(1): FTIR spectrum of compound (B3).

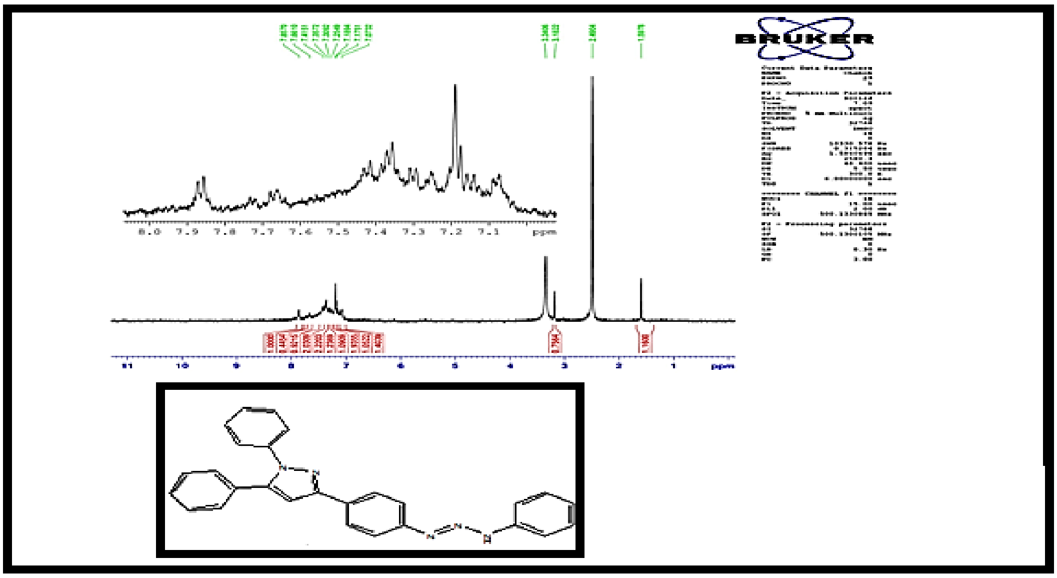


Fig.(2): FTIR spectrum of compound (B4).

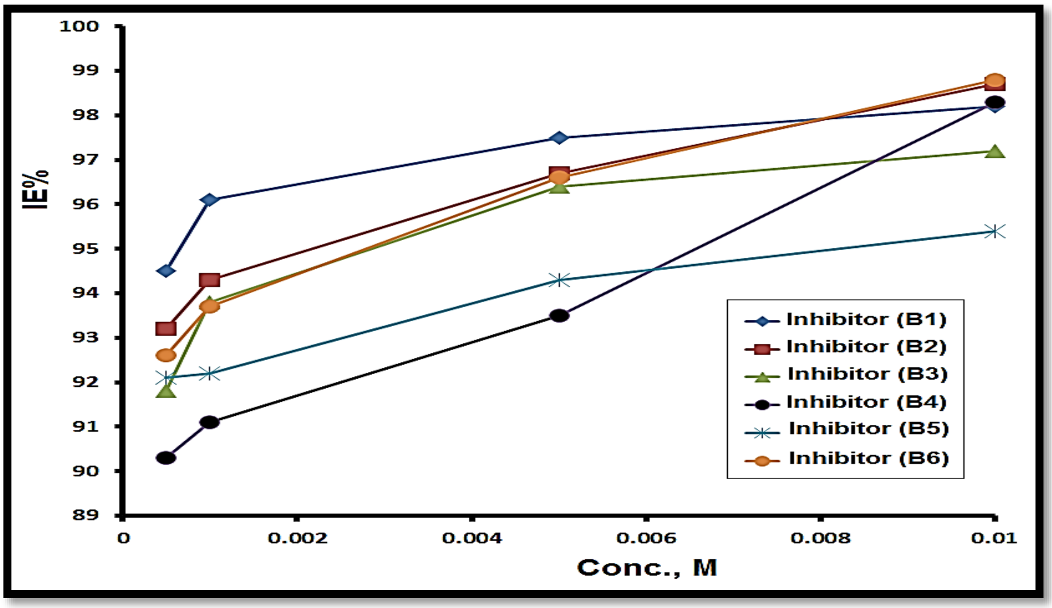


Fig.(3): Effect of inhibitor concentration on the efficiencies of mild steel obtained at 30 °C in 1M H_2SO_4 containing different concentrations of suggested inhibitors.

Table (4)

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

Concentration (M)	*Corrosion rate (mgcm^{-2} h^{-1})*	*IE%*	*θ*	*ΔG°_{ads} (kJ mol^{-1})*
Blank	0.311	-	-	-
(B1)				
5×10^{-4}	0.017	94.5	0.945	-36.26 (R^2=0.999)
1×10^{-3}	0.012	96.1	0.961	
5×10^{-3}	0.007	97.5	0.975	
1×10^{-2}	0.005	98.2	0.982	
(B2)				
5×10^{-4}	0.021	93.2	0.932	-35.56 (R^2=0.999)
1×10^{-3}	0.017	94.3	0.943	
5×10^{-3}	0.010	96.7	0.967	
1×10^{-2}	0.004	98.7	0.987	
(B3)				
5×10^{-4}	0.025	91.8	0.918	-34.54 (R^2=0.999)
1×10^{-3}	0.019	93.8	0.938	
5×10^{-3}	0.011	96.4	0.964	
1×10^{-2}	0.009	97.2	0.972	
(B4)				
5×10^{-4}	0.030	90.3	0.903	-35.07 (R^2=0.999)
1×10^{-3}	0.027	91.1	0.911	
5×10^{-3}	0.020	93.5	0.935	
1×10^{-2}	0.005	98.3	0.983	
(B5)				
5×10^{-4}	0.025	92.1	0.921	-37.06 (R^2=0.999)
1×10^{-3}	0.024	92.2	0.922	
5×10^{-3}	0.017	94.3	0.943	
1×10^{-2}	0.014	95.4	0.954	
(B6)				
5×10^{-4}	0.023	92.6	0.926	-35.05 (R^2=0.999)
1×10^{-3}	0.020	93.7	0.937	
5×10^{-3}	0.011	96.6	0.966	
1×10^{-2}	0.004	98.8	0.988	

