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Investigation of corrosion behaviour of mild steel using natural product as corrosion inhibitor in citric acidic medium

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ABSTRACT
An aqueous extract of Piper Nigrum. L (PNL) has been prepared as a corrosion inhibitor to control the rate of corrosion. This compound has been investigated as corrosion inhibitor at room temperature for preventing mild steel corrosion in Citric acid medium at different molar concentration by weight loss method and by adsorption isotherm. The result showed that the corrosion inhibition efficiency of this aqueous extract of PNL was found to vary with different molar acid concentration. Also, it was found that the corrosion inhibition behavior of PNL is greater in 1M Citric acid than 2M Citric acid due to aggressive nature of acid. So PNL can be used as a good inhibitor for preventing mild steel material. The surface analysis study confirms the corrosion of the mild steel and its inhibition by the inhibitor Piper Nigrum.L.

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Introduction

Mild steel is widely used in many applications. This intensified the research in corrosion resistance in various aggressive environments [1-3]. It is very often that several problems arise from some industries. Several researchers devoted their attention to develop more effective and non-toxic inhibitors to reduce both acid attack and protection aspects [4-9].

Corrosion involves the movement of metal ions into the solution at active areas (anode), passage of electrons from the metal to an acceptor at less active areas (cathode), an ionic current in the solution and an electronic current in the metal. The cathodic process requires the presence of an electron acceptor such as oxygen or oxidizing agents or hydrogen ions [5-13]. Corrosion can be minimized by suitable strategies which in turn stifle, retard or completely stop the anodic or cathodic reaction or both. Due to their environmental and acceptable ecological properties, naturally occurring antioxidants are cheap and readily available and renewable sources of materials [14]. These organic compounds are either synthesized or extracted from aromatic herbs, spices and medicinal plants. Plant extracts are viewed as an incredibly rich source of naturally synthesized chemical compounds that can be extracted by simple procedures with low cost. However, synergistic effects are often expected with these mixtures of inhibitors that may affect their inhibition efficiency. Several investigations have been reported using such economic plant extracts. El-Etre [6] has studied the application of natural honey as corrosion inhibitor for copper in aqueous solution. Bouyanzer *et al*. studied Pennyroyal oil from menthe pulegium [15] as corrosion inhibition action for steel in acid media. Avwiri and coworkers studied the inhibitive action of vernonia amygdaline [8] on the corrosion of aluminum alloys in HCl and HNO_3. Nypa fructicans wurmb [6] leaves were studied for the corrosion inhibition of mild steel in HCl media. Lawsonia [5] extract was studied for its inhibitive effect against acid induced corrosion of metals. El–Etre *et al* investigated khillah extract [16] for the corrosion inhibition of SS 316 steel in acid media.

Oguzie studied the inhibitive effect of trifasciata [17] extract on the acid and alkaline corrosion of aluminum alloy. P.C. Okafor *et al* phyllanthus amarus [18] extracts for the corrosion inhibition of mild steel in acid media. Ethanolic extract of Riccinus communis leaves [19] was studied for the corrosion inhibition of mild steel in acid media by sathyanathan *et al*.

Amongst the various methods available, the use of inhibitors is one of the most practical methods for protection against corrosion especially in acidic media [20-25].The natural inhibitors studies have been found to be highly eco-friendly and possess no threat to the environment.

In the present work, a systematic study has been undertaken to understand to corrosion behaviour of mild steel and the inhibitive action of Piper Nigrum.L (PNL) extract on 1M Citric acid and 2M Citric acid environment. It was found that the absorbed inhibitor on the mild steel surface accounts for protecting the metal from the corrosive medium and modifying the electrode reactions in favour of corrosion protection of the metal.

