Corrosion Inhibition of Mild Steel by Extract of Bryophyllum Pinnatum Leaves in Acidic Solution

Dakeshwar Kumar Verma
Department of Chemistry, National Institute of Technology Raipur, Raipur, 492010 CG, India
Email-id: dakeshwarverma@gmail.com

Fahmida Khan*
Department of Chemistry, National Institute of Technology Raipur, Raipur, 492010 CG, India
*Email-id: fkhan.chy@nitrr.ac.in

Abstract
Bryophyllum pinnatum leaves extract has been evaluated as mild steel corrosion inhibitor in 0.5 M HCl solution by gravimetric analysis and Scanning electron microscope techniques. Effect of temperature and inhibitor concentrations on the corrosion behaviour of mild steel were studied and found that inhibition efficiency increases as inhibitor concentration increases but decreases as the temperature increases. The activation energy and thermodynamic parameters were studied, results direct that corrosion process involve the exothermic process and adsorption of inhibitor molecules follows the physical adsorption on metal surface. Linearity of Langmuir adsorption isotherm shows the formation of monolayer over the metal surface by deposition of inhibitor molecules. SEM analysis reveal the smooth surface which indicate the protective adsorption of inhibitors molecules on metal surface. The results reveal that the extract of bryophyllum pinnatum act as an effective corrosion inhibitor for the mild steel corrosion in 0.5 M HCl medium.
Keywords: Adsorption, Corrosion, SEM, Weight loss

1. Introduction

Many acidic solutions such as sulphuric acid, hydrochloric acid and phosphoric acid are extensively used in chemical industries during the acid pickling, acidic cleaning and petrochemical process. These industrial process lead to serious impairment of the metals and there alloys [1]. Mild steel is broadly used in various industries due to its strength, tensile, and good physical property. It is very liable towards the corrosive solutions used in industries during the various process. Therefore use of corrosion inhibitors are highly encouraged for protection of metals from corrosion [2]. A great number of scientific studies have been reported for the metal corrosion and their prevention [3, 9]. Various reports reveal that inhibitor molecules adsorbing on the metal surface and prevent from the corrosion in corrosive solutions [3.6]. Adsorption mostly described by chemisorption and physisorption interaction between metal surface and inhibitor molecules [3]. Many synthetic inhibitors were studied under the anticorrosive action, but most of them showed adverse effect like kidney damage, disturb an enzyme system and biochemical process on human being [2]. Study of natural plants as green corrosion inhibitors are highly acceptable because these are eco-friendly, cheap, non-toxic and easily available. A. ostovari et al. [2] studied henna extract as mild steel corrosion in hydrochloric acidic solution and showed that maximum inhibition efficiency (92.06%) obtained at 1.2 g/L inhibitor extract. Punita mourya et al. studied marigold flower as mild steel corrosion inhibitors in sulphuric acid media [12]. In the present study Bryophyllum pinnatum leaves was selected as mild steel corrosion inhibitor. Bryophyllum pinnatum belongs to the Crassulaceae family including many common names miracle plant, air plant, life plant, and resurrection plant etc. it is extensively distributed in many parts of the world because of its easy cultivation. Flavonoids, tannins, alkaloids, saponins and many vitamins like riboflavin, thiamine, and ascorbic acid are the main phytoconstituents of the leaves [21, 23]. It is used as folk medicinal plant in many countries, these property include anti-inflammatory, antidiabetic, anti-tumour, antimicrobial, sedative, muscle relaxant, analgesic, and antiulcer etc. [21, 23].

In this paper the corrosion behaviour of bryophyllum pinnatum leaves extract was studied by weight loss method and SEM techniques. Thermodynamic and kinetics parameters are also employed for the study of corrosion mechanism.

2. Experimental

2.1. Materials preparation

The coupons were cut into 5 x 2 x 0.1 cm sizes from steel sheet and used for weight loss measurements and surface Analysis. Before the measurements, the surface of mild steel were successfully abraded using different grades of SiC papers. The metal electrode surface was cleaned by washing with double distilled water and degreased in acetone respectively dried in desiccators and weighted. Weight loss measurement done at different temperatures (298-328 K) and inhibitor concentrations respectively. 0.5 M HCl corrosive solution is prepared by analytical grade HCl with double distilled water in the absence and presence of different concentrations of inhibitors ranging from 2-8 g/L.

