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Adsorption characteristics of Kynurenic acid as green corrosion inhibitor at mild steel/hydrochloric acid interface

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ABSTRACT

The corrosion inhibition effect of kynurenic acid (KYN) has been investigated against mild steel in 1M HCl solution by using weight loss method, electrochemical impedance spectroscopy (EIS) and polarization measurements. In weight loss studies, the inhibition efficiency is increased with increase in the concentration of the inhibitor. EIS is used to investigate the mechanism of corrosion inhibition. Polarization measurements infer inhibitor acts as mixed-type inhibitor. The adsorption of inhibitor on mild steel surface followed Langmuir adsorption isotherm. The surface morphology of inhibited and uninhibited mild steel is also analyzed using scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX).

Keywords: Kynurenic acid, acid medium, weight loss, EIS and SEM.

INTRODUCTION

Metals and alloys are the backbones of engineering field. Metals especially mild steel is widely used in many industrial applications such as food, power production, petroleum, chemical and electrochemical industries. But in fact it suffers from certain type of corrosion in acidic media. Several approaches, including anodic and cathodic protection, lubrication, painting, electroplating and electroless plating have been proposed to protect the metal from corrosion. Another important method is the use of corrosion inhibitors [1]. The use of inhibitor is one of the most practical methods for protection against corrosion, especially in acidic media [2-3]. The corrosion inhibition is a surface process, which involves adsorption of the organic compounds on metal surface. The adsorption depends mainly on the electronic structure of the molecule [4]. The lone pair of electrons in heteroatoms determines the adsorption of these molecules on the metal surface [5]. There is a problem that many proven inhibitors with toxic properties include aromatic and nitrogen containing heterocyclic compounds, find applications in pickling processes and in the oil and gas industry [6-13]. In recent years, many amino acids were reported as good and safe corrosion inhibitors for metals in various aggressive media [14-17]. To solve this problem, some researchers investigated the inhibition effect of environment friendly inhibitors such as amino acids on metal corrosion [18-22]. Therefore, the development of corrosion inhibitors based on organic compounds containing nitrogen, oxygen atoms are of growing interest in the field of corrosion and industrial applications [23]. Moreover, the kynurenic acid is a commercially available amino acid. It acts as an antiexcitotoxic and anticonvulsant. Furthermore, kynurenic acid is a cheap, easily available and environmental friendly inhibitor. In the view of these favorable characteristic properties, kynurenic acid was chosen for the corrosion studies.

The main objective here is to investigate the corrosion process of mild steel in 1M HCl acid solution in the absence and presence of various concentrations of kynurenic acid. It is also the purpose of the present work to test the various electrochemical studies and surface morphologies.

MATERIALS AND METHODS

Materials preparations

Mild steel specimens having compositions of (wt. %) 0.104 % C, 0.58 % Mn, 0.035 % P, 0.026 % S and the remainder Fe were used for the gravimetric, potentiostatic polarization and impedance studies. Mild steel specimens of the dimension 1.5 Cm x 3.5 Cm x 0.2 Cm, polished to mirror finish with 1/0, 2/0, 3/0, 4/0, 5/0, 6/0 and 7/0 emery polishing papers and degreased with AR grade acetone were used in the gravimetric studies. The potentiostatic polarization and impedance studies, 1 Cm x 1 Cm x 0.2 Cm piece of the same material was welded on to a mild steel rod. The piece was polished to mirror finish with the above-mentioned emery polishing papers and degreased with AR grade acetone. Barring the 1 Cm x 1 Cm surface to be exposed for electrochemical studies, the rest of the surface was covered with epoxy resin. The acid solutions were made from analytical grade 37% HCl by diluting with double-distilled water.

Inhibitors

The compound kynurenic acid was purchased from SIGMA – ALDRICH and used as inhibitors without further purification. Stock solution were made in 1gm of inhibitor is dissolved in 1000 ml of 1M HCl solution. These stock solutions were used for all experimental purposes. Figure 1 shows the molecular structure of the used inhibitor.

