INTERNATIONAL JOURNAL OF PHARMACEUTICS & DRUG ANALYSIS

VOL.6 ISSUE 2, 2018; 180 – 185 ; http://ijpda.com; ISSN: 2348-8948

MEDFOOD'18 [1st February 2018]

National Conference on Phytochemicals in Medicinal Plants and Food

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Research Article

INHIBITION POTENTIAL OF PLANT EXTRACT OF *POLYCARPAEA CORYMBOSA*

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Date Received: 23rd January 2018; Date accepted: 29th January 2018; Date Published: 17th February 2018

Abstract

Adsorption and thermodynamics study of the inhibition of corrosion of mild steel in 1 M HCl medium using the plant extracts *Polycarpaea Corymbosa* (PC) was carried out. The inhibitive and adsorptive properties of ethanol extract of PC was investigated using weight loss technique by varying concentration inhibitor at two different temperatures. The adsorption behavior of the plant extracts on mild steel specimen was analyzed using Langumuir and Tempkin isotherm. The elemental analysis and pattern of adsorption of the inhibitors molecules to the metal surface were visualized through EDS studies. In addition, the phytochemical screening and biological activity were evaluated.

Keywords: Mild steel , EDS ,*Polycarpaea Corymbosa* (PC).

INTRODUCTION

The choice of mild steel for different industrial needs such as fabrication of vessels, pipes and reaction tanks is due to its unique qualities such as excellent formability, inexpensiveness and easy availability. Acids such as HCl and H_2SO_4 are widely used for various industrial processes such as acid pickling, cleaning and rescaling of steel [1,2]. During such industrial processes, mild steel suffers from severe corrosion in acid media. Hence, the industrial sectors do take preventive actions against corrosion. The cost involved in corrosion control is very high. For example, in India the economic loss incurred through corrosion is about 6.1 percent Gross National Product (GNP) and it worked out to be nearly Rs. 80,000 crore per annum [3]. Various methods employed towards corrosion prevention [4,5]. The most economical and practical method for reducing corrosive attack of metals in acid medium [6,7] is to use inhibitors. Inhibitors have a unique feature that they can be added to the acid media and they stay unaffected in acid. But, they continue to prevent corrosion from its early stage. These inhibitor compounds act by getting adsorbed on to the metal surface and thereby retarding metal dissolution [8]. The inhibitors are of natural or synthetic origin. The synthetic inhibitors are effective in preventing corrosion of metals and alloys in acid media. But, many of the synthetic inhibitors are toxic and harmful to man and other living systems [9]. They affect the flora and fauna of the eco system also. Hence, there is a critical need for finding an alternate to synthetic inhibitors.

The main objectives of this present work were evaluation of the equilibrium sorption data using the suitable adsorption isotherm such as Langmuir and Temkin isotherm. The adsorption behavior of inhibitor molecules on the metal surface were examined by using spectroscopic methods of Energy Dispersive X-ray Spectroscopy (EDS). Further phytochemical screening and antimicrobial activity were evaluated by using standard method.

MATERIALS AND METHODS

Plant Extract Preparation

The plant materials were collected, identified and authenticated by the Rapinat Herbarium, St. Joseph's College (Autonomous), Tiruchirappalli, Tamil Nadu, India. The fresh plants were dried, crushed and then soaked in ethanol for 3 – 4 days by cold-percolation method[10,11]. The ethanolic extracts were concentrated by distillation. Then various concentrations of the plant extract were taken for the corrosion study first. The concentrated extracts were subjected to phytochemical screening test and anti-microbial activity were evaluated by using paper disc diffusion method against two bacteria and fungi. The microbes were obtained from microbial type collection center, Chandigarh, India.

Specimen Preparation

Mild steel specimens containing C = 0.10%, Mn =0.34%, Cr = 0.22% and Fe = 99.34% were used for the study .The MS specimen of 2.5 cm × 2.0 cm × 0.06 cm were abraded by a series of emery papers (1/0, 2/0, 3/0 and 4/0 grade) and then washed with distilled water and degreased with acetone. Thus, the specimen prepared were taken for the present study.