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 (θ) at different inhibitor concentrations in 1M H_2SO_4 was achieved from weight loss measurements (θ=E (%)/100) (see Table 4) at 30°C and tested with Langmuir isotherm relationship

$$C/_{\theta} = 1/_{K_{ads}} + C \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$

Where 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/θ versus C see Fig.(7). K_{ads} is related to the standard free energy of adsorption, ΔG^o_{ads}, with the following equation: (The value 55.5 is the molar concentration of water in the solution in (1M).

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

From Table (4), the values of standard free energy of adsorption are negative to indicate that the processes of adsorption of all suggested inhibitors (B1-B6) were spontaneous processes on the mild steel surface after 24 h immersion at 30°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 [21,22].

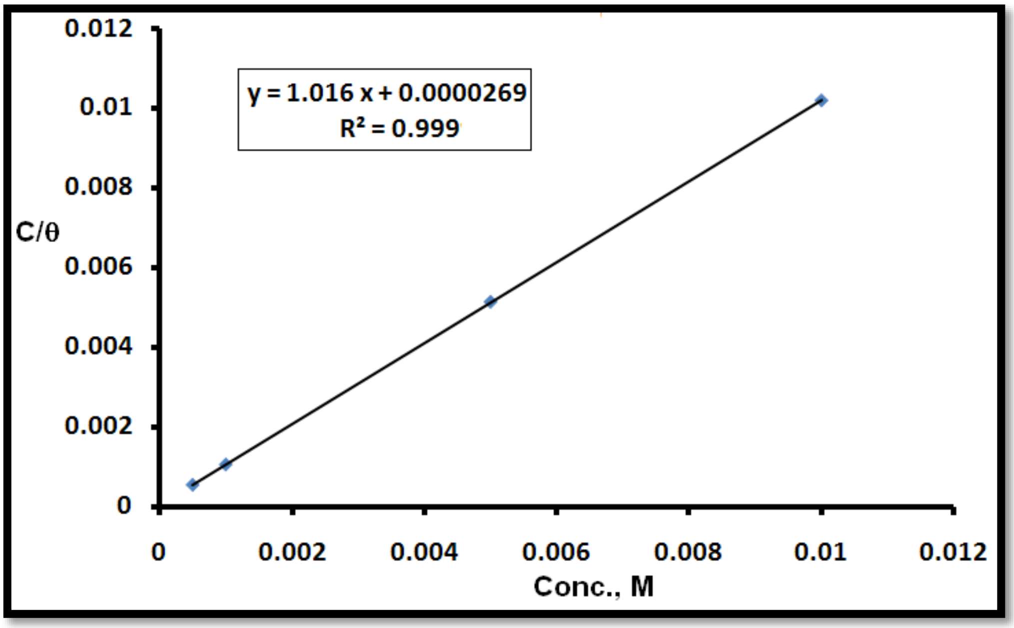


Fig.(4): Langmuir adsorption isotherm plot for mild steel in 1M H_2SO_4 solution in the presence of various concentrations of inhibitor (B1).

4- Conclusion

The prepared new pyrazole compounds (B1-B6) were used successfully as corrosion inhibitors on the mild steel surface in 1M H_2SO_4 solution at 30°C. The results of inhibitive efficiency (E %) showed interesting inhibiting effects of suggested inhibitors. The values free energy of adsorption revealed physisorption effect for (B1-B6) and gave useful information to explain the interaction between the surface of metal and the organic molecules.

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الخلاصة

تم تحضير بعض مشتقات البيرازول بعدة خطوات ابتداءا من ٤- اسيتايل انيلين لتحضير مشتقات صبغة الازو (3) ومن ثم تم تحضير الجالكونات (A1,A2,A3) بواسطة تفاعل تكاثف الالدول باستخدام الديهايدات مختلفة (البنزلديهايد, ن, ن – ثنائي مثل امينو بنزيلديهايد و الترفثلديهايد). بعد ذلك تم تحضير مشتقات البيرازول (B1,B2,B3,B4,B5,B6) من خلال تفاعل الجالكونات مع الهيدرازين والفينل هيدرازين. تم تشخيص المركبات المحضرة بطرق فيزيائية وتقنيات طيفية. المركبات المحضرة النهائية تم استخدامها كمثبطات لتأكل معدن الحديد المعتدل في وسط حامضي وبدرجة حرارة ٣٠م°. نتائج قياسات طريقة الوزن المفقود لعملية التثبيط كانت ممتازة لتثبيط التأكل في الوسط الحامضي لمعدن الحديد المعتدل حيث اظهرت النتائج التجريبية زيادة كفاءة التثبيط مع زيادة وزن المادة العضوية المثبطة.