Journal of Petroleum Research and Studies

Open Access
No. 31, June 2021, pp.1-14

P- ISSN: 2220-5381
E- ISSN: 2710-1096

DOI: http://doi.org/10.52716/jprs.v11i2.494

Paraformaldehyde as a corrosion inhibitor for carbon steel in (%15) HCl

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Received 10/9/2020, Accepted 3/11/2020, Published 20/6/2021

Abstract

The effect of paraformaldehyde in the solution of 15% HCL as an inhibitor of C-steel corrosion has been studied using the weight loss method. It was found that the efficiency of inhibitor increased by increasing the inhibitor concentration and decreasing temperatures. Also, the action of paraformaldehyde as a corrosion inhibitor has been attributed to the insoluble complexes was adsorbed on the C-steel surface. The iron complexes were identified by FTIR spectrum and the mechanism of inhibition was explained as Langmuir adsorption. The thermodynamic parameters of the adsorption process were calculated and explained.

1. Introduction

Corrosion is generally called the undesirable damage that affects metals and metal alloys due to their interaction with the medium. The meaning of this definition is very wide which is mean interaction with water, electrolytic solutions and liquid mixtures as well as includes air, some gases and some fuses [1], since the productivity of oil reservoirs decreases constantly with a period of time and the process of acidification by hydrochloric acid is one of the oldest and most important methods used to improve the productivity of oil wells through improving the permeability of the bearing layer. This method has been applied for years when the layer was treated with acid injected through the well tubes to a certain depth that dissolve the rocks (calcium carbonate rocks). It also affects the cement bonding between the rock granules or the use of acid to clean the walls of the well from the effects of drilling fluid and other pollutants. This process corrodes the equipment's that is used in drilling and productions [2]. Hence, it is very important to study the corrosion and corrosion inhibition of carbon steel in hydrochloric acid. The first adsorption theory of inhibitor action was proposed in 1923 by researchers in [3] who studied alkaline and aromatic amines in aqueous sulfuric acid and hydrochloric acid. (M. Abdallah) study the effect of adding Amino pyridine derivatives as an inhibitor of corrosion to carbon steel in acid solutions HCl, which is one of the organic inhibitors that adsorb on the surface of the metal [4]. The researchers in [5] also used polyethylene imine to reduce the wear of malleable steel in an HCl solution that creates an adsorbent layer on the steel surface so that the inhibition efficiency reaches 95% by increasing the inhibitor concentration. The relationship between the coefficient of disability and the concentration of the inhibitor takes the form of adsorption isotherm. On this basis, (Sieverts and Lueg) suggests the concept of the adsorption mechanism of the inhibitor. A rise in temperature impedes the work of corrosion inhibitor and high temperatures increase the rate of corrosion, as the corrosion is doubled by increasing the solution temperature (10) degrees Celsius [6]. Substances that are able to interact with the metal surface and form only insoluble or slightly soluble compounds are effective corrosion inhibitors [7]. The addition of corrosion inhibitors effectively protects the metal against an acid attack [8-10]. The aim of the research is using Paraformaldehyde as an inhibitor in (%15) HCl at different concentrations and temperature.

2. Method

Used (60) gr of carbon steel has ingredients (wt. %) 0.019 Cr, 1.4 Mn, 0.353 Si, 0.263 C, 0.159 Ni,0.03 P 0.001 S and remained Fe. With dimension of (2.5 x 5 x 0.7) cm C-steel coupons surface was polished with smoothing paper, degreased with acetone and rinsed with distilled water, the cleaned C-steel coupons were weighed before and after immersion in (50) ml of (%15) HCl solution at the times (3,4,5,6) hr. the weight loss of coupon in experiments was taken in milligrams. The temperature (40, 60, 80 and 90) ºC was adjusted by thermostat. Paraformaldehyde (2, 4, 6) % used as inhibitors were prepared by Fluka Company [11].