2.2. Inhibitor preparation
Bryophyllum pinnatum leaves were collected and thoroughly washed with double distilled water to remove dust and soils then allowed to shade dried for few days. The dried leaves were ground to fine powder and weighed 10 g for reflux in one litre of 0.5 M HCl solution for 4 hours then allow to stand overnight for complete extraction. Next day it was filtered and filtrate was made up to one litre by using the 0.5 M HCl solution. This solution were used as inhibitive solution for all the measurements.

2.3. Gravimetric measurements
For weight loss measurement, the specimens of 5 x 2 x 0.1 cm size were used and each experiment was carried out in a 100 ml beaker. The polished mild steel coupons were weighed and suspended in the test solution in the presence and absence of inhibitor for different temperatures and inhibitor concentrations for 24 h than specimens were taken out dried and weighed with the help of metteler Toledo AL204 electronic balance, Accuracy in weighing up to 0.0001 gm. In the total weight loss the mean value has been reported in each case.

2.4. Surface analysis
For SEM analysis mild steel specimen were first immersed in 0.5 M HCl solution in the absence and presence of inhibitor for 24 h. The surface morphology of mild steel specimens was examined by using scanning electron microscope ZEISS EVO SEM 18 model, oxford.

3. Results and discussion
3.1 Weight loss measurements
The inhibition efficiency (*%I*) and corrosion rate (ρ) with different concentrations of bryophyllum pinnatum for mild steel in 0.5 M HCl solution at temperature ranging from 298-328 K are given in table 1. It is observed that inhibition efficiency increases as bryophyllum pinnatum extract concentration increases, whereas inhibition efficiency decreases as temperature decreases. The minimum and maximum inhibition were observed at 94.27 at 298 K and 71.34 at 328 K respectively. The corrosion rate (ρ) was calculated from the equation given below [1]:

$$\rho = \Delta W/At \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

Where ΔW is the weight loss in mg, A is the total area of metal specimen in cm^2, and t is the immersion time (24 h).with the calculated corrosion rate Inhibition Efficiency (*%I*) was calculated by using the following equation [1]:

$$\%I = \left(\frac{\rho1-\rho2}{\rho1}\right) \times 100 \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

Where ρ1 and ρ2 are the corrosion rates of the mild steel specimens in the absence and presence of inhibitor, respectively. The degree of surface coverage (θ) was calculated as given

$$\theta = \frac{\%I}{100} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$

Table 1
Corrosion parameters obtained from weight loss results of mild steel in 0.5 M HCl at various temperatures for 24 h immersion time in the presence and absence of different concentrations of bryophyllum pinnatum extract.

T (*K*)	Conc. (*g/L*)	Corrosion rate (ρ)	% *I*
298	blank	2.077	-
	2	0.200	90.37
	4	0.172	91.71
	6	0.156	92.49
	8	0.119	94.27
308	blank	2.803	-
	2	0.463	83.48
	4	0.402	85.65
	6	0.238	91.51
	8	0.161	94.25
318	blank	3.736	-
	2	0.674	81.95
	4	0.651	82.57
	6	0.607	83.75
	8	0.466	87.53
328	blank	4.532	-
	2	1.299	71.34
	4	1.098	75.78
	6	0.967	78.66
	8	0.959	78.83

The inhibition efficiency with various concentrations of inhibitors at different temperature show in fig.1 and it is evident that inhibition efficiency increases as concentration increases but decreases as temperature increases.

3.2. Adsorption and thermodynamic consideration

Adsorption isotherms explained the mechanism of the interaction between inhibitor molecules and the metal surface [1]. Many adsorption isotherms Langmuir, Frumkin, Temkin and Flory-huggins were tested for the best fit and it is observed that adsorption of Bryophyllum pinnatum extract on metal surface follows the Langmuir adsorption isotherm. Usually physisorption or Chemisorption phenomenon attributing to Langmuir adsorption, the Langmuir adsorption isotherm is given by [9]:

$$\frac{C}{\theta} = \frac{1}{\mathrm{Kads}} + C \qquad \text{…………………. (4)}$$

Where θ is the surface coverage, K_{ads} is adsorptive equilibrium constant, and C is the equilibrium inhibitor concentration. K_{ads} values were calculated by the intercepts of straight lines plot of C_{inh}/θ versus C_{inh} [1].The fitting of the experimental data were determined by using the correlation coefficient r^2 to best fit the unique isotherm [1]. With the help of the K_{ads} values the free energy of adsorption, ΔG_{ads} can be calculated using the following formula and corresponding results are listed in table 2 [1,20].