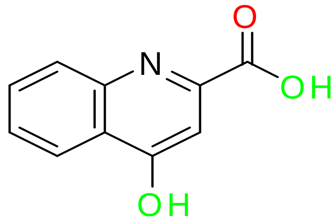


Figure 1. Molecular structure of kynurenic acid
(IUPAC Name: 4-Hydroxy quinoline-2-carboxylic acid)

Weight loss method

The weight loss method (gravimetric) is the most widely used method of inhibition assessment [24-27]. The simplicity and reliability of the measurement offered by the weight loss method is such that technique forms the baseline method of measurement in many corrosion-monitoring programmes [28, 29]. All the tests were conducted in 100 ml aerated 1M HCl solution at room temperature with various concentrations (50-300 ppm) of kynurenic acid for 3 hours immersion period. These samples were polished with emery paper of 1/0, 2/0, 3/0, 4/0, 5/0, 6/0 and 7/0 grades, washed thoroughly with double-distilled water, degreased with acetone and finally dried. At the end of the tests the specimen were carefully washed in acetone and then weighed. Duplicate experiments were performed in each and the mean value of the weight loss has been reported. From the weight loss measurements, the corrosion rate (W) was calculated by using the following equation:

$$\text{C.R.} = W = \frac{m_1 - m_2}{St} \quad (1)$$

where, m_1 is the mass of the specimen before corrosion, m_2 is the mass of the specimen after corrosion, S is the total area of the specimen, t is the corrosion time, and W is the corrosion rate. The (IE %) was determined by using the following equation [30] :

$$\text{IE \%} = \left[\frac{W_o - W_i}{W_o}\right] \times 100 \quad (2)$$

where, W_0 is the corrosion rate in the absence of inhibitor and W_i is the corrosion rate in the presence of inhibitor.

Electrochemical impedance spectroscopy (EIS)

EIS is now a sophisticated and established laboratory technique, with the relevant software to determine important parameters like corrosion charge transfer resistance (R_{ct}) rate and double-layer capacitance (C_{dl}) [31-35]. The working electrode was polished with different grades of emery papers, washed with water and degreased with AR grade acetone. All electrochemical measurements were carried out using a CHI 760D Electrochemical impedance analyzer model. Prior to the electrochemical measurement, a stabilization period of 30 minutes was allowed, which was proved to be sufficient to attain a stable value of open circuit potential (OCP) [36].

The electrochemical studies were made using a three-electrode cell assembly at room temperature with a platinum counter electrode and a saturated calomel electrode (SCE) as the reference electrode. The working electrode was mild steel with the exposed surface of $1Cm^2$ and the rest being covered by using commercially available resin. The EIS measurements (charge transfer resistance and double –layer capacitance) were carried out from Nyquist plot by using ac signal of 0.1V amplitude for the frequency spectrum from 100 kHz to 0.01Hz. The Tafel polarization curves were recorded in the potential range of $\pm$ 200 mV from the open circuit potential at a sweep rate of 0.1mV/s.

Surface analysis - Scanning Electron Microscope (SEM)
The scanning electron microscopy (SEM) JEOL/EO JSM-6390 model was used to study the morphology of mild steel surface in the absence and presence of optimum concentration of kynurenic acid for the immersion of 3 hours at room temperature. The plates were washed with running water and dried for SEM analysis. The SEM images were taken from that portion of the specimen where better information was expected.

RESULTS AND DISCUSSION

Weight loss method
The values of corrosion rate and percentage of inhibition efficiency were calculated from weight loss method at various concentrations of kynurenic acid in 1M HCl after 3 hours immersion at room temperature. They are summarized in Table 1. It is evident from table 1 that the inhibition efficiency is increased from 62.27% to 87.42% with the addition of 50 ppm to 300 ppm of kynurenic acid, which confirmed that the number of molecules adsorbed increased over the mild steel surface, blocking the active sites from acid attack and thereby, protecting the metal surface from corrosion. The maximum inhibition efficiency was shown at 300 ppm concentration of kynurenic acid. Indeed, corrosion rate values of mild steel decreases from 39.76 mmy^{-1} to 5.0 mmy^{-1} on the addition of 50 ppm to 300 ppm of kynurenic acid. The increased inhibition efficiency (IE %) and decreased corrosion rate (CR) might be due to the result of increased adsorption and increased coverage of kynurenic acid on the mild steel surface with increasing concentration of kynurenic acid [37].

