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Gravimetric and Electrochemical studies of a Schiff Base as green corrosion inhibitor for mild steel in 0.5 M H_2SO_4 solution.

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Abstract: The corrosion inhibition of mild steel in 0.5M H_2SO_4 by Schiff bases, namely,N1,N1'-(1,4-phenylene)bis(N4-(4-chlorobenzylidene)benzene-1,4-diamine) [PCBA] has been studied by using weight loss and Tafel polarization method . These studies were carried out at various temperatures and concentrations of this inhibitor. The highest inhibition efficiency obtained was 96.86% (PCBA) at 200 mg L^{-1}. Results show that the inhibition efficiency increases with increasing the inhibitor concentrations and decreases with increase in temperatures. Tafel polarization indicated this inhibitor acted as a mixed-type inhibitor. It is a very environmentally friendly compound.The adsorption of inhibitor on mild steel surface obeys the Langmuir adsorption isotherm.

Key words: Mild steel, gravimetric measurements, electrochemical studies.

1. Introduction

Mild steel and its alloys are widely used in various industries such as power production, petroleum, chemical and elechtrochemical industries [1]. Sulphuric acid and hydrochloric acid are used for acid pickling, acid cleaning, oil well acidification and acid descaling to remove undesirable scale from metal that causes the corrosion [2]. The use of inhibitor is one of the effective method to prevent the metal from corrosion. Inhibitors are added to the acid solution to slow down the corrosion by acid attack on the metal surface [3-4]. The literature shows that most of the organic compounds containing heteroatoms (like nitrogen, oxygen, sulphur etc.), congugated multiple bonds and aromatic ring behave as good corrosion inhibitors for metals in acid solution.Organic compounds containing functional group and multiple bonds are effective inhibitors because they adsorb on metal surface through lone pairs of electrons and delocalised π electrons. [5-8].

Literature revealed that Schiff base compounds have been reported as effective corrosion inhibitors and they are condensation product of aldehyde and ketone with amine show excellent corrosion efficienceis due to –C=N– group that lead to absorption on the metal surface. The greatest advantages of Schiff bases are that they can be easily synthesized, have low toxicity and are eco-friendly in nature [9-11]. Inhibitors adsorbed on metal surface by the two types of adsorption Physical adsorption which involves the electrostatic interaction between the metal surface and charged inhibitor molecule and chemical adsorption which involves the transfer the lone pair of electrons to the vacant d-orbital of metal surface to form a coordination bonds. The review of literature reported that Schiff bases are efficient corrosion inhibitorsfor metal in acidic medium [12].In the present study, synthesized inhibitor (PCBA) has been used as corrosion inhibitor, this shows good inhibition efficiency as it has two (-Cl) in the aromatic ring, two (HC=N) and π electrons which favour the adsorption on the surface on the mild steel.

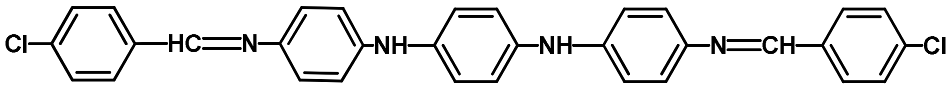
The aim of the present study is to investigate the corrosion behaviour of mild steel in 0.5M H_2SO_4 at temperature range (298 K -328 K) in the absence and presence of Schiff base,N1,N1'-(1,4-phenylene)bis(N4-(4-chlorobenzylidene)benzene-1,4-diamine) by using weight loss and Tafel polarization studies.

2. Experimental:

2.1 Inhibitor synthesis

The investigated inhibitor was synthesized, N1,N1'-(1,4-phenylene)bis (N4-(4chlorobenzylidene) benzene-1,4-diamine) [PCBA]according to the previously reported literature [13-15]. The chemical structure and nomenclature is given in Table 1. Inhibitor PCBA was characterised by FT-IR (Perkin-ElmerFT-IR Spectrum BX Spectrophotometer) and ^{1}H NMR (Bruker Advance II 400MHz system, Ultra shield, Switzerland).