$$\Delta G_{ads} = -RT\ln(55.5K_{ads}) \qquad \text{…………………. (5)}$$

Where R is gas constant, T is temperature, and K is the binding constant. Generally speaking, that the negative values of ΔG_{ads} values indicate the strong and stable interactions between the inhibitor molecules and the mild steel surface and involve the spontaneous process [3, 7]. It has been observed as the negative value of ΔG_{ads} increases, the effectiveness of corrosion inhibition also increases [7]. Usually, the standard free energy of adsorption values of around -40 kJ mol^{-1} or higher involves charge transfer or sharing between inhibitor molecules and metals shows the chemical adsorption those of -20 kJ mol^{-1} or less negative values are associated with electrostatic interaction (physisorption) [1, 3, 7]. Therefore for present study the calculated values of ΔG_{ads} mol^{-1} has been considered less negative values then-20 kJ mol^{-1} indicating that the adsorption of inhibitor is physical adsorption [3]. The kinetic- thermodynamic model is given by the following equation [14]:

$$\log[\theta/(1-\theta)] = \log K' + y\log C \qquad \text{……………………. (6)}$$

Where θ the surface coverage, C the concentration and y is the number of inhibitor molecules occupying one site. Here the binding constant is expressed as $K = K'^{(1/y)}$. Linear fitting kinetic- thermodynamic model of bryophyllum pinnatum extract show in fig 3, and parameters shown in Table 3. Plot between log (θ / (1 - θ) vs. log C at all studied concentrations of inhibitor and temperatures gives the straight line fit. Larger value of binding constant K, indicated the strong and stable interaction between inhibitor molecules and metal surface [9].

Table 2
Thermodynamic parameters for the adsorption of bryophyllum pinnatum leaves extract in 0.5 M HCl on the mild steel surface after 24 h immersion time at different temperature.

T (*K*)	R^2	k_{ads} (L mol^{-1})	ΔG_{ads} (kJ mol^{-1})
298	0.999	6.66	-11.79
308	0.997	2.05	-09.45
318	0.997	3.39	-10.41
328	0.999	2.75	-10.03

Table 3
Linear fitting parameters of bryophyllum pinnatum leaves extract to kinetic-thermodynamic model.

T (K)	R^2	*1/y*	*K*
298	0.710	3.174	621.0
308	0.794	1.200	2.945
318	0.512	3.690	103.3
328	0.955	3.246	9.957

3.3. Effect of temperatures
Values of apparent energy provide the further evidence concerning the corrosion protection mechanism of inhibitor on the metal surface in their presence and absence at dependent temperatures. For the corrosion mechanism the activation energy Ea was calculated from the Arrhenius plot according to the following equation [1].

$$\log \rho = \log A - \left(\left(\frac{Ea}{2.303RT} \right) \right) \quad \text{.......................... (7)}$$

Where ρ is the corrosion rate, *E*a is the apparent activation energy, *R* is the gas constant, *A* is the constant and *T* is the absolute temperature. From weight loss measurement (table 1) corrosion rate values obtained for mild steel in the presence and absence of inhibitor at different concentrations and temperatures [3]. Fig. 4 shows the plot of log ρ versus 1000/*T* for the mild steel corrosion in the presence and absence of inhibitor at different concentrations and parameters were given in the table 4 [4]. By applying the transition state equation the enthalpy of activation (ΔH^*) and the entropy of activation (ΔS^*) were obtained for the corrosion of mild steel. The transition state equation is given as [1, 2]:

$$log\left(\frac{\rho}{T}\right) = \left[\left(log\ \left(\frac{R}{Nh}\right)\right) + \left(\frac{\Delta S^*}{2.303}\right)\right] - \frac{\Delta H^*}{2.303RT} \quad \text{.......................... (8)}$$

Where ΔH^* is the enthalpy of activation, ΔS^* is the entropy of activation, *h* is the plank constant, and *N* is the Avogadro's number. The values of ΔH^* enthalpy of activation and ΔS^* entropy of activation calculated from the plot of log (*ρ/T*) versus 1000/*T* and the values of ΔH^* and ΔS^* given in table 4 [2]. The values of apparent energy is greater in the presence of inhibitor and lower in inhibited solution at different concentrations. Activation energy increases from 38.50 to 80.99 kJ mol^{-1} by the addition of bryophyllum pinnatum extract up to 8 g/L. the results reveal that addition of inhibitor decreases the metal dissolution due to the formation of the stable metal complex layer in acidic solution [2]. Activation energy values around 40-80 kJ mol^{-1} suggested to obey the physisorption. Positive value of ΔH^* suggested that the corrosion mechanism involves the exothermic process hence it needs more energy to achieve equilibrium or activation state [20].