3. Results and discussion

3.1 Weight loos measurements:

In this work, paraformaldehyde was used as a corrosion inhibitor for coupons of (C-Steel) alloy. Tables (1), (2) show the weight loss results and efficiency in the presence and absence of the corrosion inhibitor at different concentrations, temperatures and times in (15%) HCl. Figure (1) shows a weight loss curve against time in the absence and different concentrations of inhibitors at temperature (40) °C. Similar curves were obtained for other temperatures (60, 80, 90) °C. It is clear that the weight loss of the C-steel samples is linearly proportional with time and is much less than that obtained for the control solution in the absence of paraformaldehyde. This action indicates that the adsorption of paraformaldehyde on the active sites of metal as anti-corrosion layer prevent corrosion process [12]. The percentage efficiency (%E) of corrosion inhibitor and metal degree of surface coverage (ϴ) was calculated using the following equations:

$$\% E = [(1- (W_{add} / W_{free})] \times 100 \text{ -----------}(1)$$

$$\Theta = [1 - (W_{add} / W_{free})] \text{ ----------------------}(2)$$

Where W_{add} and W_{free} are the weight loss of C-steel in the presence and absence of inhibitor. Tables (1), (2) show that the corrosion increases with increasing temperature and decreases with increasing inhibitor concentration.

3.2 The effect of temperature on adsorption

The effect of temperature on the corrosion rate of C-steel in the acid (15%) HCl was studied in the absence and presence of different concentrations of paraformaldehyde over a temperature range from (40 -90) °C. Using weight loss measurement, the corrosion rate (R_{corr}) was calculated from the following equation [13]:

$$R_{corr} = \Delta w / St \quad \text{----------------------------}(3)$$

Where S is the surface area (cm^2) t is the immersion time of C-steel in acid (min) and Δw is the weight loss of metal. The results of corrosion rate and efficiency in Tables (1 and 2) show that the corrosion rate (R_{corr}) and efficiency (E) increase with increasing the concentration of the inhibitor and decrease with increasing temperature (T). The values of activation energy (Ea) of the corrosion process were calculated from the Arrhenius equation [14]:

$$\log R_{corr} = \log A - (Ea / 2.303\ RT) \qquad \text{-------------}(4)$$

Where R_{corr} is the corrosion rate of weight loss, A is Arrhenius constant, R is the gas constant and T is absolute temperature. Figure (4) shows the Arrhenius curve (log R_{corr} vs 1 /T) in the presence (%6) of paraformaldehyde and blank at time of (3) hr. in (%15) HCl at different temperature, Similar curves were obtained for other concentration (2, 4) % at different times and temperatures (Ea) values were obtained from the slope of straight lines and are listed in Tables (3 to 6). The activation energy increases with increasing in the concentration of the inhibitor for the same time, but in general it decreases when moving from time (3) hours to a time of (6) hours and this indicates a delay or slow adsorption of the anticorrosive on the surface of C-steel depending on the amount of degradation of paraformaldehyde so the adsorption increases in long periods of time, the rate of corrosion increases with increasing in temperature but decreases with increasing the concentration of the inhibitor due to the corrosion inhibitor covering the metal surface[15]. We also noticed that the rate of corrosion increased with the increase in the exposure certain time at the temperature (40 and 60) ºC and it decreased at the temperature (80 and 90) ºC relatively. Due to the increasing in the dissolution of paraformaldehyde at high temperatures and its coverage of more surface area on the metal.

3.3 Adsorption isotherm

The surface covered values by the corrosion inhibitor (Θ) on samples of C-steel inside hydrochloric acid (15% HCl) listed in Tables (1) and (2) increased with increasing the concentration of the paraformaldehyde and decreased with increasing temperature from (40 to 90) °C. When a monolayer adsorption occurs on the surface of C-steel, the Langmuir adsorption isotherm can be expressed from the following equation [16]:

$$\Theta / 1- \Theta = AC \exp (- \Delta H / RT) \qquad \text{-------------}(5)$$

Where A is an independent constant, C is the concentration of the inhibitor and ΔH is the heat of adsorption. Equation (5) can be written on the logarithmic scale as:

$$\log \Theta /1- \Theta = \log A + \log C - (\Delta H / 2.303 RT) \quad \text{--------}(6)$$

Figure (2) represents the relationship between log Θ / 1 – Θ vs 1 / T for paraformaldehyde (4%) at different temperature in time (3) hr as an example. Similar curves were obtained for other concentrations of paraformaldehyde in different time and temperature and the obtained data are listed in Tables (1) and (2). The linear relationship implies that the adsorption of paraformaldehyde on C-steel obeys Langmuir adsorption isotherm and the (ΔH) values of adsorption can be calculated from the slope of straight line ($-\Delta H / 2.303R$) that listed in Tables (3 to 6) and negative value for adsorption heat reflect the exothermic nature of the C-steel dissolution process.

