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Green corrosion inhibitor from leaves of Purple Knight Hedge plant for mild steel in 1 M HCl medium: Electrochemical, gravimetric, adsorption and SEM studies

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Lyophilized hot water extract of Purple Knight leaves (PKLE) has investigated as an environment friendly and cost effective corrosion inhibitor against corrosion of mild steel in 1 M HCl solution. Corrosion inhibition efficiency of PKLE has studied using Gravimetric, potentiodynamic polarization and electrochemical impedance spectroscopic methods.

PKLE acts as mixed inhibitor and its adsorption on mild steel surface in 1 M HCl solution follows the Langmuir adsorption isotherm. Thermodynamic parameters of the adsorption process and apparent activation energy for the corrosion process have been determined. Both physical and chemical adsorption contributes to the overall adsorption process. Scanning Electron Microscopy reveals a significant protection of metal surface by PKLE molecules.

The chemical characterization of PKLE is carried out by gas chromatography and FT-IR spectroscopy.

Keywords: Adsorption, Electrochemical studies, Green corrosion inhibitor, Mild steel, Purple knight plant, SEM

Mild steel is an indispensable alloy in modern civilization. This alloy is widely used in several industrial processes like acid descaling, acid pickling, petroleum oil well acidization and paper and pulp industries. Hydrochloric acid is one of the raw materials in these processes. Dissolution of metal in acidic corrosive medium has a severe impact on the economy of these industries[1,2]. Therefore, protection of mild steel from corrosive acid environment is a challenging problem to the scientific community. Several methods are available for mitigation of this problem. The use of inhibitor offers a simple and cost effective way for the protection of metal surface. Several synthetic organic and inorganic inhibitors are being reported with high efficiency[3,4]. Non-bonding electron and/or pi-electrons of this inhibitor are responsible for their adsorptionon metal surface[5]. This adsorbed film acts as a physical obstruction to the corrosion process. However, toxicity, non-biodegradability and environmental hazards associated with these synthetic compounds compelled several governments to put restriction on them. Therefore, scientists are now inclined to the use of green corrosion inhibitors. Extracts from different plant parts are rich in phytochemicals like tannins, phenolics, anthocyanins, flavones, alkaloids, terpenoids, amino acids and carbohydrates[6-10]. These phytochemicals can mimic the properties of synthetic inhibitors because of their similar structures. In addition to this wide availability, biodegradability, environment friendly nature and simple method of extraction are the reasons for which more and more plant extracts are being explored as corrosion inhibitors[11]. Purple Knight plant is widely available, weather/climate tolerant and efficient in propagation without having any extra care. Therefore, Purple Knight plant was selected as a source of green corrosion inhibitor against mild steel corrosion in present study.

Purple Knight (*Alternanthera dentata*) is a purple hedge plant which is mostly used for decorating of the boundaries and gardens. This plant is widely available all over the world. It is characterized by its purple colored leaves along with purple stems. Aqueous extract of purple knight was used for the synthesis of silver nano-particles and for antimicrobial activity[12]. The dyes present in this plant were also used as natural sensitizers for dye-sensitized solar cells[13]. In the present study the lyophilized aqueous extract of Purple Knight leaves was used as green corrosion inhibitor for mild steel in 1 M HCl medium.

Experimental Section

Coupon preparation

Mild steel coupons (C = 0.07%,V = 0.004%,Mn = 0.46%, Al = 0.002%, P = 0.06%, Ni = 0.038%, Cr = 0.034%, Mo = 0.007%, Cu = 0.115%, Ti = 0.002%, Nb = 0.0001%, Co = 0.005% and the remaining Fe) of 1×1× 0.1 cm^3 size were used for gravimetric measurements whereas coupons of 1 cm^2 exposed surface areas were used as working electrode for electrochemical polarization and impedance measurements. The coupons were polished mechanically with emery papers of 220, 400, 600, 800, 1200 and 1500 grade. They were then washed with distilled water followed by acetone, air dried and finally kept in a vacuum desiccators before exposing to the 1.0 M acidic medium.

Preparation of extracts

Fresh leaves were collected from the campus of National Institute of Technology Durgapur, West Bengal, India in the month of June, 2015. They were cleaned thoroughly with running tap water to remove the dirt, dried for 2 days in sunlight and finally grounded to powder. The dried powder (60 g) was extracted in distilled water (1000 mL) maintained at 80°C for an hour. Aqueous extract was collected by centrifugation followed by filtration through G-3 sintered bed. The residue was again extracted under similar set of conditions. Aqueous extracts were combined and concentrated under reduced pressure. This concentrated solution was then freeze dried and the solid material (PKLE) thus obtained was preserved in a desiccator. Solutions of PKLE in 1.0 M HCl were used for further corrosion and structural investigation.