Table 4
Activation parameters *E*a, ΔH^* and ΔS^* of the dissolution of mild steel in 0.5M HCl in the absence and presence of different concentration of bryophyllum pinnatum leaves extract.

Conc. (g/L)	Ea (kJ mol-1	ΔH^* (kJ mol^{-1})	ΔS^* (kJ mol^{-1})
Blank	38.50	18.78	-21.13
2	84.03	46.18	-12.36
4	85.09	46.68	-12.49
6	83.16	49.39	-11.44
8	80.99	56.67	-08.89

3.4. SEM Analysis
Fig 6 shows the SEM images of mild steel specimen surface in the absence and presence of bryophyllum pinnatum extract in 0.5 M HCl solution [2]. SEM analysis of micrographs in fig 6b reveal the damage and rough surface in the absence of inhibitor solution for 24 h of immersion period. However fig 6c exhibit the smooth

surface compare to fig 6b clearly indicates the protective adsorption of inhibitors molecules on metal surface [24].

4. Conclusion

Bryophyllum pinnatum extract exhibit the mild steel corrosion inhibitor property in 0.5 M HCl solution. Weight loss measurement indicated that inhibition efficiency increases as inhibitor concentrations increases but decreases as temperatures increases. Inhibition efficiency studied at temperatures 298-328 K and inhibitor concentrations of 2-8 g/L in 0.5 M HCl solution. The adsorption of bryophyllum pinnatum extract obey the Langmuir isotherm and values of free energy of adsorption indicates the physical adsorption process of inhibitor molecules on the metal surface. From the values of activation energy and thermodynamic parameters it is evident that corrosion process involve the exothermic process. SEM micrographs shows the formation of protective layer over the metal surface.

Acknowledgement
Authors are greatly thankful to Ministry of Human Resource Development (MHRD) and Govt. of India for financial support.

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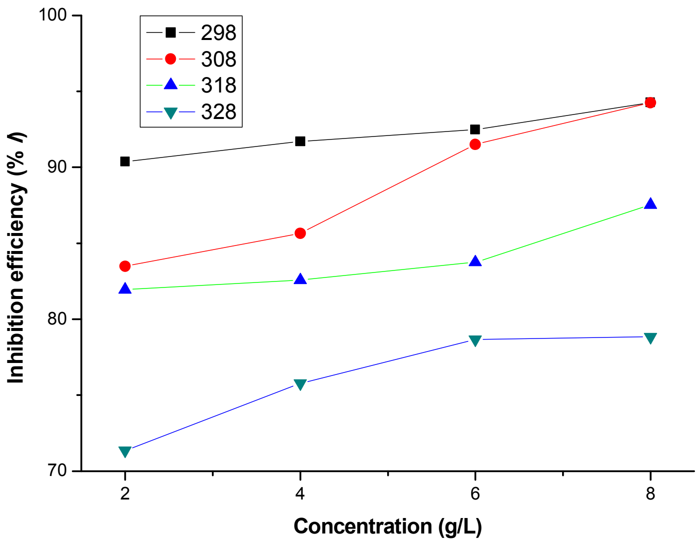

Fig. 1. The relationship between inhibition efficiency and inhibitor concentrations at different temperatures.

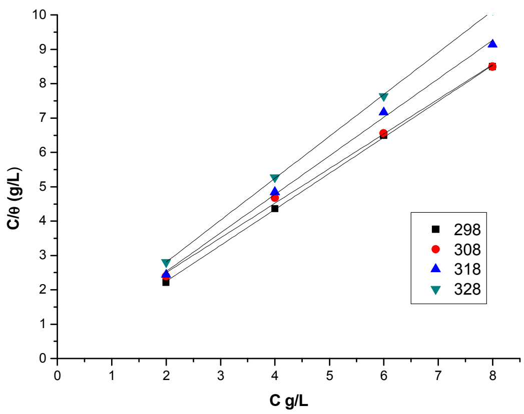

Fig. 2. Linear fitting of bryophyllum pinnatum leaves extract to Langmuir adsorption isotherm at different temperature.