Experimental

Specimen Preparation

According to ASTM method as reported already [26], cold rolled mild steel strips were cut into pieces of 5 cm × 1 cm having the following composition (in percentage) % C=0.017; Si=0.007; Mn=0.196; S=0.014; P=0.009; Ni=0.013; Mo=0.015; Cr=0.043 and Fe=99.686 was used. The samples were polished, drilled a hole at one end and numbered by punching. During the study, the samples were polished with various grades of SiC abrasive papers (from grits 120 to 1200) and degreased using Acetone.

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Preparation of extract:

The material was dried in shade to enrich the active principle in them, by reducing its moisture content and made into powder. An aqueous extract of Piper Nigrum.L was prepared by boiling 20 g of powdered substances, with distilled water and making up to 100 ml, after filtering the suspending impurities. From this various milli molar concentration of inhibitor solutions have been prepared. All the solutions were prepared using NICE brand AR grade chemicals in double distilled water and bubbling purified by nitrogen gas for 30 minutes to carry out de-aeration of the electrolytes. 1M Citric acid and 2M Citric acid solution was prepared with double distilled water.

Weight loss measurement:

Mild steel specimens were immersed 1M Citric acid and 2M Citric acid for 2 hours at room temperature (30 ± 2 ºC) for each inhibitor concentration. Then the specimens were removed, rinsed in double distilled water, acetone and the loss in weight of the specimen were determined. From this the inhibition efficiency (IE %) was calculated using the formula,

$$IE\ \% = \frac{W_o - W_i}{W_o} \times 100 \qquad (1)$$

Where, W_O and W_i (in g) are the values of the weight loss observed of mild steel in the absence and presence of inhibitor respectively.

Scanning Electron Microscope (SEM analysis):

The mild steel specimens were immersed in the blank solution (1M Citric acid and 2M Citric acid) containing the inhibitor (PNL) for 2 hours after which they were taken out, washed with distilled water and then the specimens were observed under Scanning Electron Microscope (SEM-HITACHI S3000H, Japan).

FT-IR Studies:

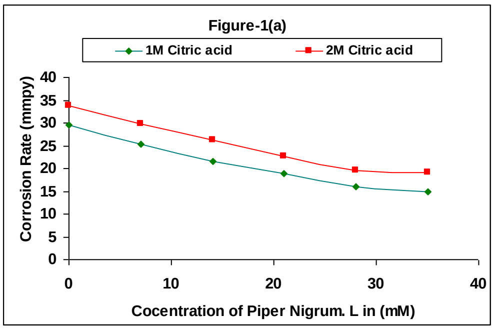
The corrosion products formed on the steel surface during weight loss measurement were removed by scrapping and were used for recording FT-IR spectra. This study reveals the possibility of the adsorption of the inhibitor on the metal surface. The Fourier transform infrared (FT-IR) spectra of the scraped films were recorded using a (Perkin Elmer-1400) FT-IR spectrophotometer.

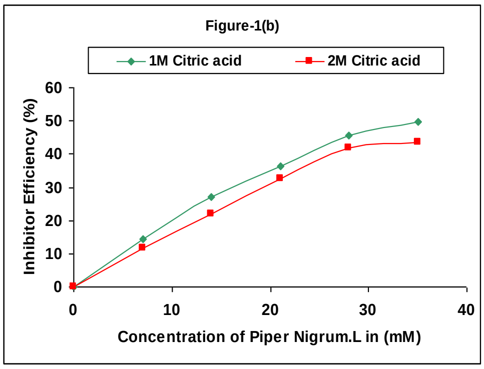
Result and Discussion

Weight loss method

The comparison graph of corrosion behaviour and inhibitor efficiency of mild steel in 1M Citric acid and 2M Citric acid acid with (PNL) was given in Figure1(a) and in Figure 1(b), which was studied by weight loss method at 2 hours at room temperatures. From the graph, it was observed that the weight loss of mild steel in the acid decreases with increasing concentration of additives. The values were tabulated in Table 1. From Table 1, it was clear that the corrosion rate was decreased with increasing concentration of inhibitor and inhibition efficiency increased with increasing the concentration of the inhibitor. In addition, the maximum corrosion inhibition efficiency of Piper Nigrum.L (PNL) was 43.56 % at 2M Citric acid and 49.81 % at 1M Citric acid respectively at 35.04 mM concentration of the inhibitor solution at two hour at room temperature.