Table 1. Inhibition efficiency values of mild steel in presence and absence of various concentrations of kynurenic acid in 1M HCl solution (weight loss method)

Conc. (ppm)	*Weight loss ($mg\ cm^{-2}$)*	*CR ($mm\ y^{-1}$)*	*Surface coverage (θ)*	*IE (%) η*
Blank	16.7	39.76	-	-
50	6.3	15.0	0.6227	62.27
100	4.2	10.0	0.7484	74.84
150	3.5	8.33	0.7904	79.04
200	2.9	6.90	0.8264	82.64
250	2.8	6.67	0.8322	83.22
300	2.1	5.0	0.8742	87.42

Electrochemical impedance spectroscopy (EIS)
Table 2 shows the experimental results obtained from EIS measurements for the corrosion of mild steel in the absence and presence of kynurenic acid at room temperature. The impedance spectra for mild steel in 1M HCl solution without and with the various concentrations (50-300 ppm) of kynurenic acid are presented as Nyquist plots in Figure 2. The impedance spectra exhibit a large capacitive loop at high frequencies followed by a small inductive loop at low frequency values. The diameter of the capacitive loop in the presence of inhibitor is bigger than in the absence of inhibitor (blank solution) and increases with the inhibitor concentration [38]. It is seen that addition of inhibitor, increases the values of charge transfer resistance (R_{ct}) and reduces the double layer capacitance (C_{dl}). The interfacial double layer capacitance (C_{dl}) values have been estimated from the impedance value using Nyquist plot by the formula:

$$C_{dl} = \left(2\pi f_{\max} R_{ct}\right)^{-1} \quad (3)$$

The values of C_{dl} decreased with an increase in the inhibitor concentration. This is due to an increase in the surface coverage by this inhibitor, resulting in to an increase in the inhibition efficiency.

$$\delta_{inh} = \frac{\varepsilon_0 \, \varepsilon_r}{C_{dl}} \quad (4)$$

where, ε_0 is the dielectric constant and ε_r is the relative dielectric constant. This decrease in C_{dl} values from 1230.91 to 25.016 μF cm^{-2} is due to the reduction in local dielectric constant and/or an increment in the thickness of the electrical double layer. The change in C_{dl} is due to the gradual replacement of water molecule by the adsorption of the inhibitor molecule on the metal surface, decreasing magnitude of metal dissolution [39]. The increase in R_{ct} values from16.080 Ω cm^2 to 113.076 Ω cm^2 is due to the formation of protective film on the metal/solution interface [40]. These observations suggest that kynurenic acid molecules function by adsorption at metal surface thereby causing the decrease in C_{dl} values and increasing in R_{ct} values. R_{ct} values were used to calculate the IE %, according to the following expression:

$$\text{IE}(\%) = \left[\frac{R_{ct}^{i} - R_{ct}^{o}}{R_{ct}^{i}} \right] \times 100 \quad (5)$$

where, R_{ct}^{i} and R_{ct}^{o} are the charge transfer resistance values with and without kynurenic acid, respectively. The Table 2 confirms that the inhibition efficiency (IE %) increases with increase the concentrations of kynurenic acid and maximum efficiency (85.77%) reaches at 300 ppm of inhibitor. All the above results infer that with increase in kynurenic acid concentration, the protective film is more and more protective.