3.4 Thermodynamic data

The Langmuir equation for isotherm adsorption can be written as follows:

$$C / \Theta = 1 / K + C \quad \text{------------------}(7)$$

where K is the equilibrium constant for adsorption process. Through the curve of log C / Θ against log C, a straight line was obtained Figure (3), indicate the adsorption of paraformaldehyde on C-steel surface follows Langmuir, from this result it can be assumed that there is no interaction between the adsorbent materials, so the equilibrium constant (K_{eq}) calculated from equation (7) [11] and the values are listed in Tables (3 to 6). The values of the equilibrium constant (Keq) changed with changing of the inhibitor concentration and the temperature of solution which were decreased with increasing the temperature and the concentration of the inhibitor for each certain times of corrosion process.. The other thermodynamic variables such as (ΔG_{ads}) and (ΔS_{ads}) for the adsorption process were obtained from the following relationships:

$$K_{eq} = \exp - \Delta G_{ads} / RT \quad \text{-----------}(8)$$

$$\Delta G = \Delta H - T\Delta S \quad \text{-----------------}(9)$$

The values of the ΔG calculated over the range of temperatures (40-90)ºC and in the used concentrations attributed to spontaneous adsorption of paraformaldehyde inhibitor on the surface of C-steel and the ΔG values range between (15.07 - 19.58) kJ, this is means that the adsorption on C-steel is physical adsorption because the values are less than (40) kJ [17]. The ΔS values changed from less random to more random and it reversed depending on the paraformaldehyde concentration and temperature at each period time as long as exist uncovered surface area on C-steel, and the adsorption in all cases of the adsorption process were spontaneous on the surface of C-steel.

3.5 FTIR spectrum information

Figure (5) shows the infrared spectrum of sediments scraped from the surface of C-steel after the adsorption process and the appearance of absorption peak for Fe-O group in (464) cm^{-1} which indicates the adsorption of the inhibitor on the surface of the C-steel [18], as well as the absorption peaks of paraformaldehyde have been identified, as shown in Table (7) and Figure (6) shows the IR spectrum of paraformaldehyde before the adsorption process.

4. Conclusions

1- Paraformaldehyde can be used as acid corrosion inhibitor.
2- The efficiency of inhibitor depends on the concentration of paraformaldehyde and to the temperature of medium.
3- Paraformaldehyde makes insoluble and stable complexes on C-steel surface.
4- The adsorption of paraformaldehyde on C-steel surface follows Langmuir equation.

Table (1) Inhibition efficiency of paraformaldehyde on coupon of C-steel in (%15) HCl at different temperature and in (3,4) hr. and surface coverage (Θ)

Conc. (Inh.) %	T °C	3hr				4hr			
		Weight loss /mg wt$_o$=60g	E %	Θ	R_{corr} mg/cm^2.hr	Weight loss/mg	E %	Θ	R_{corr} mg/cm^2.hr
Blank	40	1090	-----	-----	10.23	1120	-----	------	7.89
2		30	97.24	0.9724	0.28	57	94.91	0.9491	0.40
4		20	98.16	0.9816	0.18	40	96.42	0.9642	0.28
6		15	98.62	0.9862	0.14	30	97.32	0.9732	0.21
Blank	60	1180	-----	-----	11.08	1210	-----	------	8.52
2		50	95.76	0.9576	0.47	80	93.38	0.9338	0.56
4		40	96.61	0.9661	0.38	65	94.62	0.9462	0.46
6		35	97.03	0.9703	0.33	50	95.86	0.9586	0.35
Blank	80	1850	-----	-----	17.37	1880	-----	------	13.24
2		140	92.43	0.9243	1.31	160	91.49	0.9149	1.13
4		110	94.05	0.9405	1.03	140	92.55	0.9255	0.96
6		90	95.13	0.9513	0.85	110	91.15	0.9115	0.77
Blank	90	1910	-----	------	17.93	1950	-----	------	13.73
2		200	89.52	0.8952	1.88	230	88.20	0.8820	1.62
4		170	91.09	0.9109	1.60	205	89.49	0.8949	1.44
6		145	92.42	0.9240	1.36	180	90.77	0.9077	1.27