Preparation of electrolytic solution

The 1.0 M HCl solution was prepared by dilution of analytical grade HCl (Merck, India) with double distilled water. Inhibitive solutions were prepared by adding PKLE in 1.0 M HCl under stirring at 293 K to make 25 ppm, 50 ppm, 75 ppm and 100 ppm inhibitive solutions.

Weight loss measurements

Finely polished and dried metal coupons were accurately weighed and immersed in 1.0 M HCl for 6 h in absence and presence of 25 ppm, 50 ppm, 75 ppm and 100 ppm of PKLE. These experiments were conducted at 293 K, 303 K, 313 K and 323 K. The metal coupons (corroded/inhibited) were taken out of electrolytes and washed thoroughly with distilled water followed by acetone, and dried in a vacuum desiccator. The weight loss of the coupons was then measured. In all of the above measurements, the average values of the inhibition efficiencies of three separate experiments were taken. The rate of corrosion (C_R) in (g $cm^{-2}h^{-1}$) was measured according to the given equation[14]:

$$C_R = \frac{\Delta w}{s \times t} \quad \text{... (1)}$$

where Δw is weight loss (average) of coupon, 's' the area of the coupon, and 't' immersion time of coupon in electrolyte solution. The inhibition efficiency (η_w) was calculated from corrosion rate as follows

$$\eta_w(\%) = \frac{C_R^0 - C_R}{C_R^0} \times 100 \quad \text{... (2)}$$

where, C_R and C_R^0 are the rates of corrosion of mild steel samples in electrolyte solutions with and without inhibitor respectively.

Electrochemical measurement

Electrochemical measurements were performed in a glass cell consisting of three openings for working (mild steel coupon), reference (calomel electrode) and auxiliary electrodes (platinum electrode). A working electrode of mild steel with 1 cm^2 exposed surface area was attached to holder of the system and the rest of the surface was covered with electrolyte solution for 40 min to attain open circuit potential (OCP) to reach steady state. Polarization studies (both cathodic and anodic) were carried out by Electrochemical Analyzer (Gill AC version 5) after attaining the steady state. The experiments were conducted at 293 K, 303 K, 313 K and 323 K without inhibitor and with 25 ppm, 50 ppm, 75 ppm and 100 ppm of the inhibitor in 1.0 M HCl. Impedance measurements were conducted at frequencies ranging from 10 mHz to 100 kHz with an A.C. amplitude of ±10 mV at the rest potential. The values of charge transfer resistance (R_{ct}) were calculated from thediameters of the semicircles of Nyquist plots. The inhibition efficiency, η_z(%) of the inhibitor was determined as follows,

$$\eta_z(\%) = \frac{R_{ct} - R_{ct}^0}{R_{ct}} \times 100 \quad \text{...(3)}$$

where,R_{ct} and $R_{ct}^0$are the charge transfer resistance values with and without inhibitor in 1.0 M HCl respectively. Charge transfer resistance (R_{ct}) is related to the double layer capacitance (C_{dl}) according to the following equation

$$C_{dl} = (Q.R_{ct}^{1-n})^{1/n} \quad \text{... (4)}$$

where, Q is the parameter which is proportional to the double layer capacitance on the surface of metal and $n$is a parameter which is related to the surface irregularity. The value of n varies from zero to unity.

Electrochemical polarization plots were obtained within -250 mV to +250 mV using a sweep rate of 30 mV per min. Extrapolation ofthe Tafel slope to the point of intersection of anodic and cathodic current gave the corrosion current density (i_{corr}) and corrosion potential (E_{corr}) values. Inhibition efficiency, $\eta_p(\%)$ was then calculated according to the given equation,

$$\eta_p(\%) = \frac{i_{corr}^0 - i_{corr}}{i_{corr}^0} \times 100 \quad \text{... (5)}$$

wherei_{corr} and i_{corr}^0represent the values of corrosion current densities in presence and absence of inhibitor respectively.

Surface study by Scanning Electron Microscopy (SEM)

The surface morphology of the inhibited and uninhibited mild steel surfaces in 1.0 M HCl was measured by scanning electron microscope. Polished mild steel coupons were immersed in 1.0 M HCl with and without addition of 100 ppm PKLE for 6 h at 293 K. The samples were then taken out of the electrolyte solutions, cleansed with double distilled water and dried in a desiccator under reduced pressure Anelectron microscope, SEM Hitachi, S-3000 N instrument, was used for SEM study.