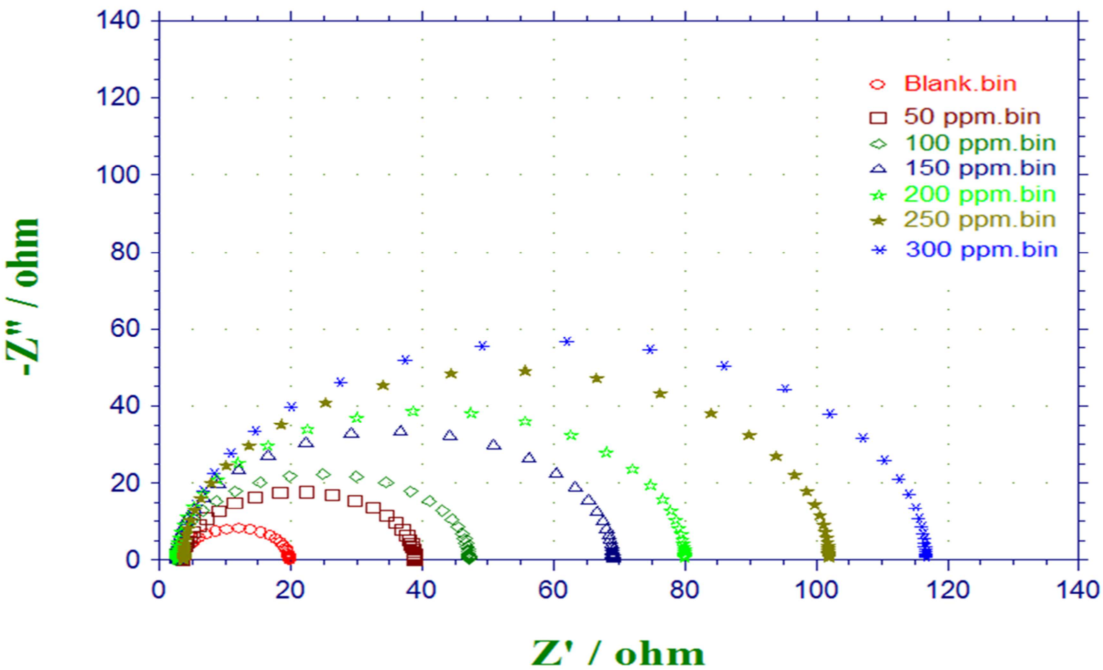


Figure 2. Nyquist plots of mild steel in 1M HCl with various concentrations of inhibitor at room temperature

Table 2. Electrochemical impedance parameters for mild steel in 1M HCl containing various concentrations of kynurenic acid

Conc. (ppm)	**Y_{max}** (Ωcm^2)	**R_{Ct}** (Ωcm^2)	**C_{dl}** ($\mu F\ cm^{-2}$)	**IE (%)** η
Blank	8.045	16.080	1230.91	_
50	17.638	35.313	255.65	54.46
100	22.268	44.643	160.17	63.98
150	33.175	66.407	72.279	75.78
200	38.404	77.338	53.613	79.2
250	48.789	98.471	33.144	83.67
300	56.292	113.076	25.016	85.77

Tafel polarization

The corrosion potential (E_{corr}), corrosion current density (I_{corr}), anodic (β_a) and cathodic (β_c) slopes are obtained by the anodic and cathodic regions of the Tafel plots. The corrosion current density (I_{corr}) can be obtained by extrapolating the Tafel lines to the corrosion potential [41] and the inhibition efficiency (IE %) values were calculated from the relation:

$$IE(\%) = \left[\frac{I^o_{corr} - I^i_{corr}}{I^o_{corr}}\right] \times 100 \quad (6)$$

where, I^o_{corr} and I^i_{corr} are the corrosion current densities in the absence and presence of inhibitor, respectively. The values obtained from polarization measurements such as corrosion potential (E_{corr}), corrosion current density (I_{corr}), anodic (β_a), cathodic (β_c) Tafel slopes and inhibition efficiency (IE %) are given in Table 3. Figure 3 shows the polarization curves for mild steel in 1M HCl containing with and without inhibitor. From Table 3 that the values of IE % increased with increase in the concentration of the inhibitor. At the optimum concentration of 300 ppm the value of IE % was 80.95 %, which confirmed the strong adsorption on the mild steel surface to control the corrosion rate. The increase in the concentration of inhibitor decrease I_{corr} values. E_{corr} values do not vary significantly in the increase of concentration of inhibitor that they are indicate the used inhibitor is a mixed-type inhibitor. The change in the values of β_c in the presence of inhibitor clearly indicates the effect of the inhibitor compound on the kinetics of hydrogen evolution. The shift in the anodic Tafel slope (β_a) values may be due to the adsorption of sulphide ions/or inhibitor molecules onto the mild steel surface [42].

The inhibition efficiency calculated from the electrochemical impedance spectroscopy and tafel polarization is 85.77 % and 80.95%, respectively. These values are correlated with IE % obtained by weight loss method (87.42 %).

Table 3. Tafel polarization values for the corrosion of mild steel in 1M HCl containing various concentrations of kynurenic acid

Conc. (ppm)	***β_a (1/V)***	***β_c (1/V)***	***E_{corr} (mV/SCE)***	***I_{corr} (mA/cm^2)***	***R (Ohm)***	***IE (%) η***
Blank	6.531	6.511	-449.6	1.087	31	-
50	8.348	7.739	-356.5	0.4940	55	54.55
100	7.898	8.430	-486.5	0.4288	62	60.55
150	10.492	8.950	-476.6	0.3255	69	70.05
200	9.831	9.105	-469.2	0.2966	77	72.71
250	9.256	7.900	-489.9	0.2332	109	78.54
300	8.995	8.606	-479.6	0.2070	119	80.95