Table (2) Inhibition efficiency of paraformaldehyde on coupon of C-steel in (%15)HCl at different temperature and in (5,6)hr. and surface coverage (Θ)

Conc. (Inh.) %	T °C	5hr				6hr			
		Weight loss/mg	E %	Θ	R_{corr} mg/cm^2.hr	Weight loss/mg	E %	Θ	$R_{corr.}$ mg/cm^2.hr
Blank	40	1150	-----	-----	6.48	1180	-----	-----	5.54
2		80	93.04	0.9304	0.45	100	91.53	0.9153	0.47
4		60	94.78	0.9478	0.34	87	92.63	0.9263	0.41
6		50	95.65	0.9565	0.28	78	93.39	0.9339	0.37
Blank	60	1240	-----	------	6.99	1260	------	------	5.92
2		110	91.13	0.9113	0.62	140	88.89	0.8898	0.66
4		88	92.90	0.9290	0.50	110	91.27	0.9127	0.52
6		70	94.35	0.9435	0.39	90	92.86	0.9286	0.42
Blank	80	2100	-----	-----	11.83	2300	-----	-----	10.80
2		190	90.95	0.9095	1.07	210	90.87	0.9087	0.99
4		170	91.90	0.9190	0.96	190	91.74	0.9174	0.89
6		140	93.33	0.9333	0.79	170	92.61	0.9261	0.80
Blank	90	2300	------	-----	12.96	2500	-----	------	11.74
2		260	88.87	0.8870	1.46	280	88.80	0.8880	1.31
4		230	90.00	0.9000	1.30	260	89.60	0.8960	1.22
6		210	90.87	0.9087	1.18	240	90.40	0.9040	1.13

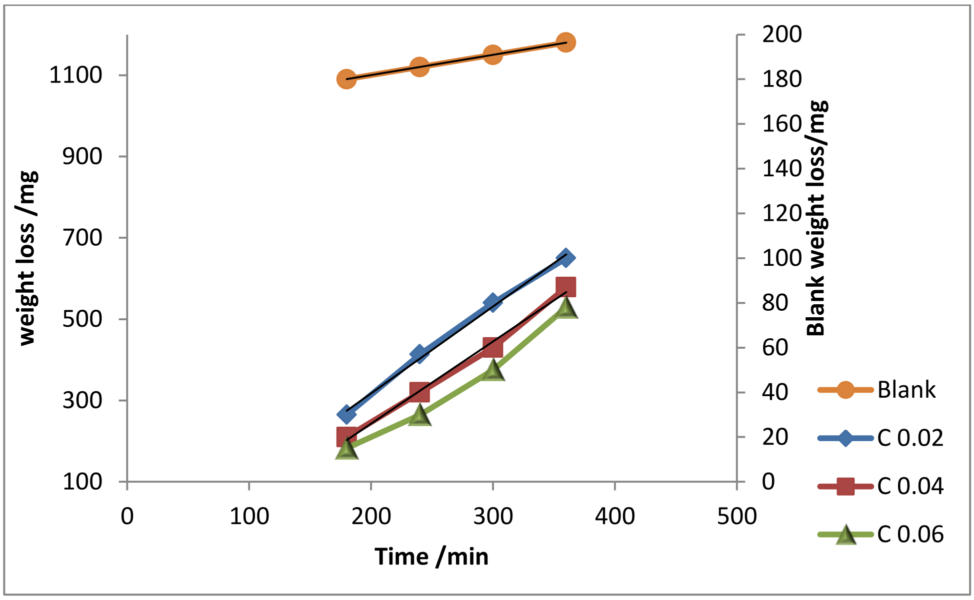

Fig. (1) The weight loss – time plot for coupon of C-steel in the presence and absence different concentration of Paraformaldehyde at (40) °C in (%15) HCl.

Table (3) Thermodynamic parameters of paraformaldehyde adsorption on coupon of C-steel in (3) hr.