FTIR spectroscopic analysis

Fourier transform infrared (FTIR) spectroscopy was used to identify the functional group present in PKLE. Thermo Nicolet, iS10 spectrophotometer was used for FTIR spectrum. KBr disk technique was used for recording the spectrum.

Carbohydrate and phenolics estimation and monosaccharide compositional analysis

Total carbohydrate content of PKLE was determined by colorimetric method. In this method PKLE was treated with 5% phenol and concentrated sulfuric acid[15]. Glucose solution was used as standard. Absorbance or optical density was measured at 485 nm in a Shimadzu UV 1800 spectrophotometer. Total carbohydrate content was expressed as mg per mg of PKLE. The amount of phenolics present in PKLE was determined spectrophotometrically by treating PKLE with Folin- ciocalteau reagent. Gallic acid served as standard[16]. Total phenolic content was expressed as mg of gallic acid equivalents per mg of PKLE. Monosaccharide composition of the carbohydrates was analyzed by gas chromatography following the method of Blakeney[17]. Briefly, dried PKLE was hydrolyzed in 4M trifluroacetic acid in a sealed tube under nitrogen atmosphere at 121°C for 3 h. TFA was then removed and the monosaccharides released were reduced to their alditols using $NaBH_4$ in NH_4OH. The alditols were further converted to their acetate derivatives by treating them with acetic anhydride and 1-methyl imidazole as catalyst. The alditol acetates were then analyzed by gas chromatography using capillary column. Myo- inositol was used as an internal standard. Total anthocyanins were determined according toreported methods [18, 19] and expressed as cyanidin-3-glucoside (Cy-3-glc) equivalents.

Results and Discussion

Weight loss study

Weight loss study is a non-electrochemical technique to determine the rate of corrosion and inhibition efficiency. The data obtained from weight loss studies of mild steel corrosion in 1.0 M HCl without and with PKLE of different concentrations at 293 K are shown in Table 1. It was found that with increase in concentration of PKLE, the inhibition efficiency $\eta_w(\%)$ increased with concomitant decrease in the rate of corrosion (C_R).When the PKLE

Table 1 — Gravimetric experiment at various temperatures using different concentration of PKLE

Temperature(K)	Inhibitor conc. (ppm)	C_R (mg cm^{-2}h^{-1})	η_p(%)
293	00	1.633	-
	25	0.15	90.82
	50	0.09	94.49
	75	0.075	95.41
	100	0.055	96.63
303	00	3.3	-
	25	0.257	92.22
	50	0.14	95.76
	75	0.12	96.36
	100	0.095	97.12
313	00	5.15	-
	25	0.3267	93.66
	50	0.222	95.69
	75	0.18	96.50
	100	0.143	97.18
323	00	8.25	-
	25	0.462	94.40
	50	0.315	96.18
	75	0.2633	96.80
	100	0.223	97.29

concentration was 100 ppm the inhibition efficiency attained its maximum value 96.63% at 293 K. The increase in inhibition efficiency on going from 75 ppm to 100 ppm inhibitor concentration was negligible. Therefore, further increase in PKLE concentration for weight loss study seemed to be impractical. Formation of a thin film of adsorbed inhibitor molecules can be proposed to explain this observation[20]. This adsorbed film acts as a barrier to the corrosion process leading to higher inhibition efficiency.

Electrochemical experiment

Potentiodynamic polarization study

Potentiodynamic polarization studies were carried out to measure the inhibition behavior of PKLE and to find out the values of kinetic parameters related to the corrosion process. The values of kinetic parameters thus obtained are tabulated in Table 2 and the corresponding Tafel diagrams are given in Fig. 1(a). Table 2 clearly indicates that corrosion current density (i_{corr}) decreases in all inhibitive solutions compared to that in non-inhibitive solution and higher the concentration of PKLE lower is the value of i_{corr}. Corrosion current density attained a value of 0.0879 mA cm^{-2}at 100 ppm inhibitor concentration. Since i_{corr} is a measure of extent of corrosion, such a low value of i_{corr}points to the high efficiency of PKLE as corrosion inhibitor. Cathodic and anodic current densities shifted toward lower values in each inhibitive solution compared to those in non-inhibitive solution. Therefore, PKLE can be termed as mixed inhibitor[21]. Table 2 shows that maximum shift of corrosion potential is 42.07 mV which is less than 85 mV. This also suggests that PKLE acts as mixed inhibitors[22]. Figure 1(a) shows that cathodic lines are themselves parallel and similar is the case with anodic lines. This indicates that same mechanism is operative in both of inhibitive and non-inhibitive solutions[23]. This is further supported by the insignificant changes in cathodic and anodic slope (b_c and b_a respectively) given in Table 2. The inhibition efficiency in this