Table 1: Molecular structures and analytical data of PCBA

Molecular structure of inhibitor	**Analytical data**
 ***N*^{1},*N*$^{1'}$-(1,4-phenylene)bis(*N*^{4}-(4-chlorobenzylidene)benzene-1,4-diamine)** **(PCBA)**	IR (KBr ,cm^{-1}) : 1618.56(-C=N-), ^{1}HNMR(400MHz,CDC$_3$);δvalues(ppm)=9.98(s,2H,-CH=N), 8.39(s,2H,-NH),7.82(d,5H, Ar-H), 7.52(d,5H,Ar-H),7.45(d,2H,Ar-H),7.35(d,2H,Ar-H),7.13(dd,3H,Ar-H), 7.02(dd,3H,Ar-H),6.66(d,2H, Ar-H)

2.2 Materials and methods

The experiments were performed on mild steel samples having composition (in %): C-0.15, Si-0.08, S-0.02, Mn-1.02 and rest Fe -98.72. Mild steel samples were used with dimension of 1 cm × 1 cm × 1 cm for gravimetric experiments and for electrochemical experiments having dimensions 1 cm × 1 cm × 4 cm were used for Tafel polarization expriments. The samples were cuboidal in shape which is covered by epoxy resin whose one end is connected internally with the copper wire and exposed area (1 cm^{2}) of mild steel in acid solution for electrochemical experiments. The samples were abraded by emery paper of grade number 100, 220, 320, 400, 600, 1000 and 1500, then washed with distilled water andacetone and dried. The solution of 0.5 M H_2SO_4 was prepared by diluting concentrated H_2SO_4 (AR) using double distilled water. Weight loss and electrochemical measurements were determined in the presence and absence of inhibitor at different temperatures (298K, 308K, 318K and 328K) and using 50 mgL^{-1},100 mgL^{-1},150 mgL^{-1}, 200 mgL^{-1} as inhibitor concentrations.

2.3 Weight loss measurements

The weight loss measurements were carried out on the MS samples having dimensions 1 cm × 1 cm × 1 cm. These coupons were immersed in 100 mL of 0.5 M H_2SO_4 for 6 hours in the presence and absence of various concentrations of inhibitor (50 mgL^{-1} -200 mgL^{-1}) at 298 K, 308 K, 318 K and 328 K. The samples were weighed before and after 6 h of immersion time and difference in weight loss were calculated. Weight Loss Measurements were carried out by using analytical weighing machine Mettler Toledo.

2.4 Electrochemical measurements

Tafel polarization measurements were performed using a CH instruments electrochemical workstation CHI 760c (CH Instruments, Inc.USA). Three electrode cell assembly was used to carry out the electrochemical experiments including mild steel sample as working electrode, platinum electrode as counter electrode and saturated calomel electrode (SCE) was used as the reference electrode. All electrochemical experiments were done after immersing the working electrode for 1 h in 0.5 M H_2SO_4 in the absence and presence of inhibitor to obtain a stable value for the open circuit potential (OCP). The cathodic and anodic curves of the linear Tafel segments were extrapolated to corrosion potential to achieve the corrosion current densities. The inhibition efficiency was determined at different temperatures and variation of inhibitor concentrations for this technique.

3. Results and discussion

3.1 Weight loss measurements

Weight loss data obtained by performing the experiment with the variation of temperature and concentrations of inhibitor in 0.5 M H_2SO_4 solution and resultant parameters are shown in the given histogram in Fig.1. Inhibition efficiency is shown in Fig.1 reveals that corrosion inhibition efficiency (η%) increases significantly with rising the concentration of inhibitor and decrease the corrosion rate.The weight of each MS coupons was determined before and after immersion in test solutions. On increasing the inhibition efficiency, the adsorption amount of inhibitor molecule increases on the surface of metal and protect the MS from corrosion [16-17].