Conc. (Inh.)%	T °C	K_{eq}	E_a kj	- ΔH kj	– ΔG kj	- ΔS j
2	40	$1.76x10^3$	35.08	25.19	19.45	18.34
	60	$1.13x10^3$			19.46	17.21
	80	$0.79x10^3$			19.58	15.90
	90	$0.43x10^3$			18.30	18.98
4	40	$1.33x10^3$	39.30	28.81	18.72	32.24
	60	$0.71x10^3$			18.18	31.92
	80	$0.40x10^3$			17.58	31.81
	90	$0.26x10^3$			16.80	33.09
6	40	$1.19x10^3$	40.62	30.27	18.43	37.83
	60	$0.54x10^3$			17.42	38.59
	80	$0.33x10^3$			17.02	37.54
	90	$0.20x10^3$			15.99	39.34

Table (4) Thermodynamic parameters of paraformaldehyde adsorption on coupon of C-steel in (4) hr.

Conc. (Inh.)%	T ºC	K_{eq}	E_a kj	- ΔH kj	– ΔG kj	ΔS j
2	40	$0.93x10^{3}$	25.14	15.03	17.79	8.82
	60	$0.71x10^{3}$			18.18	9.46
	80	$0.54x10^{3}$			18.46	9.72
	90	$0.37x10^{3}$			17.85	7.77
4	40	$0.67x10^{3}$	29.03	18.35	16.93	-4.54
	60	$0.44x10^{3}$			16.85	-7.06
	80	$0.31x10^{3}$			16.84	-4.28
	90	$0.21x10^{3}$			16.14	-6.09
6	40	$0.61x10^{3}$	31.67	25.48	16.69	-28.08
	60	$0.39x10^{3}$			16.52	-26.91
	80	$0.17x10^{3}$			15.07	-29.49
	90	$0.16x10^{3}$			15.32	-27.99

Table (5) Thermodynamic parameters of paraformaldehyde adsorption on coupon of C-steel in (5) hr.

Conc. (Inh.)%	T ºC	K_{eq}	E_a kj	- ΔH kj	– ΔG kj	ΔS j
2	40	$0.67x10^{3}$	20.99	7.97	16.93	28.63
	60	$0.51x10^{3}$			17.26	27.90
	80	$0.50x10^{3}$			18.24	29.09
	90	$0.39x10^{3}$			18.00	27.63
4	40	$0.45x10^{3}$	24.18	11.48	15.90	14.12
	60	$0.33x10^{3}$			16.06	13.75
	80	$0.28x10^{3}$			16.54	14.33
	90	$0.23x10^{3}$			16.41	13.58
6	40	$0.37x10^{3}$	25.60	12.66	15.39	8.72
	60	$0.28x10^{3}$			15.60	8.83
	80	$0.23x10^{3}$			15.96	9.35
	90	$0.17x10^{3}$			15.50	7.82

Table (6) Thermodynamic parameters of paraformaldehyde adsorption on coupon of C-steel in (6) hr.

Conc. (Inh.)%	T ºC	K_{eq}	E_a kj	- ΔH kj	- ΔG kj	ΔS j
2	40	$0.54x10^3$	17.9	4.24	16.37	38.75
	60	$0.40x10^3$			16.59	37.09
	80	$0.50x10^3$			18.24	39.66
	90	$0.40x10^3$			17.31	36.00
4	40	$0.31x10^3$	19.3	7.25	14.93	24.54
	60	$0.26x10^3$			15.40	24.47
	80	$0.28x10^3$			16.54	26.32
	90	$0.22x10^3$			16.28	24.88
6	40	$0.24x10^3$	20.12	7.75	14.26	20.80
	60	$0.22x10^3$			14.93	21.56
	80	$0.21x10^3$			15.69	22.49
	90	$0.16x10^3$			15.32	20.85