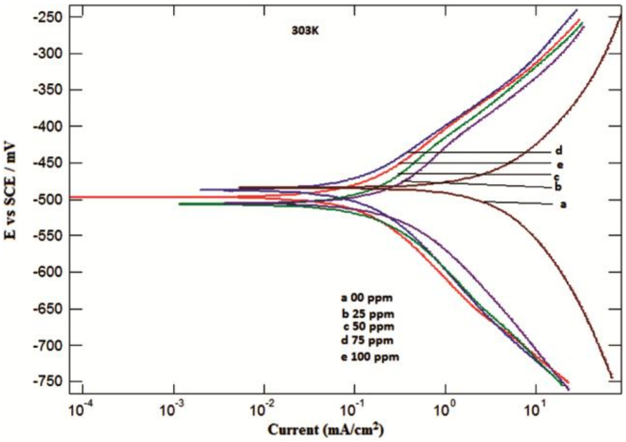

Fig. S1 — Potentiodynamic polarization curves for mild steel in 1 M HCl in presence of PKLE at 303K.

Table 2 — Kinetic parameter obtained from potentiodynamic polarization studies

Temperature (K)	Inhibitor conc.(ppm)	E_{corr} (mV per SCE)	I_{corr}(A cm^{-2})	b_a(mV dec^{-1})	b_c (mV dec^{-1})	Efficiency η_P (%)
293	00	-538.22	1.8710	152.47	137.1	-
	25	-516.19	0.2139	110.13	85.09	88.57
	50	-499.17	0.1447	98.977	83.307	92.27
	75	-496.15	0.1268	125.17	116.47	93.22
	100	-519.36	0.0879	123.01	82.558	95.30
303	00	-482.9	2.5330	100.28	119.18	-
	25	-507.05	0.2419	119.06	112.98	90.45
	50	-507.94	0.1482	113.56	113.89	94.15
	75	-487.36	0.1393	104.83	124.4	94.50
	100	-497.45	0.0986	90.40	104.8	96.10
313	00	-434.36	4.0236	89.79	102.5	-
	25	-492.31	0.3342	83.376	80.146	91.69
	50	-502.56	0.1924	100.48	88.48	95.22
	75	-512.98	0.1657	96.13	86.27	95.88
	100	-511.68	0.1131	93.04	86.82	97.19
323	00	-528.98	6.2490	154.86	140.03	-
	25	-504.68	0.4963	74.922	77.458	92.06
	50	-498.3	0.3103	122.00	98.396	95.03
	75	-515.57	0.2486	115.76	89.475	96.02
	100	-501.53	0.1721	78.445	63.631	97.25

study was inhibitor concentration dependent and is in agreement with weight loss study. At 293 K inhibitions efficiency attained its maximum value 95.30 % when concentrations of PKLE was 100 ppm.

Electrochemical Impedance Study (EIS)

The data obtained in EIS study are represented in Table 3 and the corresponding Nyquist plots are given in Fig. 1 (b). Figure 1(b) shows that depressed semicircular shapes were obtained in each EIS experiment with the centers of the semi circles under the real axis. This points to the non- working electrode and operation of single charge transfer process during anodic dissolution. Diameter of the semicircle is a measure of charge transfer resistance which increases with increasing number of PKLE molecules. This means that increasing concentration of inhibitors leads to increasing inhibition efficiency. Nyquist plots were analyzed by invoking an equivalent circuit which is composed of charge transfer resistance (R_{ct}) and constant phase element of electrical double layer (CPE) which remain in parallel combination with themselves and each of them is in series with solution resistance (Rs) (inset of Figure 1 (b)) .

Constant phase element is considered here because of non-ideal nature of the electrolyte. The impedance of CPE (Z_{CPE}) can be expressed by the equation[24]

$$Z_{CPE}= Y_0^{-1}(iw)^{-n} \quad \text{... (6)}$$

where, Y_0 is proportionality constant, $i$is the imaginary numbers, w is the angular frequency and n is constant which varies from 0 to 1. Higher the deviation of the value of n from 1, higher is the deviation from ideal behavior. A close look of Table 3 shows that $\mathrm{R_{ct}}$values increases with increasing inhibitors concentration. $\mathrm{R_{ct}}$ attained its highest value (153 Ω cm2) at 100 ppm inhibitor concentration. This can be correlated with progressive adsorption of inhibitor molecules on metal surface with increase in concentration of inhibitor. The adsorbed inhibitor layer acts as a barrier in between metal surface and electrolyte. Opposite trend is observed with double layer capacitance (C_{dl}). The value of $C_{dl}$was calculated according to the equation (4). C_{dl}value is related to permittivity constant of air (ε_0), dielectric constantof the adsorbed film (ε), thickness of the adsorbed film (d),surface area (A) of the working electrode according to the Helmoltz equation,[25]