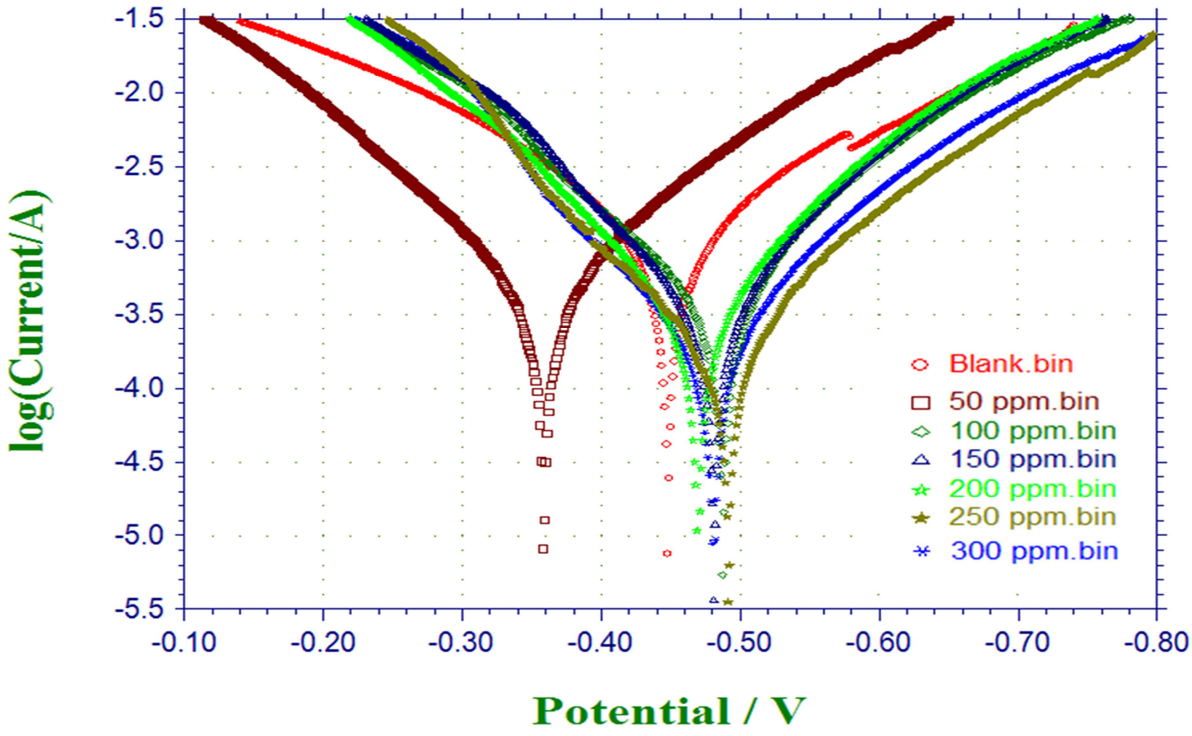


Figure 3. Anodic and cathodic Tafel polarization plots of mild steel in 1M HCl with various concentrations of kynurenic acid

Adsorption isotherm

Adsorption isotherms are very important to understanding the mechanism of inhibition of corrosion reaction of metals and alloys. The adsorption isotherm study describes the interaction between inhibitor molecules and metal surface. The most frequently used adsorption isotherms are Frumkin, Temkin and Langmuir isotherms. Attempts to fit data obtained from the weight loss measurements into different adsorption isotherms revealed that the data best fitted to the Langmuir adsorption isotherm. Assumptions of Langmuir relate the concentration of the adsorbate in the bulk of the electrolyte (C_{inh}) to the degree of surface coverage (θ) as in equation:

$$\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh} \tag{7}$$

where, K_{ads} is the equilibrium constant of the inhibitor adsorption and C_{inh} is the inhibitor concentration. The linear regressions parameter (R^2) between C_{inh}/θ and C_{inh} were listed in Table 4. Figure 4 shows the relationship between C_{inh}/θ and C_{inh} for optimum concentration of inhibitor, which gives a straight line at room temperature. The slope of the C_{inh}/θ versus C_{inh} plots shows a small deviation from unity, which means non-ideal simulating and is unexpected from the Langmuir adsorption isotherm [43]. Adsorption equilibrium constant (K_{ads}) and free energy of adsorption (ΔG^{o}_{ads}) were calculated using the following relationship:

$$\Delta G^{o}_{ads} = -\mathrm{RT}\ln(55.5\mathrm{K}_{ads}) \tag{8}$$

where, 55.5 is the concentration of water in solution in mol L^{-1} and R is the universal gas constant. Generally, values of ΔG^{o}_{ads} around -20 kJ mol^{-1} or lower are consistent with the electrostatic interaction (or) physisorption and when it is around -40 $kJmol^{-1}$ or higher values then this is chemical interaction [44].