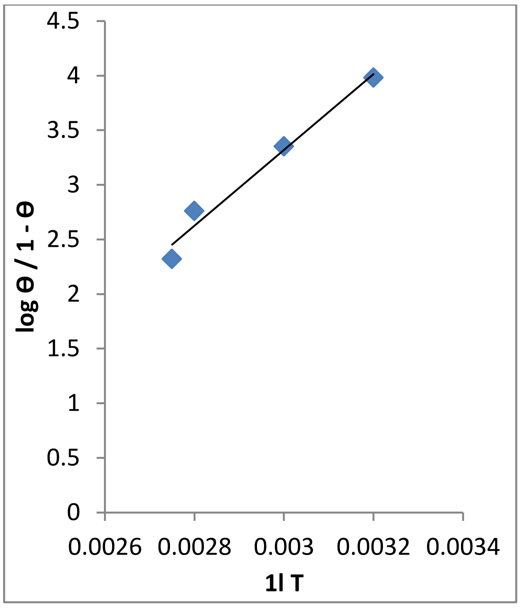

Fig. (2) The (log Ө/(1-Ө) – 1/T) plot of coupon C-steel in the presence of (%4) of paraformaldehyde and in (3)hr at different temperature

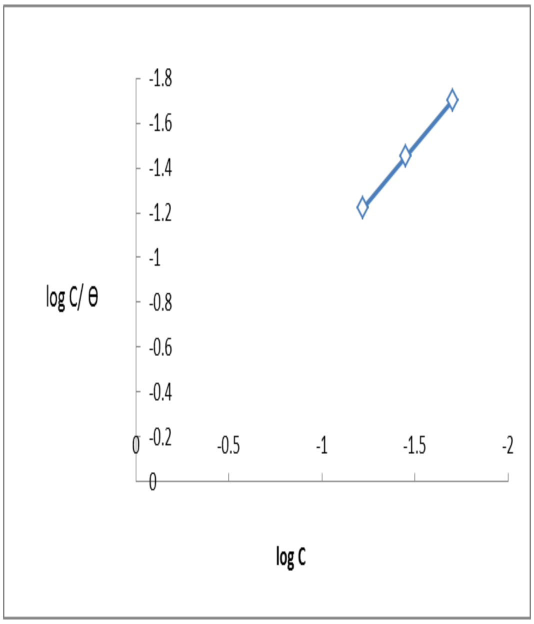

Fig. (3) The (log C/Ө –log C) plot of coupon C-steel in the presence of paraformaldehyde at different temperatur

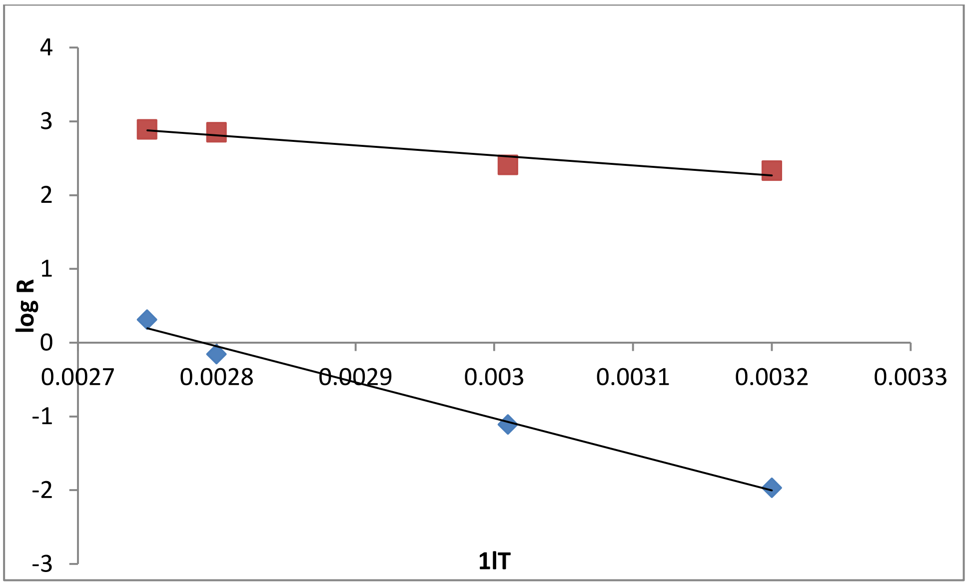

Fig. (4) The (log R – 1/ T) plot for coupon of C-steel in the presence (%6) of paraformaldehyde and blank at time of (3)hr. in (%15)HCl