$$C_{dl} = \frac{\varepsilon_0 \varepsilon}{d} A \quad \text{...(7)}$$

Decreasing C_{dl}value with increasing inhibitor concentration is due to increasing value of thickness of adsorbed film of inhibitor and concomitant decrease in dielectric constant value of the adsorbed film. This is needless to mention at this point that

Table 3 — Kinetic parameter obtained from electrochemical impedance study

Temp.(K)	Inhibitor conc.(ppm)	R_{ct} (Ω cm^2)	Q($\mu\Omega^{-1}$ S^n cm^{-2})	n	C_{dl} (μF cm^{-2})	η_z (%)
293	00	6.18	1460	0.720	234.00	-
	25	62.4	629	0.755	219.96	90.10
	50	94.6	478	0.778	197.57	93.46
	75	113.0	321	0.785	129.42	94.53
	100	153.0	239	0.790	99.18	95.96
303	00	4.60	1250	0.780	291.76	-
	25	56.3	396	0.785	140.00	91.83
	50	93.5	275	0.815	123.12	95.08
	75	102.0	261	0.825	120.95	95.49
	100	119.0	170	0.845	83.12	96.13
313	00	3.23	763	0.825	213.43	-
	25	29.5	291	0.830	109.82	92.05
	50	66.5	181	0.835	75.57	95.14
	75	87.1	165	0.840	73.54	96.29
	100	110.0	147	0.851	71.40	97.06
323	00	1.58	2040	0.761	336.57	-
	25	22.2	690	0.770	198.1	92.88
	50	54.9	436	0.775	147.53	97.12
	75	58.0	365	0.800	139.22	97.27
	100	60.1	307	0.815	124.03	97.37

chloride ions and water molecules possess higher dipole moment than inhibitor molecules[26]. The values of inhibition obtained in electrochemical studies are completely in accord with those obtained in gravimetric studies.

Figure 2 depicts the variation of absolute value of impedance and phase angle with frequency. At the lower value of frequency absolute impedance increased with increasing concentration of the PKLE. At intermediate frequencies the phase angle value at the maxima gradually changes to higher values with increasing concentration. Both of these facts corroborate the findings obtained in Nyquist Plot. Single time constant is observed both in Figure 2 and in Fig. 1(b).

Activation energy

Apparent activation energy of the corrosion process was obtained by plotting the logarithm of corrosion rate (C_R)obtained in weight loss study against $1/T$ where T is absolute temperature. This plot was obtained at different concentrations of PKLE used in this study. Figure 3 show that these plots gave straight lines. The corresponding slope of the straight lines are the measure of activation energy (E_a) of the corrosion process according to the following Arrhenius equation,

$$logC_R = -\frac{E_a}{2.303RT} + \log A \qquad ...(8)$$

where A is a pre exponential factor. Table 4 shows that E_a decreased in presence of PKLE. Decrease in activation energy in presences of inhibitor was ascribed to chemical adsorption in literature[8,27]. Therefore, in the present investigation it can be said that chemical adsorption has same contribution to the overall adsorption of PKLE on mild steel surface.

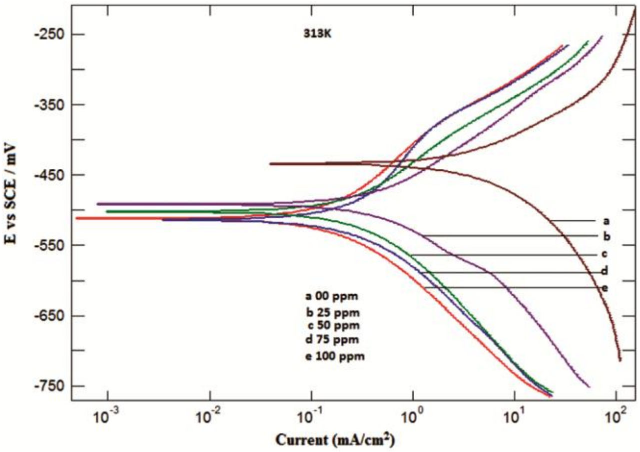

Fig.S2 — Potentiodynamic polarization curves for mild steel in 1 M HCl in presence of PKLE at 313K.