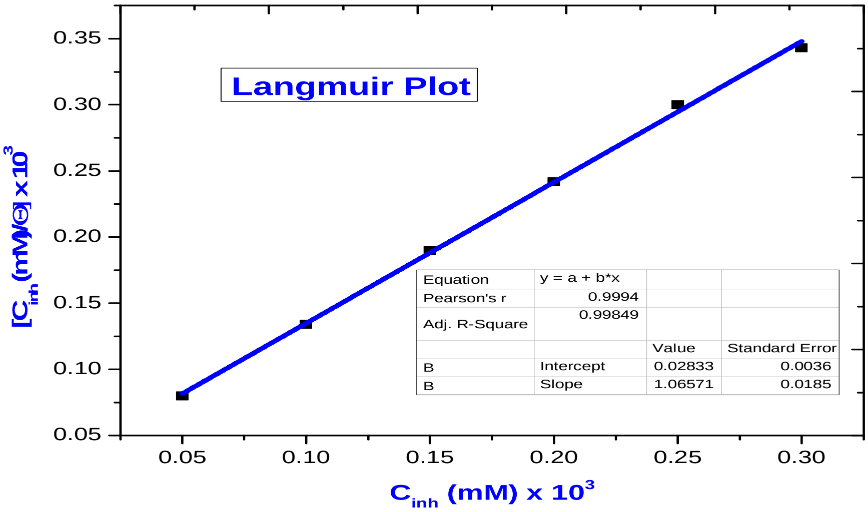


Figure 4. Langmuir adsorption isotherm plots for the adsorption of kynurenic acid in 1M HCl on the surface of mild steel

Here, the calculated ΔG^{o}_{ads} value is -19.2560 KJ/mol indicating that the adsorption mechanism of kynurenic acid on mild steel surface in 1M HCl solution followed physical adsorption (ionic). The ΔG^{o}_{ads} negative value of ensure the adsorption of inhibitor molecule to the mild steel surface is a spontaneous process.

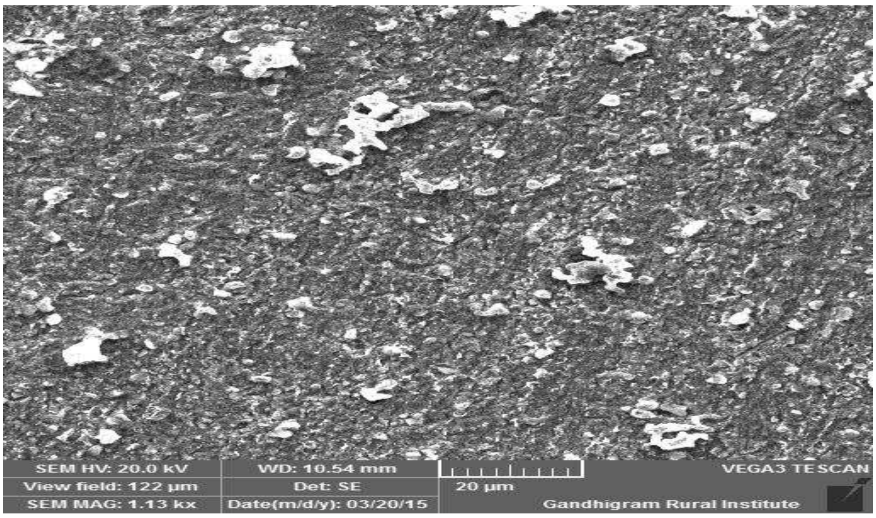
Table 4. Langmuir adsorption isotherm parameters for the adsorption of kynurenic acid in 1M HCl on the surface of mild steel

Inhibitor	R^2	K_{ads} ($10^4 M^{-1}$)	ΔG^0_{ads} (kJ mol^{-1})
KYN	0.9984	37.6177	-19.256

Surface analysis

Scanning Electron Microscope (SEM)

The SEM images were recorded in Figure 5a&b to be establishing the interaction of inhibitor molecules with metal surface. The SEM images show the features of mild steel surface after 3 h in 1M HCl in absence and presence of 300 ppm kynurenic acid at 303K. The SEM images revealed that the mild steel specimen immersed in inhibited solutions is in better conditions having smooth surface while the metal surface immersed in blank acid solutions is rough covered with corrosion products and appeared like full of bits and cavities. This indicated that the kynurenic acid molecules hinder the dissolution of iron by forming protective film on mild steel surface and thereby reduce the corrosion rate.