Table (7) Infrared absorption peaks of sediments scraped from the surface of C-steel after the adsorption process

Compounds	I R cm $^{-1}$	Assignments
sediments scraped from the surface of C-steel after the adsorption process	2953	CH Str.
	1631.3	C=O str.
	1350.6 , 1461	CH_2
	464	Fe-O

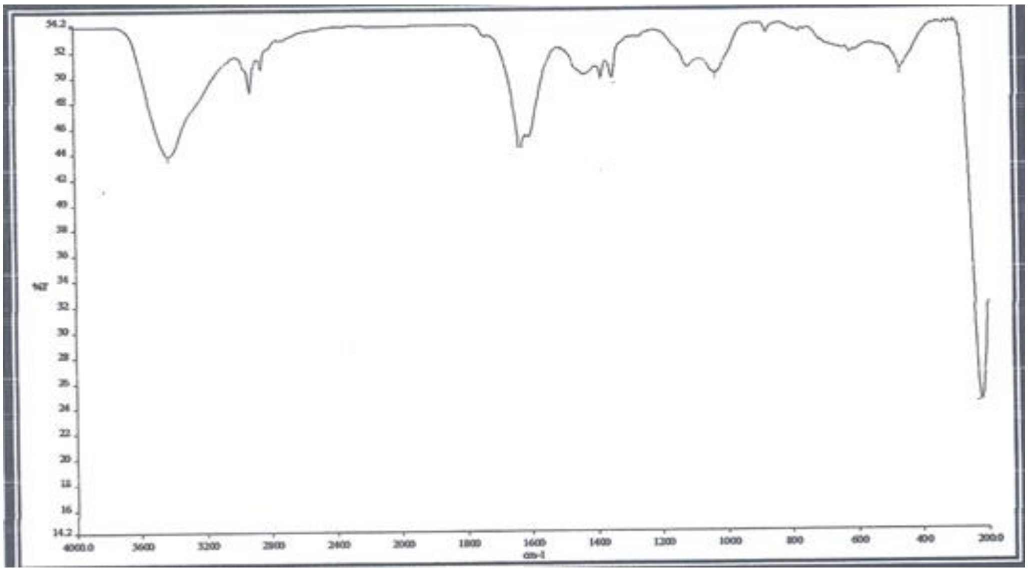

Fig. (5) The FTIR spectrum of paraformaldehyde complex that scraped from the surface of C-steel after the adsorption process.

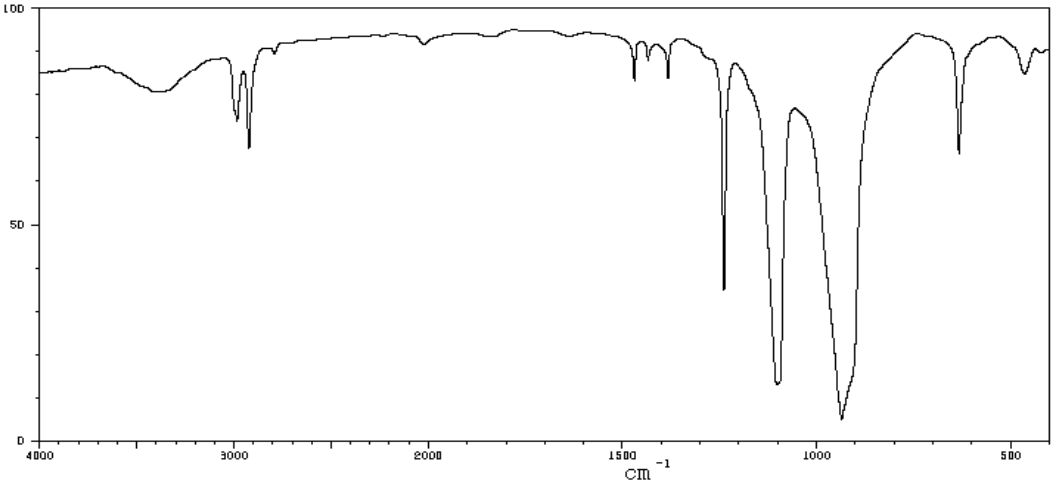

Fig. (6) The FTIR spectrum of paraformaldehyde before the adsorption process.

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