Adsorption isotherm study

It is believed that adsorption of inhibitor molecules on metal surface is responsible for their corrosion inhibitory properties. Therefore, different adsorption isotherms were tried to fit the data. When concentrations of inhibitor (C) were plotted against C/θ(θ= surface coverage) straight line were obtained (Fig. 4) with slope values ranging from 1.0127 to 1.0176 and correlation coefficients values very close to unity. These straight lines represent the following equation

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \qquad ...(9)$$

where, K_{ads} stands for equilibrium constant for the adsorption process. This confirms that PKLE molecules follow Langmuir adsorption isotherm for mild steel surface in 1.0 M HCl medium[28]. The values of thermodynamic parameters in this adsorption process are given in Table 5. The free energy of adsorption (ΔG_{ads}) was calculated from the value of equilibrium constant given in Table 5 using the following equation[27]

$$\Delta G_{ads} = -RTln(10^6 K_{ads}) \qquad ...(10)$$

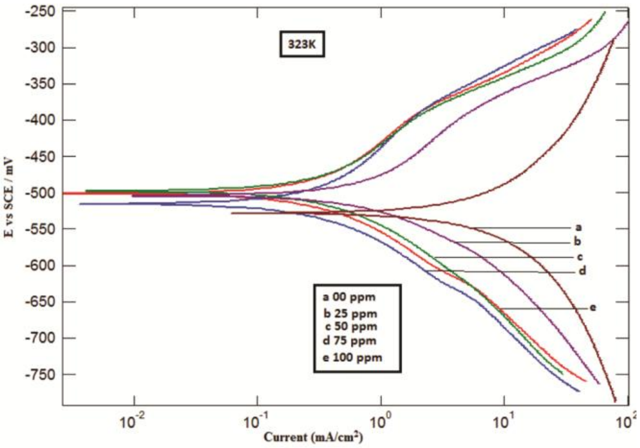

Fig.S3 — Potentiodynamic polarization curves for mild steel in 1 M HCl in presence of PKLE at 323K.

Table 4 — Apparent Activation Energy for corrosion in presence and absence of different concentration of PKLE

Inhibitor Conc (ppm)	E_a (kJ mol^{-1})
0	41.840
25	28.528
50	33.228
75	32.865
100	36.412

Table 5 — Thermodynamic parameters of adsorption PKLE over mild steel surface

Temperature(°K)	R^2	K_{ads}(Lmg^{-1})	$-\Delta G^0_{ads}$(kJmol^{-1})	$\Delta H°$(kJmol^{-1})	$\Delta S°$(Jmol^{-1}K^{-1})
293	0.9999	3.50×10^{-1}	31.09	8.11	134.40
303	0.9998	4.62×10^{-1}	32.85	8.11	134.40
313	0.9999	4.82×10^{-1}	34.05	8.11	134.40
323	0.9999	4.88×10^{-1}	35.17	8.11	134.40

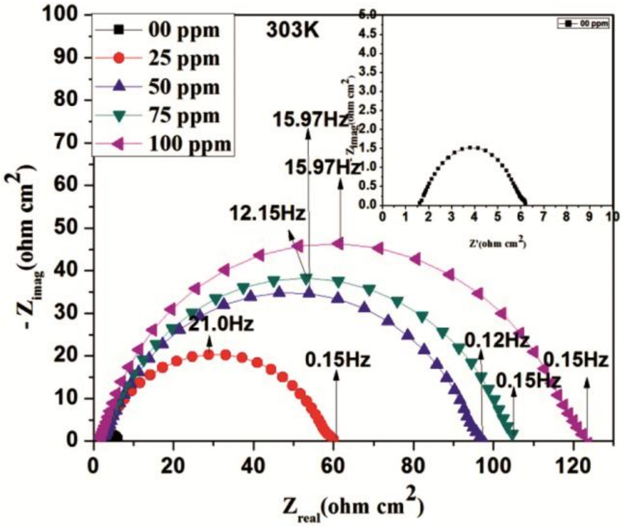

Fig.S4 — Nyquist plots for mild steel in 1M HCl in presence of PKLE at 303K.