Experimental Methods

Adsorption Isotherm

The experiment was carried out by varying concentrations of inhibitor (100, 200, 300 and 400 ppm) and two different temperatures (298 and 308 K).The Inhibition Efficiency (I.E.%) and surface coverage (θ) were calculated by using the equation 1 and 2.

$$\text{I.E}(\%) = \frac{\Delta W_0 - \Delta W_1^{'}}{\Delta W_0} \times 100 \quad \text{(Eq 1)}$$

$$\theta = \frac{\text{I.E}(\%)}{100} \quad \text{(Eq 2)}$$

ΔW_0 and $\Delta W_1^{'}$ difference of the initial and final weight of the mild steel specimen in the absence and presence of the inhibitor.

From the surface coverage (θ) values were tested graphically for two different adsorption isotherms such as Langmuir and Temkin isotherms using the following equations 3and 4.

$$K = \frac{\theta}{1-\theta} \times \frac{1}{C} \quad \text{(Eq 3)}$$

$$K_{ads} C = e^{f\theta} \quad \text{(Eq 4)}$$

Where θ - degree of coverage on the metal surface , C - concentration of inhibitor, f - constant factor for the slope and K_{ads} - adsorption constant at equilibrium. The calculation of K_{ads} from the Langmuir plot(ln (θ /1-θ) Vs ln C) and Temkin plot (θ Vs ln C).

From the Langmuir and Temkin plots the free energy of adsorption ΔG_{ads} was calculated by using the following equation 5.

$$\Delta G_{ads} = -RT\ \text{In}(55.5\ K_{ads}) \quad \text{(Eq 5)}$$

where R is the gas constant (8.314 J K^{-1} mol^{-1}) and T is the temperature and the constant value of 55.5 represents the concentration of water in solution in mol/dm^3. Other thermodynamic functions enthalpy of adsorption (ΔH_{ads}) and entropy of adsorption (ΔS_{ads}) were calculated by the following equations 6 and 7 .

$$\ln (K1_{ads}/K2_{ads}) = \Delta H_{ads}/R(1/T2-1/T1) \quad \text{(Eq 6)}$$

$$\log (K_{1ads}/K_{2ads}) = \Delta H_{ads}/R\ 2.303\ (1/T2-1/T1)$$

$$\Delta S_{ads} = (\Delta H_{ads} - \Delta G_{ads})/T \quad \text{(Eq7)}$$

Energy Dispersive Spectroscopy (EDS)

The elemental analysis of the specimen was examined by the Hitachi S3 400 N Scanning Electron Microscope (SEM) attachment of Energy Dispersive Spectroscopy (EDS), CECRI- Karaikudi, Tamilnadu, India.

RESULT AND DISCUSION

Adsorption Isotherm

The results of inhibition efficiency, surface coverage were presented in Table 1. The effect of temperature on the performance of the inhibitors PC clearly indicated that the inhibition efficiency decreases with increase in temperature. It was noted that surface coverage decreases with increase in temperature. Higher the surface coverage greater the adsorption and lower the surface coverage greater the desorption at any given temperature, the adsorption and desorption were taking place continuously. Both these phenomena were said to be in a dynamic equilibrium. Temperature raise would favor desorption more than the adsorption. Thus, the dynamic equilibrium shifted towards the desorption side more than the adsorption side. This trend would reflect on the corrosion of the mild steel. It explains the lower inhibition efficiency at higher temperature. Hence, the studied inhibitors PC exhibited maximum inhibition efficiency of 84.55% at the temperature of 298 K in 1 M HCl solution of 400 ppm. This suggests that the acceleration in corrosion rate and weakening of bonding forces between the inhibitors and mild steel surface. Further, when the temperature was increased the metal surface remained uncovered for longer duration resulting in increase in corrosion. This suggests that the inhibitors provide a complete protective action on the metal surface effectively at 298 K [12-15].

From the surface coverage (θ) values the various thermodynamic parameters such as Gibbs free energy (ΔG_{ads}), enthalpies of adsorption (ΔH_{ads}) and entropy of adsorption (ΔS_{ads}) were obtained from the Langmuir and Temkin plots 1 and 2.

The results of thermodynamic parameters are presented in the Table 2 for four different concentrations 100, 200, 300 and 400 ppm of inhibitors at two different temperatures (298 and 308 K).

The negative values of free energy of adsorption ΔG_{ads} indicated that the adsorption of the inhibitors PC on the mild surface was a spontaneous process [16]. It was due to the strong interaction between inhibitor molecules and metal surface. The magnitude of ΔG_{ads} around −20 kJmol^{-1} or less could be attributed to the physisorption of inhibitors molecules to the metal surface. The magnitude of ΔG_{ads} to be around −40 K Jmol^{-1} or higher could be justified to the chemisorption of inhibitor molecules to the metal surface [17].