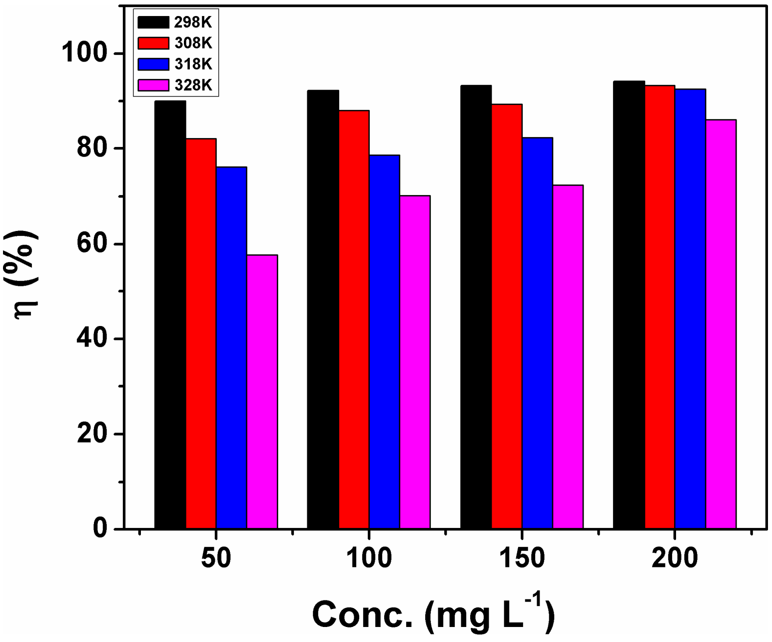


Fig.1. Variation of inhibition efficiency with varying concentrations of inhibitor (PCBA) at different temperatures for MS in 0.5 M H_2SO_4.

The corrosion rate is calculated by the given equation:

$$C_r \text{ (acid or inh.)} = \frac{W_{initial} - W_{final}}{S \times t} \quad (1)$$

W$_{initial}$ = weight of the plain polished MS coupons (g)

W_{final} = weight of the MS coupons after 6 hours immersion (g)

S = Surface area of the MS coupon (cm^2)

t = Time (h)

The inhibition efficiency (η %) was calculated by using the following relation [18]

$$\eta_{\%} = \frac{C_r^0 - C_r^i}{C_r^0} \text{ X } 100 \quad (2)$$

Where C_r^0 and C_r^i is the corrosion rates of mild steel in the absence and presence of the inhibitor respectively.

Temperature range studied from 298K to 328K . The inhibition efficiency (IE) was obtained which is 94.17% at 298 K, 93.32% at 308 K, 92.56% at 318 K, 86.07% at 328 K of PCBA at optimized concentration 200 mgL^{-1}. The result shows that inhibition efficiencies of this studied inhibitor decreased with increase in temperatures because at high temperature, the hydrogen evolution increases on the metal surface which leads to the desorption of the absorbed inhibitor molecule from the mild steel surface [19-25] leaving more surface available for corrosion.

3.2 Tafel polarization

The Tafel polarization curves for the MS in 0.5M H_2SO_4 in the absence and presence of different inhibitor concentrations at different tempratures are given in Fig. 2. All Tafel parameters such as corrosion potential (E_{corr}), corrosion current density (I_{corr}), cathodic and anodic Tafel constants (βc and βa), surface coverage (θ), and inhibition efficiency (η) % can be seen from the Fig. 2.