It was also concluded that the inhibitor was the best inhibitor in mild steel corrosion in 1M Citric acid and 2M Citric acid. But when comparing with acids the inhibitor efficiency was the best in 1M Citric acid than 2M Citric acid. Figure 1(a) revealed the comparison of corrosion rate (CR) with concentration of Piper Nigrum.L (PNL) (in %) in 1M Citric acid and 2M Citric acid solution at two hour at room temperature. Comparison of inhibition efficiency (IE) with concentration of PNL (in %) in 1M Citric acid and 2M Citric acid solution at two hours at room temperature is shown in Figure 1(b).





Adsorption Isotherm:

Basic information on the interaction between the inhibitor and the mild steel surface can be proved by the adsorption isotherm and in general, inhibitors can function either physical (electrostatic) adsorption or chemisorption with the metal. To obtain more information about the interaction between the inhibitor molecules and the metal surface, different adsorption isotherms were tested. The fractional surface coverage θ at different concentrations of inhibitors 1M Citric acid and 2M Citric acid solutions were determined by the weight loss measurements data [27] using the formula,

$$(\theta) = \frac{Wo - Wi}{Wo} \qquad (2)$$

where, Wo and Wi are the values of weight loss of uninhibited and inhibited specimens, respectively.

$$Kc = \frac{\theta}{1-\theta} \qquad (3)$$

where, c is the concentration of the inhibitor, θ is the fractional surface coverage. The Langmuir isotherm, Eq. (4), which is based on the assumption that all adsorption sites are equivalent and that molecular binding occurs independently from the fact whether the nearby sites are occupied or not, was verified for all the studied inhibitors. The adsorption equilibrium constant K is related to the free energy of adsorption ΔG_{ads} as,

$$K = \frac{1}{C_{solvent}} \exp\left(\frac{-\Delta G_{ads}}{RT}\right) \qquad (4)$$

Where, $C_{solvent}$ represents the molar concentration of the solvent, which in the case of water is 55.5 mol dm^{-3}, R is the gas constant and T is the thermodynamic temperature in K. The Langmuir isotherm, Eq. (5), can be rearranged to obtain the following expression,

$$\frac{c}{\theta} = \frac{1}{K} + c \text{ ---------------} \qquad (5)$$

So that a linear-relationship can be obtained on plotting c/θ as a function of c, with a slope of unity. The thermodynamic parameters K and ΔG_{ads} for the adsorption of the studied inhibitors on mild steel is obtained by Langmuir's adsorption isotherm are plotted in Figure 2 and the obtained values are given in Table 2.

It was found that the linear correlation coefficients clearly prove that the adsorption of the Piper Nigrum.L(PNL) from 2 M acid solutions on the mild steel corrosion obeys the Langmuir adsorption isotherm.

The negative values of ΔG^0_{ads} for the addition of inhibitors indicates that the process of adsorption of studied inhibitors are spontaneous in nature [28]. The free energy of adsorption of (ΔG_{ads}), in 1M Citric acid was found to be -9.059 $kJmol^{-1}$while for 2M Citric acid it was found to be -7.045 $kJmol^{-1}$ respectively.

It is well known that the values of ΔG_{ads} in the order of −20 kJ mol^{-1} or lower indicate a physisorption while those about −40 kJ mol^{-1} or higher involve charge sharing or transfer from the inhibitor molecules to the metal surface to form a co-ordinate type of bond [29].

The calculated adsorption values for all the studied inhibitor show that the adsorption is of physical in nature, and there is no chemisorption between the inhibitor molecule and the metal surface. This indicates that the adsorption of PNL at 2 h takes place through electrostatic interaction between the inhibitor molecule and the metal surface. Hence it indicates that the interaction between the inhibitor molecule and metal surface is physisorption.