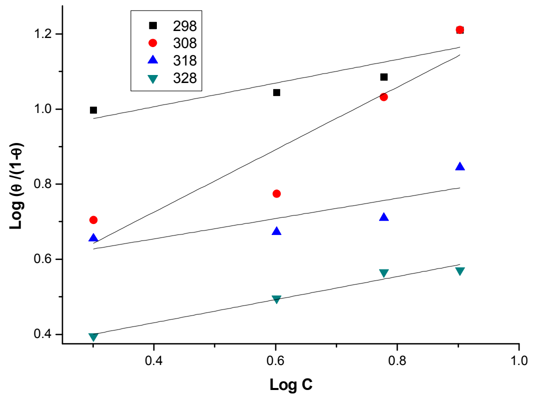

Fig. 3. Linear fitting of bryophyllum pinnatum leaves extract to kinetic-thermodynamic model at different concentrations and temperature.

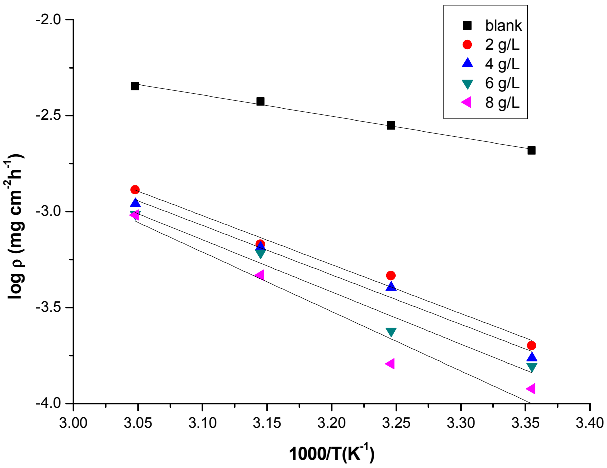

Fig. 4. Arrhenius plot for mild steel corrosion rates in 0.5 M HCl in the absence and presence of different concentrations of inhibitor at temperature 298-328 K.

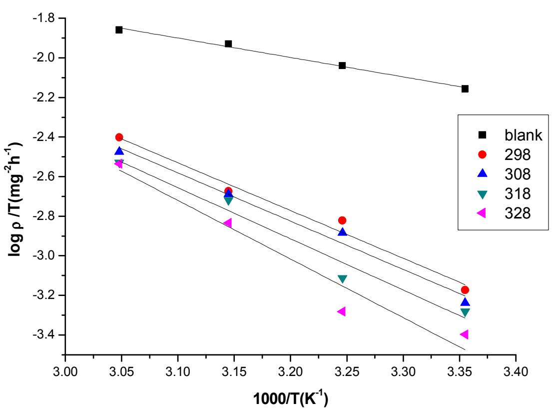

Fig. 5. Transition state plot for mild steel corrosion rates in 0.5 M HCl in the absence and presence of different concentrations of inhibitor at temperature range 298-328 K.

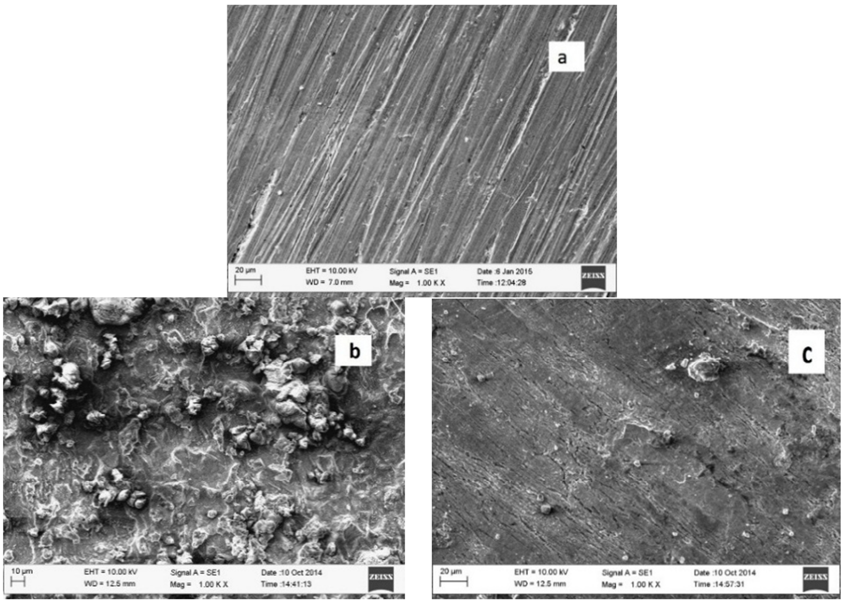

Fig.6. SEM images of (a) mild steel (b) mild steel in 0.5 M HCl, and (c) mild steel in the presence of inhibitor for 24 h period.