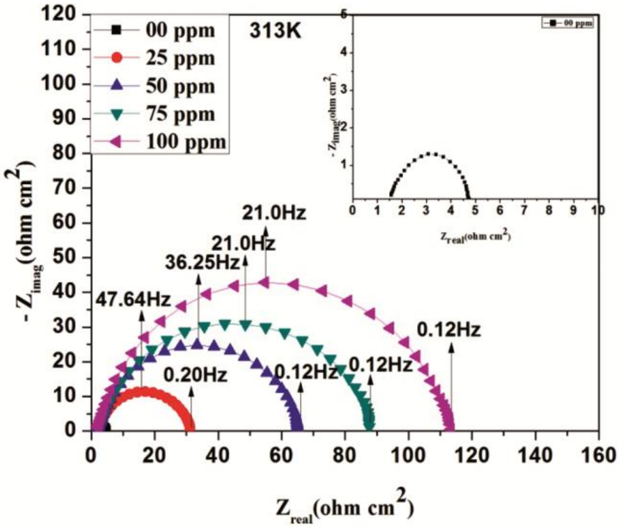

Fig.S5 — Nyquist plots for mild steel in 1M HCl in presence of PKLE at 313K.

where R is universal gas constant, T is temperature in absolute scale and 10^6 mg L^{-}1 was incorporated as the concentration of water. At a temperature of 293 K, ΔG_{ads} has the value -31.09 kJmol^{-1}. The negative free energy is indicative of spontaneous process. It had been reported that if ΔG_{ads}corresponds to -20 kJmol^{-1} or less negative the process is controlled by week electrostatic interaction (physical adsorption)[29]. On the other hand a value of -40 kJmol^{-1} or more negative corresponds to chemical adsorption resulting from reciprocal orbital interaction between inhibitor and metal atom (coordinate bond)[30]. At 293 K, ΔG_{ads} has the value -31.09 kJmol^{-1} which indicates that adsorption of PKLE molecules on metal surface is controlled by both physical and chemical adsorption[31]. Corresponding values of enthalpy (ΔH_{ads}) were obtained from the slope when lnK_{ads} values were plotted against $1/T$according to the following equation

$$lnK_{ads} = \frac{-\Delta H_{ads}}{RT} + D \qquad \text{... (11)}$$

where, D is integration constant. Values of enthalpy of adsorption suggest that the adsorption process is endothermic in nature[32]. Entropy of adsorption (ΔS_{ads}) was calculated using the following equation,

$$\Delta S_{ads} = \frac{\Delta H_{ads} - \Delta G_{ads}}{T} \qquad \text{... (12)}$$

Positive sign of ΔS_{ads} is again in conformity with the spontaneous adsorption process. The positive sign associated with ΔS_{ads} points to the fact that adsorption of PKLE molecules is associated with desorption of water molecules and the number of desorbed water molecules are greater than the number of adsorbed PKLE molecules. This is possible only when the inhibitor molecules because of their large size covers the metal surface forming a thin film by replacing greater number of small water molecules from that metal surface[33]. It is seen in Table 5 that with progressive increase in temperature ΔG_{ads} becomes more negative. This trend is again in agreement with contribution of chemical adsorption in the overall process[34].

Scanning Electron Microscopic Study (SEM)

The surface structure of mild steel coupons in absence and presence of inhibitor in 1.0 M HCl solutions was studied. The corresponding SEM micrographs are shown in Figure 5. It is understood from the images that in 1.0 M HCl solution the mild steel surface was damaged significantly with the formation of several pits and corrosion products. In presence of inhibitor the surface of metal became more smooth with the formation of insignificant amount of corrosion products. Therefore, it can be said that PKLE molecules protected the mild steel surface in 1.0 M HCl medium. This is due to the formation of a protective film of PKLE molecules on mild steel surface as a result of adsorption.

Chemical Structure determination of PKLE molecules

The amount of carbohydrate contain in PKLE is 90%, total phenolics contain (TPC) in PKLE is 10 g/100 g GAE and total anthocyanin content is7 mg/LCy-3-glc equivalents. Therefore, carbohydrates are the most significant component of PKLE. Gas chromatographic analysis was carried out to find out the monosaccharide composition of PKLE (Figure 6(a)). It was found that D-mannose is the most abundant monosaccharide followed by D-glucose and D-galactose (Table 6). FT-IR spectrum in Figure 6(b) indicates the presence of large number of –OH groups (broad band around 3434 cm^{-1}), carboxylic acid moieties attached to the monosaccharide in the form of uronic acid (strong and sharp C=O stretching frequency at 1739 cm^{-1}), -CH bonds (2936 cm^{-1}), C=C and carbonyl groups attached to conjugated environment like aromatic rings (1628 cm^{-1}). Bands at 1407 cm^{-1} , 1240 cm^{-1}and 1096 cm^{-1} in the IR spectrum are due to –CH_2 bending, framework vibration of aromatic ring and C-O stretching vibrations respectively[8]. It should be kept in mind that IR spectroscopy indicates only the presence of functional groups in a qualitative way but not in the quantitative sense.