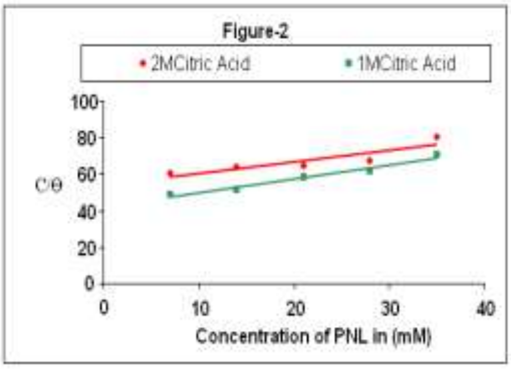


Figure 2- Comparison of Langmuir isotherm for adsorption of PNL on mild steel surface studied at different concentration of citric acid media

SEM Analysis:

The polished mild steel specimens were immersed in the acid solution (1M Citric acid and 2M Citric acid) and in the acids containing inhibitor Piper Nigrum.L for 2 h, then the specimens were taken out, dried and observed under Scanning Electron Microscope (SEM). The micrographs are shown in the Figure 3 & 4 shows polished specimen which was kept in the blank solution of 1M Citric acid and 2M Citric acid, which is associated with polishing scratches.

Figure 5 & 6 shows specimen which was kept in the 35.04 mM concentration of inhibitor solution with 1M Citric acid and 2M Citric acid depends upon the concentration of the inhibitor solution suggesting that the presence of adsorbed layer of the inhibitor on mild steel surface which impedes corrosion rate of metal appreciably.

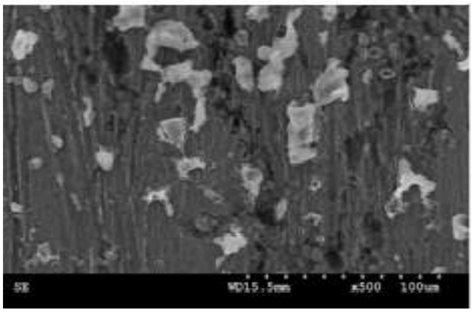


Figure 3 SEM images obtained for the mild steel surfaces immersed for 2 h in 2M Citric acid (blank acid solution)

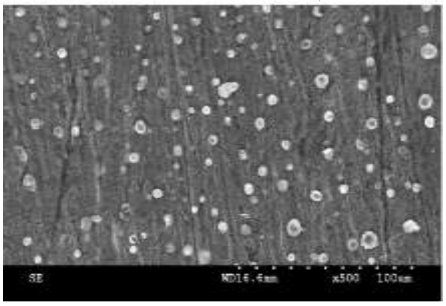


Figure 4 SEM images obtained for the mild steel surfaces immersed for 2 h in 1M Citric acid (blank acid solution)

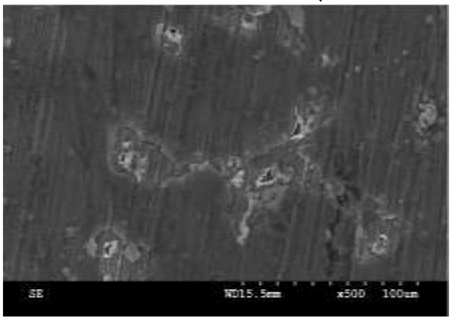


Figure 5 SEM images obtained for the mild steel surfaces immersed for 2 h in 2M Citric acid with 35.04 mM (PNL) inhibitor solution

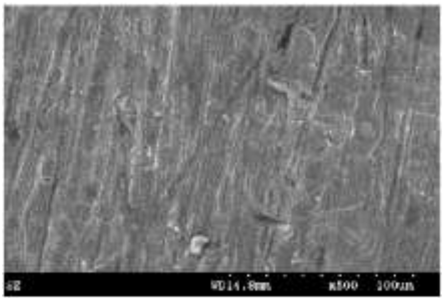


Figure 6 SEM images obtained for the mild steel surfaces immersed for 2 h in 1M Citric acid with 35.04 mM (PNL) inhibitor solution