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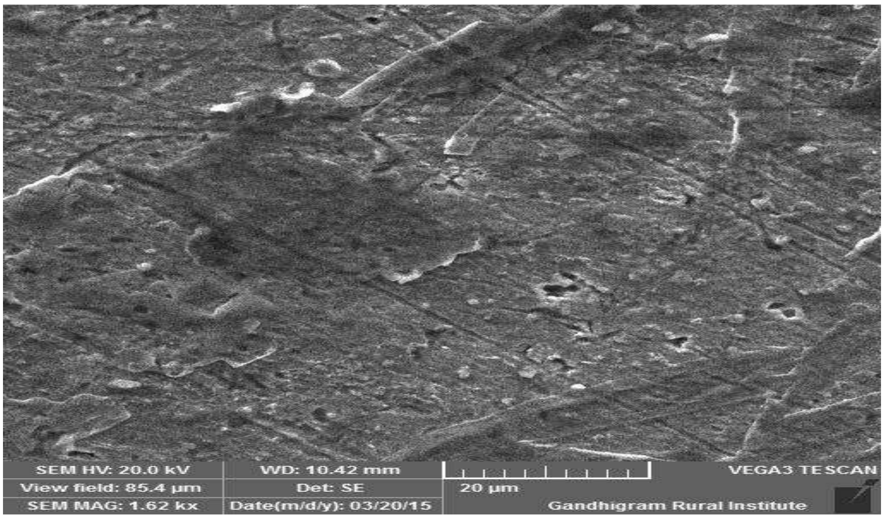
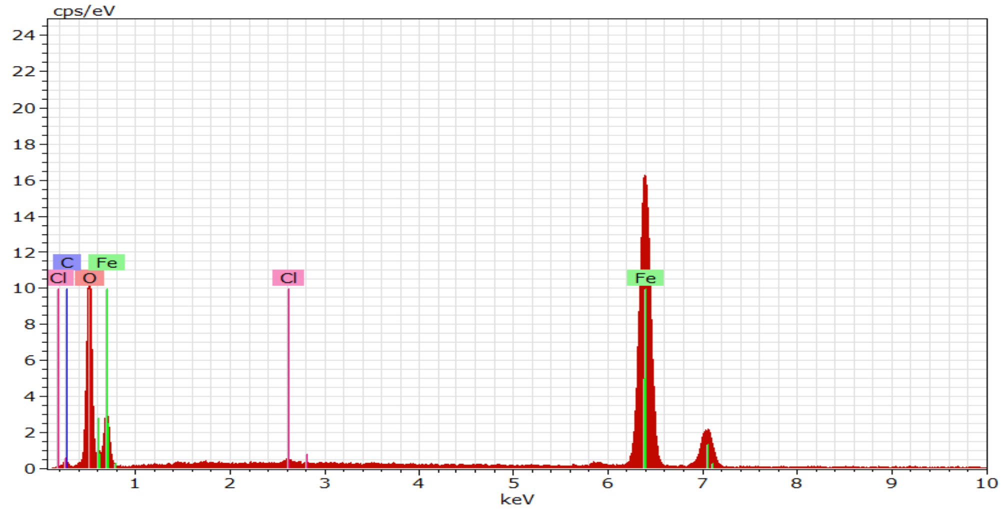
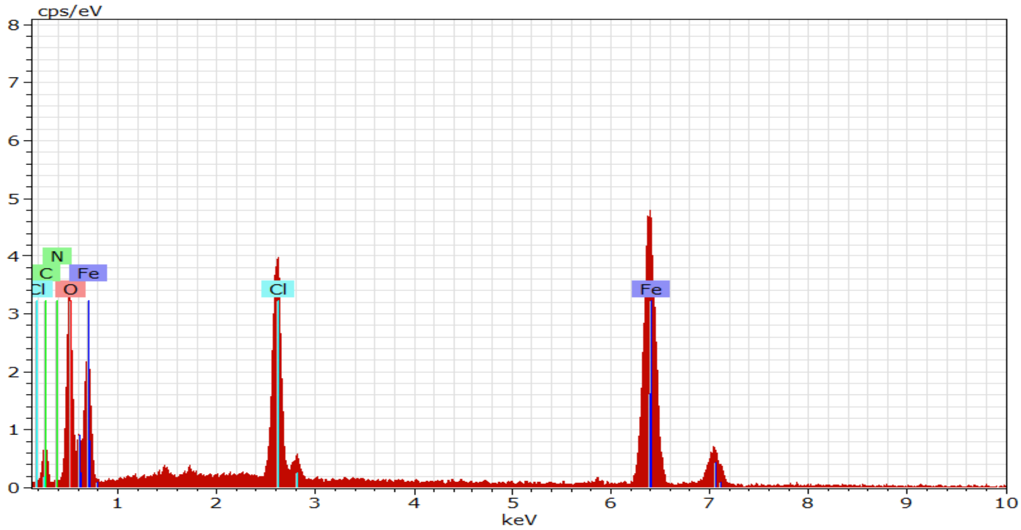