In the present study the ΔG_{ads} calculated for the inhibitor PC were in the range of −21.17 to −36.74 kJmol^{-1}. It indicated that the adsorption was the mixed type of physisorption and chemisorptions [18] process. The enthalpy of adsorption (ΔH_{ads}) values were observed to be negative for the inhibitors PC. This trend was revealing exothermic nature of the adsorption phenomenon. The negative values of entropy of adsorption (ΔS_{ads}) indicated that the onset of more orderly arrangement of inhibitor molecules PC on the surface of metal during adsorption.

The nature and pattern of adsorption of the inhibitors molecules to the metal surface were visualized through EDS studies.

Table 1.Inhibition efficiency and surface coverage of mild steel for various concentrations of plant extracts at two different temperature

Temperature(K)	100 ppm		200 ppm		300 ppm		400 ppm	
	I .E (%)	θ	I .E (%)	θ	I .E (%)	θ	I .E (%)	θ
298	77.56	0.7756	80.48	0.8048	82.19	0.8219	84.55	0.8455
308	73.86	0.7386	76.86	0.7686	79.57	0.7957	81.98	0.8198

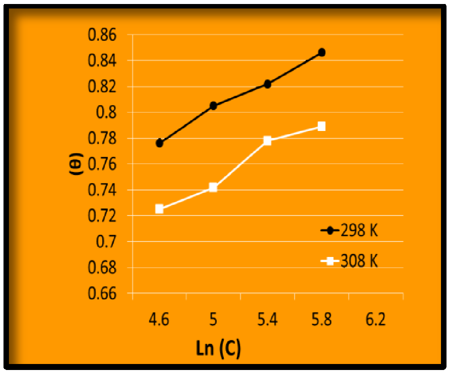


Figure.1. Langmuir plot

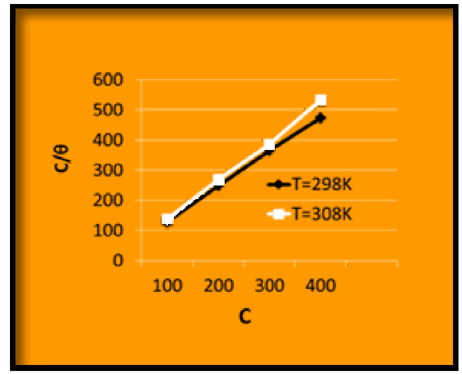


Figure .2.Temkin plot

Table 2 .Thermodynamic parameters for the adsorption of inhibitor PC on mild steel in 1 M HCl at two different temperatures

Langmuir Adsorption isotherm					Temkin Adsorption isotherm		
	T(K)	- ΔG_{ads} (KJ mol^{-1})	-ΔH_{ads} (KJ mol^{-1})	-ΔS_{ads} (J mol^{-1}K^{-1})	- ΔG_{ads} (KJ mol^{-1})	-ΔH_{ads} (KJ mol^{-1})	-ΔS_{ads} (J mol^{-1}K^{-1})
Inhibitor PC	298	32.45	31.36	296.51	36.74	31.74	253.28
	308	26.18			21.17		

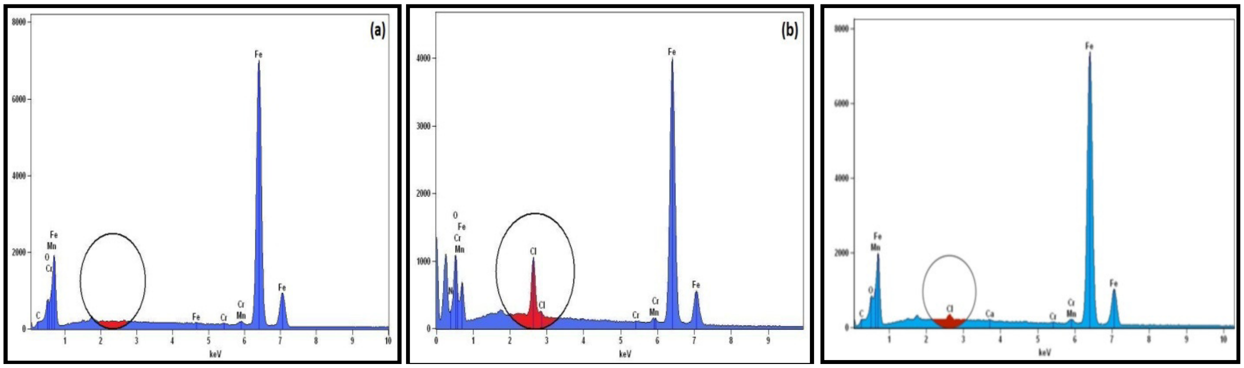
Energy Dispersive Spectroscopy (EDS)