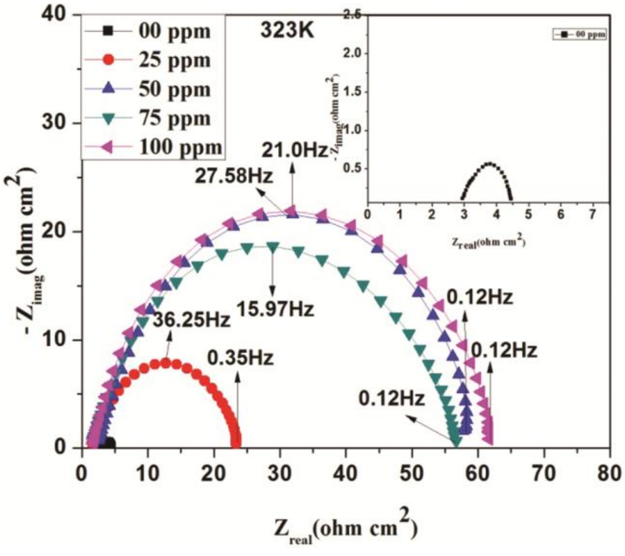

Fig. S6 — Nyquist plots for mild steel in 1M HCl in presence of PKLE at 323K.

Table 6 — Monosaccharide composition of PKLE

Monosaccaride	Mole Percentage
Glucose	21.44
Galactose	14.28
Mannose	64.28

Mechanism

Plant extract consist of chemical composition of complex nature. Therefore proposing a mechanism for corrosion inhibition by plant extract is difficult task. Since carbohydrates were found as major chemical constituent of PKLE, it can be assumed that carbohydrates are responsible for exerting inhibition behaviour. Inhibition studies and isotherm analysis indicate that both physical and chemical adsorption contribute to the overall adsorption process. Metal surface becomes negatively charged in 1.0 M HCl medium because of adsorption of Cl$^-$ on it. In acidic medium some of the hydroxy groups of polyhydroxylated carbohydrate and anthocyanin molecules remain protonated. Therefore, an electrostatic attraction generates between metal surface and PKLE molecules. When these inhibitor molecules are in sufficient proximity to the metal atoms nonbonding electrons of inhibitor molecules are transferred to the lower lying vacant orbitals of metal atom. The electron rich orbitals of metal then donate electrons to the antibonding orbital of inhibitor molecule (Fig. 7). A thin layer of PKLE molecules is formed because of these physical and chemical interactions. This adsorbed layer of inhibitor molecules serves as a physical obstruction to the corrosive medium leading to the protection of mild steel surface.

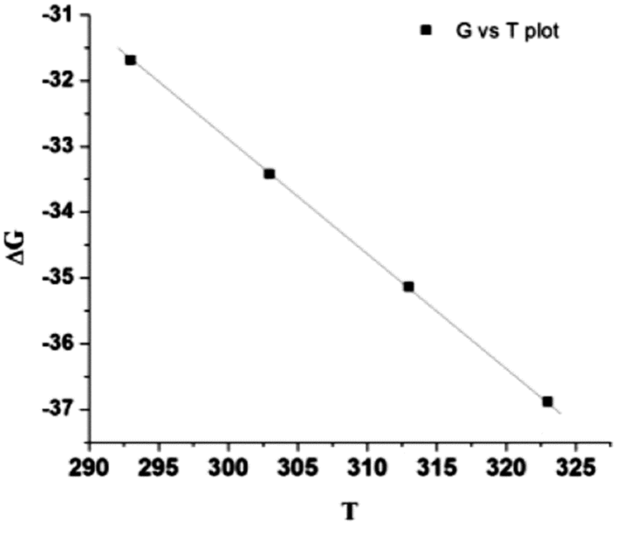

Fig. S7 — Plot of free energy of activation against absolute temperature.

Conclusion

Purple Knight Plant extract is found to act as an efficient green corrosion inhibitor for mild steel in 1.0 M HCl solution. Electrochemical studies show that PKLE has the property of mixed inhibitor. Adsorption of PKLE molecules on metal surface obeys Langmuir adsorption isotherm. Both of free energy of adsorption and entropy of adsorption suggest spontaneous adsorption of PKLE molecules on mild steel surface. Increasing concentration of inhibitor as well as temperature leads to increase in efficiency. Adsorption studies and electrochemical investigation indicate that both electrostatic interaction and orbital interaction contribute to the overall adsorption. SEM images proved the protection of mild steel surface as a result of adsorption of PKLE molecules on mild steel surface.

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