5b

Figure 5. SEM Micrographs of mild steel: a after immersion in 1M HCl solution in absence of kynurenic acid, b after immersion in 1M HCl solution in presence of 300 ppm kynurenic acid



6a



6b

Figure 6. EDX spectra of the surface of mild steel: a after immersion in 1M HCl solution in absence ofinhibitor, b after immersion in 1M HCl solution in presence of 300 ppm kynurenic acid

Energy dispersive X-ray spectroscopy (EDX)

EDX spectra recorded for mild steel samples exposed to 1M HCl in the absence and presence of 300 ppm kynurenic acid is shown Figure 6a&b. The EDX spectra in absence of inhibitor, Figure 6a shows the characteristic peaks of the elements constituting mild steel sample. However, the EDX spectra in presence of inhibitor, Figure 6b show some additional and strong lines of nitrogen and oxygen. These additional and strong lines are due to nitrogen and oxygen of the adsorbed inhibitor species. From the EDX spectra data, the inhibitor was strongly adsorbed on the mild steel surface.

Mechanism of Corrosion Inhibition

A clarification of mechanism of inhibition requires full knowledge of the interaction between the protective compound and the metal surface. Many of the organic corrosion inhibitors have atleast one polar unit with atoms of nitrogen, sulphur, oxygen and phosphorous. It has been reported that the inhibition efficiency decreases in the order to O < N < S < P. In addition, iron is well known for its co-ordination affinity to heteroatom bearing ligands [45].

In HCl acid medium, inhibitor molecule exist as protonated species and it is assumed that Cl^- ions are first adsorbed on the metal surface and the net positive charge on the metal surface enhances the specific adsorption of Chloride ions [46]. Generally, in acid solution inhibition of metallic corrosion occurs through (i) electrostatic interaction of protonated molecules with already adsorbed chloride ions, (ii) donor-acceptor interactions between the π-electrons of aromatic ring and vacant *d*-orbital of surface iron atoms, (iii) interaction between unshared electron pairs of heteroatoms and vacant *d*-orbital of iron surface atoms [47]. In the present study, the values of ΔG^o_{ads} are around -20 kJ mol^{-1}. Hence, showing that adsorption of kynurenic acid molecules on the surface of mild steel predominantly take place by physical adsorption.

CONCLUSION

The inhibition effect of kynurenic acid on mild steel in various concentrations of HCl was studied by weight loss method. From this study, the inhibition efficiency of the inhibitor increases with an increase in concentration. The adsorption of kynurenic acid on the mild steel surface in 1M HCl obeys the Langmuir adsorption isotherm. The value of ΔG^o_{ads} indicates that kynurenic acid is inhibiting the corrosion of mild steel by purely physisorption. Tafel polarization technique suggests that kynurenic acid act as a mixed-type of inhibitor. Electrochemical impedance spectroscopy was used to investigate the mechanism of corrosion inhibition. The SEM and EDX images were confirm the formation of protective layer on the mild steel surface. Based on all experimental results, kynurenic acid was found to act as good corrosion inhibitor for mild steel in 1M HCl media.

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