The EDS spectra of the mild steel surface, in the presence of inhibitors and in the blank for 2hrs were observed and given in Figures 3(a), (b) and (c). The atomic percentage of elemental (chloride) are presented in Table 3. From the Figure 3(a) it was observed that chloride peak did not exist in the absence of 1 M HCl solution. But, in the case of mild steel surface in 1 M HCl solution in the absence of inhibitors a very high peak was observed in Figure 3(b) due to aggressive nature of acid medium (HCl). These observations could be explained on the basis of chloride ion (Cl^-) activity and enhanced metal dissolution. The metal dissolution in HCl solutions depended principally upon the chloride ion activity. It was in agreement with results obtained from weight loss method. From the EDS spectra Figures 3(c) of the mild steel in the presence of inhibitors(PC) for the same period of time in 1 M HCl solution very small peaks were observed. It was attributed to the addition of the inhibitors molecules did inhibit the metal dissolution reaction in 1 M HCl. Finally, the adsorption predominately depended upon factors such as the phytoconstients of extract , composition, type of anion of the acid, etc.

Table 3 .Results of EDS analysis of mild steel, mild steel in 1M HCl in the absence and presence of inhibitors

Medium	Atomic percentage of the elements					
	Fe	O	C	Cl	Mn	Cr
Mild Steel (a)	99.34	–	0.10	–	0.34	0.22
Blank (b)	76.73	15.83	-	7.12	0.32	–
Inhibitor (PC)	83.49	3.25	12.15	0.53	0.43	0.15

Figure 3(a), (b)and (c).
EDS spectrum of mild steel , mild steel in 1 M HCl , mild steel in 1 M HCl with PC extract



As seen from the Table 3 the atomic percentage of chloride (7.12%) in blank was significantly high because of Cl^{-} ion activity, more pronounced in 1M HCl solution without inhibitors. But, in the of presence of inhibitors the atomic percentage of chloride remarkably reduced. This suggested that the formation of an adsorption layer by inhibitors molecules blocked the active sites on the metal surface, which effectively protected the metal from corrosion. The possible reason was that the extract PC contained active ingredients of phytoconstituents is rich amount. The atomic percentage of Fe was 99.34% in the mild steel specimen before immersion. It decreased to 76.73% when immersed in 1 M HCl. It indicated the enhanced corrosion of the mild steel. For the mild steel that was immersed in HCl along with inhibitors the percentage of Fe was in the range 83.49 which indicated the corrosion of mild steel was reduced by the inhibitors (PC).

Phytochemical screening and Biological activity

The results of plant metabolites such as alkaloids, glycosides, phytosterols,saponins, phenolics compounds,terpenoids and flovonoids, proteins and amino acids were tested positively in the plants extracts of *Polycarpaea corymbosa* (PC) .

The results of antimicrobial activity of extract were active against two bacteria and two fungi. Ciprofloxacin was used as positive control, for measuring the activity against the bacterial strains, with zone of inhibition ranges from 36.07 mm to 37.10mm. The extract showed high degree of inhibition against *Staphylococcus aureus* (31.11mm) and *Salmonella typhi* (31.07). Ketoconazole was used positive control, for measuring the activity against the fungal strains, with zone of inhibition at 38.10mm. The extract showed the heighst zone of inhibition against *Aspergillus niger* (29.05mm) followed by *Candid albicans* (27.10).

CONCLUSION

From the experimental observation, it was found that the significant reduction and control of corrosion of mild steel in acid medium is due to the adsorption of active ingredients present in the plant extract of *Polycarpaea corymbosa* (PC) . Moreover the adsorption behavior of inhibiter molecules on the mild steel surface fits Langmuir and Temkin isotherm. EDS analysis show that the formation of an adsorption layer by inhibitors molecules blocked the active sites on the metal surface, which effectively protected the metal from corrosion. Futher the extract showed high degree of zone of inhibition against tested bacteria and fungi.

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