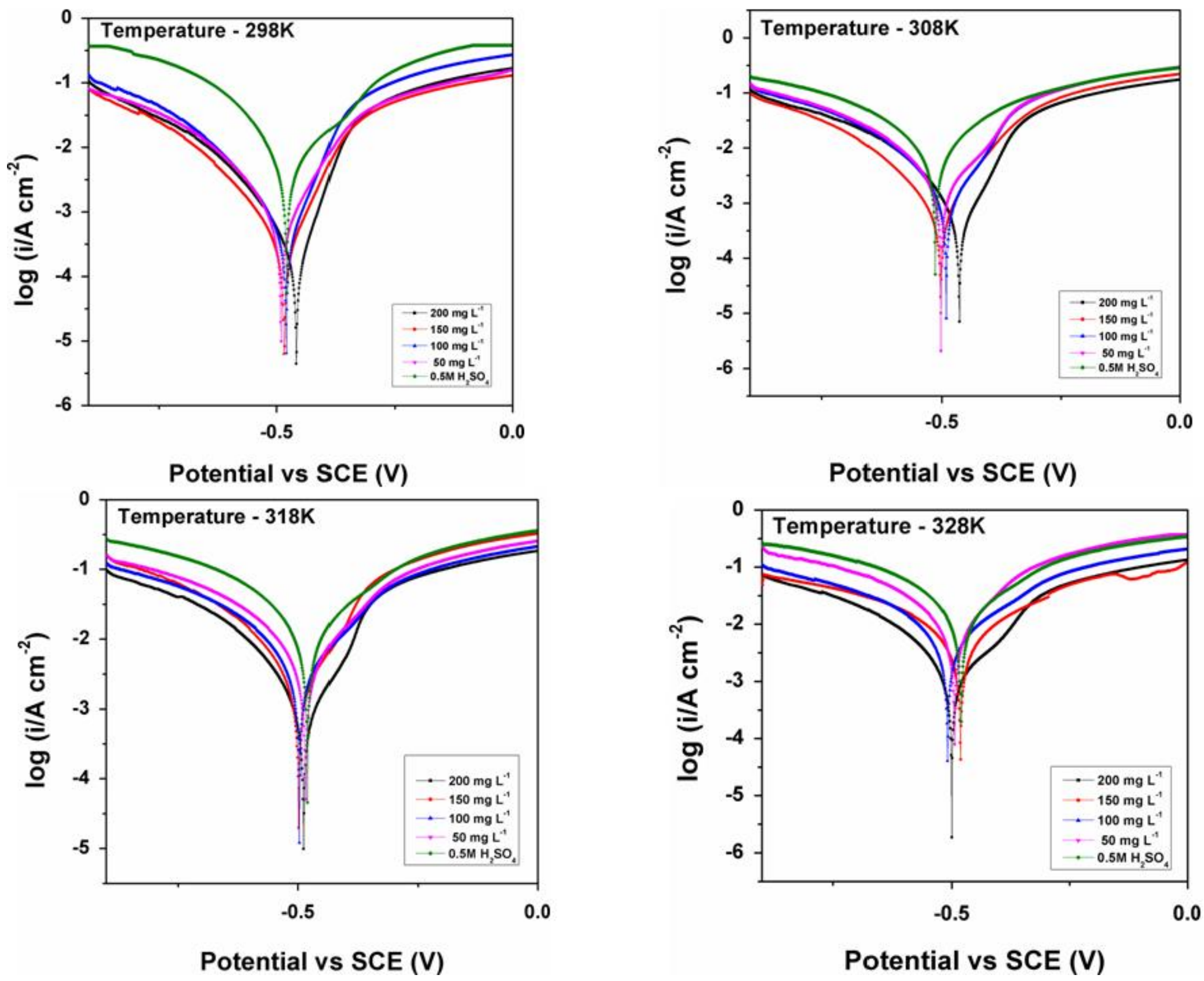


Fig.2. Tafel Polarization curves for MS in 0.5M H_2SO_4 in the absence and presence of different concentrations of PCBA at (a) 298K (b) 308K (c) 318K (d) 328K

The following relation was used to evaluate the inhibition efficiencies [26]

$$\text{Inhibition efficiency } (\eta)\ \% = \frac{i_{ocorr} - i_{corr}}{i_{ocorr}} \times 100 \qquad (3)$$

Where i_{0corr} and i_{icorr} are the values of the corrosion current density for MS in 0.5M H_2SO_4 solution in the absence and presence of the inhibitor respectively.

Polarization curves for mild steel in 0.5M H_2SO_4 in the absence and presence of different concentrations of the inhibitor show that both the anodic and cathodic currents in the presence of inhibitor as compared with the blank solution. It is reported in the literature that if the values of $E_{corr} > 85$ mV with respect to blank solution, the inhibitor behave as a cathodic or anodic type otherwise the inhibitor acts as mixed type inhibitor [27-28].

The temperature effect (298-328 K) has been studied on MS in the absence and presence of various concentrations of PCBAas given in Table 3. The highest inhibition efficiency 96.86 % is obtained at 298 K and 94.10 % at 308 K, 93.48% at 318 K, 90.58 % at 328 K for PCBA at optimum concentration 200 mgL^{-1}. The results show that the inhibition efficiency decreases with increasing the temperature which is due todesorption of the absorbed inhibitor molecule from the mild steel surface [19].

The results show that decrease of I_{corr} value with increase in the in concentration of PCBA leads to higher inhibition efficiency attributing this to the formation of protective layer on the mild steel surface that makes a barrier between the metal and the corrosive solution and thus reduce the corrosion rate [29-30].