FT-IR Studies:

The FT-IR analysis of metal surface (scraped corrosion product) can be useful for predicting whether organic inhibitors are adsorbed or not adsorbed on the metal surface [30]. Therefore, FT-IR spectra were used to support the fact that corrosion inhibition of mild steel in acid medium is due to the adsorption of inhibitor molecules on the mild steel surface as well as providing new bonding information on the steel surface after immersion in 1M Citric acid solution containing inhibitor. Figure 7(a) shows the FT-IR spectrum of the Piper Nigrum.L. In this spectrum the peak appeared at 3433cm^{-1} corresponds to –OH group, 1637 cm^{-1} corresponds to C=0 group and from 1230 cm^{-1} to 1000 cm^{-1} indicates the presence of C-O bonding nature.

Figure 7(b) is similar to Figure 7(a) which indicates that the scarped corrosion product contains Piper Nigrum.L. Moreover, there is no additional peak observed in the spectrum. Therefore from these spectra, it is reveled that the inhibition is due to the physical adsorption occurred on the surface of the metal. This is already confirmed from the Langmuir adsorption isotherm studies.

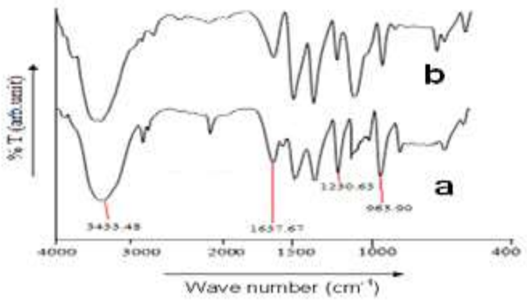


Figure 7 IR spectrum of the corrosion product showing adsorption in the presence of aqueous extract of Piper Nigrum.L

Conclusions

The present study leads to the following conclusion in controlling the corrosion of mild steel by Piper Nigrum.L (PNL) in 1M Citric acid and 2M Citric acid.

1. Piper Nigrum.L (PNL) was found to be effective inhibitor in the acidic medium giving inhibition efficiency upto 49.81 % in 1M Citric acid and 43.56 % in 2M Citric acid respectively.
2. The inhibitor Efficiency is greater in 1M Citric acid than 2M Citric acid due to aggressive nature of an acid medium.
3. The inhibition efficiency increased with increase in concentration of inhibitors for 7.00 mM to 35.04 mM at 2 h at room temperature.
4. From the comparative studies of weight loss method, it was concluded that the inhibitor efficiency is better in 1M Citric acid than 2M Citric acid.
5. The adsorption of the compound investigated follows the Langmuir isotherm and the adsorption is physical in nature.
6. The FT-IR results also reveal the adsorption of inhibitor molecule on the metal surface and blocking the active sites.

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Table1. Corrosion parameters in absence and presence of Piper Nigrum.L 1M Citric acid and 2M Citric acid

Inhibitor	Conc. of inhibitor (mM)	Corrosion Rate (mm/y)		Inhibitor Efficiency (%)	
		1M Citric acid	2M Citric acid	1M Citric acid	2M Citric acid
Piper Nigrum.L	Blank	29.5343	33.7694	---	---
	7.00	25.2992	29.8687	14.33	11.55
	14.01	21.5099	26.3022	27.16	22.11
	21.02	18.8351	22.7358	36.22	32.67
	28.03	16.0488	19.5038	45.66	41.66
	35.04	14.8229	19.0580	49.81	43.56

Table 2: Thermodynamic parameters for the adsorption of PNL in Citric acid mediums on the mild steel.

Name of the Acid	Concentration in (mM)	Surface coverage (θ)	ΔGads KJ / mol^{-1}	Kx (10^{-2} M^{-1})
1M Citric	35.04	0.4981	-9.059	1.79
2M Citric	35.04	0.4356	-7.045	1.79