3.3 Adsorption isotherm and thermodynamic parameters

The mechanism of interaction between the PCBA and mild steel surface was studied by using adsorption Isotherms. The adsorption of inhibitor on metallic surface increases with increased inhibitor concentration.Langmuir adsorption isotherm was utilized to fit the experimental data obtained by Tafel polarization curve. Langmuir adsorption isotherm is best fitted isotherm which shows a straight line with regression coefficient (R^2) value near to one from the plots of C/θ against C and all values are given in Table 4. According to

Langmuir adsorption isotherm, the relationship between degree of surface coverage (θ) and concentration of inhibitor (C) which is represented by following equation :

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \qquad (4)$$

$$\theta = \frac{IE(\%)}{100} \qquad (5)$$

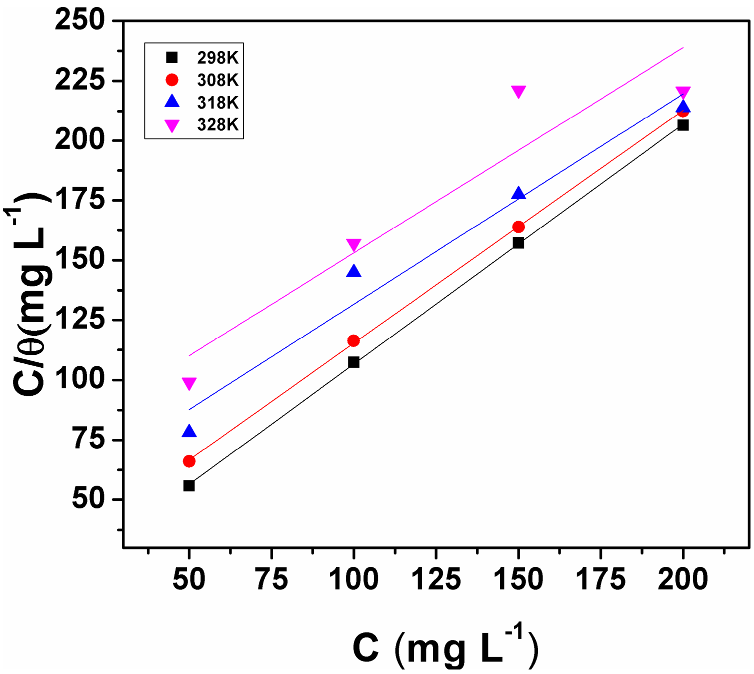


Fig.3. Langmuir adsorption isotherm for mild steel surface in 0.5M H_2SO_4 containing various concentrations of PCBA at 298-328K.

Where C is the inhibitor concentration, θ is the degree of surface coverage of inhibitors and K_{ads} is the equilibrium adsorption constant is shown in Fig.3. The K_{ads} values were calculated at different temperatures from the intercept of the Langmuir isotherm plots. The higher values of K_{ads} for inhibitor shows that inhibitor molecules have high adsorption potential on the MS surface [26]. The standard free energy of adsorption (ΔG^0_{ads}) and equilibrium constant (K_{ads}) are correlated by the following equation:

$$\Delta G^{\,0}_{ads=} - 2.303\ RT\ log(55.5\ K_{ads}) \qquad (6)$$

Where R is the gas constant, T is the absolute temperature and 55.5 is the molar concentration of water in molar.

Table 2: Thermodynamic parameters obtained for the adsorption of inhibitor on MS surface in 0.5M H_2SO_4 at four temperatures (298-328 K)

Inhibitor	Temperature (K)	K_{ads} (Lg^{-1})	$-\Delta G°_{ads}$ (KJ mol^{-1})
PCBA	298	158.9	22.51
	308	55.70	20.58
	318	22.80	18.88
	328	14.88	18.31

The obtained negative value of ΔG^0_{ads} at four different temperatures shows spontaneous adsorption on the surface of mild steel [31]. The K_{ads} and ΔG^0_{ads} values are listed in Table 2. It is reported in literature that the value of $\Delta G^0_{ads}$is less negative than -20 kJ mol^{-1}, it is indicatative of physical adsorption while those around -40 kJ mol^{-1} or higher value indicate chemical adsorption. In the present study, the calculated ΔG^0_{ads} values are given in Table 2 at four different temperatures for PCBA and these ΔG^0_{ads}values are slightly more negative or less negative than -20 kJ mol^{-1} indicating that the adsorption of this inhibitor is purely physical or slightly chemical adsorption. In other words it is physical leading to chemical adsorption at lower temperature.

4. Mechanism of corrosion inhibition

The adsorption mechanism is based on the interaction between the PCBA and mild steel surface in 0.5M H_2SO_4 solution.The phenomenon of adsorption is influenced by chemical structure of inhibitors and surface charge of the metal. The inhibition efficiency obtained from weight loss and electrochemical study indicates that the inhibition mechanism involves blockage of active site of mild steel surface by adsorption of inhibitor molecule. In sulphuric acid solution, the investigated inhibitor exists either as neutral molecules or in the cationic form.Inhibitors adsorb on the metal or on the metal /acid solution interface by the following ways: (i) electrostatic interaction of the positively charged inhibitor molecule with already adsorbed sulphate ions (SO_4^{-2}) on the metal surface, indicative of physisorption and. (ii) The donation of lone pair of electrons of oxygen atom to vacant d-orbital of the metal surface leading to chemisorption. (iii) donor–acceptor interactions between the vacant d-orbitals of Fe atoms and the π-electrons of aromatic ring, this phenomenon is known as retero-donation. Adsorption of the inhibitor molecule on the mild steel surface is presented in Fig.4. From the experimental observation, the inhibition efficiency of studied inhibitor PCBA is due to the presence of electron donating group –Cl at para position in the inhibitor molecule which increase the electron density on the benzene ring due to +R effect.

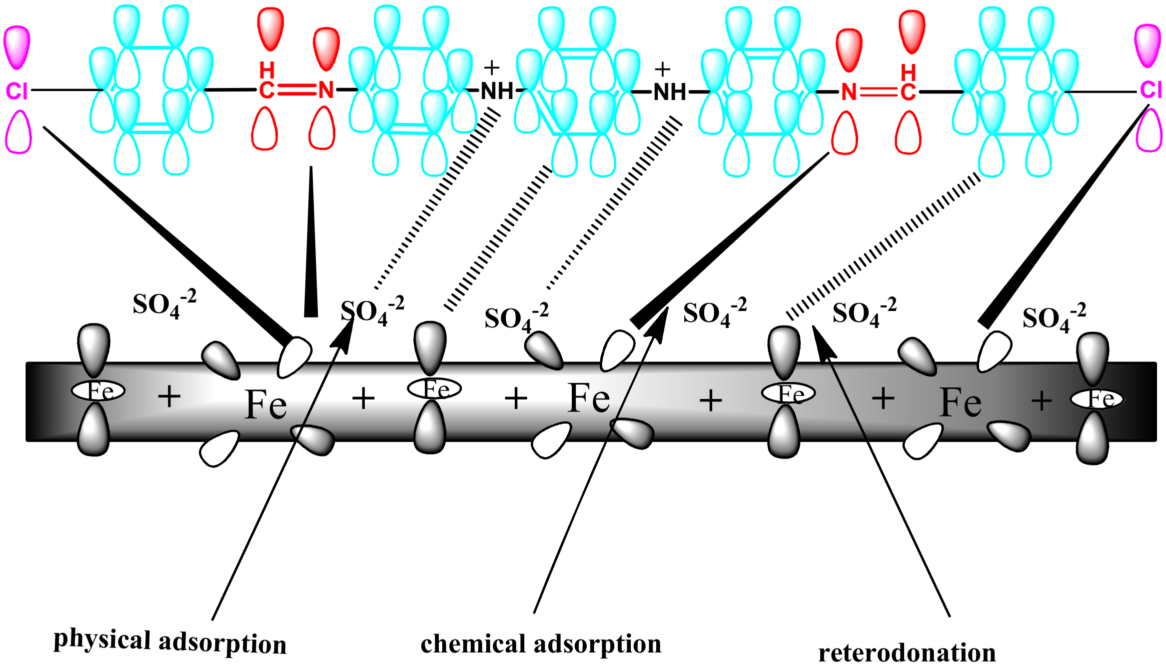


Fig.4. Pictorial representation of adsorption of inhibitor (PCBA) on mild steel surface.

5. Conclusions

The inhibition efficiency of studied inhibitor obtained from weight loss and Tafel polarisation studies are very well correlated with the data obtained experimentally. It is concluded from the studied inhibitor acts as an effective corrosion inhibitor for mild steel in 0.5M H_2SO_4 .The inhibition efficiency of studied inhibitor increases with the increase the concentration of inhibitor (PCBA). Tafel polarization study shows that PCBA behaved as a mixed type of inhibitor and followed the Langmuir adsorption isotherm.

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