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Study on corrosion inhibition of mild steel using natural product as corrosion inhibitor in acidic medium

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ABSTRACT

An aqueous extract of Allamanda Blanchetti (AB) 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 Sulphuric acid and Hydrochloric acid medium by weight loss method and by adsorption isotherm. The result showed that the corrosion inhibition efficiency of this aqueous extract of AB was found to vary with different acid concentration. Also, it was found that the corrosion inhibition behavior of AB is greater in 2M H_2SO_4 than 2M HCl. So AB can be used has 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 Allamanda Blanchetti.

Introduction

Mild steel is widely used in many applications; the 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].

Amongst the various methods available, the use of inhibitors is one of the most practical methods for protection against corrosion especially in acidic media [10-15].

Natural products like lignin and tannin [16], cinchona alkaloids [17] and pomegranate alkaloids [18] have been evaluated as very effective acid corrosion inhibitors in standard as well as in stringent conditions. Inhibition of corrosion was studied with the extracts of Antrographis paniculata [19], Thespesia populnea [20], Mangifera indica [21], Datura metal [22], Mentha pulgeium [23], Sesbania grandiflora seeds [24], Ficus benghalensis bark [25], Psidium gerajanra (bark) and Callistemos (leaves) [26], Canavalia ensiformis [27] etc. The natural inhibitors studied 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 Allamanda Blanchetti (Purple Color Flower) extract on 2M HCl and 2M H_2SO_4 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 [28], 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.

Preparation of flower extract

The plant was collected, shaded dried and powdered. The material was dried in shade to enrich the active principle in them, by reducing its moisture content. An aqueous extract of Purple Allamanda Blanchetti was prepared by boiling 20 g of dried flower petals, with distilled water and making up to 100 ml, after filtering the suspending impurities. From this various milli molar concentration of inhibitor solutions has 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. 2M HCl and 2M H_2SO_4 solution was prepared by double distilled water.

Weight loss measurement

Mild steel specimens were immersed 2M HCl and 2M H_2SO_4 for 2 h at room temperature (28 ± 2 °C) 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 inhibiton 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 (2M HCl and 2M H_2SO_4) containing the inhibitor Allamanda Blanchetii for 2 h after which they were taken out, washed with distilled water and then the specimens was observed under Scanning Electron Microscope (SEM- HITACHI S3000H, Japan).

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FT-IR Studies:

The corrosion products formed on the steel surface during weight loss measurement was removed by scrapping and was 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

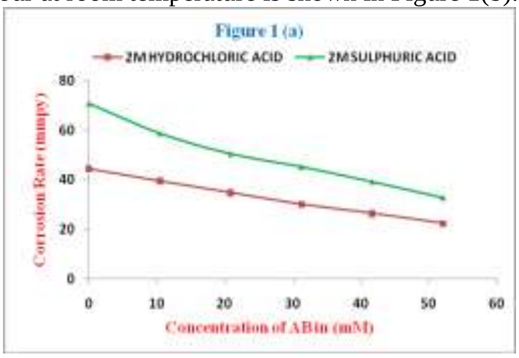
Weight loss method

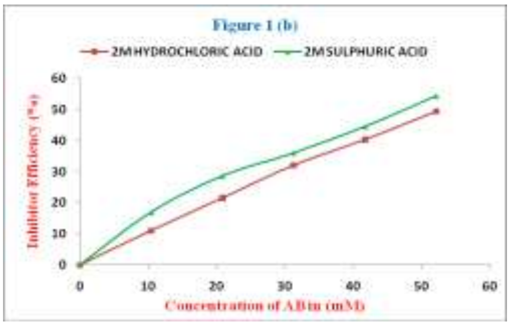
The comparison graph of corrosion behaviour and inhibitor efficiency of mild steel in 2M HCl and 2M H_2SO_4 acid with Allamanda Blanchetti was given in Figure1(a) and in Figure 1(b), which was studied by weight loss method at 2 h at room temperatures.

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 Allamanda Blanchetti (AB) was 49.49 % at 2M HCl and 54.41 % at 2M H_2SO_4 respectively at 52.05 mM concentration of the inhibitor solution at two hour at room temperature.

It was also concluded that the inhibitor was best inhibitor in mild steel corrosion in 2M H_2SO_4 and 2M HCl. But when comparing with acids the inhibitor efficiency was best in 2M H_2SO_4 than 2M HCl. Figure 1(a) revealed the comparison of corrosion rate (CR) with concentration of Allamanda Blanchetti (AB) (in %) in 2M HCl and 2M H_2SO_4 solution at two hour at room temperature. Comparison of inhibition efficiency (IE) with concentration of (AB) (in %) in 2M HCl and 2M H_2SO_4 solution at two hour 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 by 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 2M HCl and 2M H_2SO_4 solutions were determined from the weight loss measurements data [29] 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. (5.2), 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,

$$K = \frac{1}{C_{solvent}} \exp\left(\frac{-\Delta G_{ads}}{RT}\right) \qquad (4.3)$$

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. (5.4), can be rearranged to obtain the following expression,

$$\frac{c}{\theta} = \frac{1}{K} + c \qquad (4.4)$$

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 Allamanda Blanchetti (AB) 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 [30]. The free energy of adsorption of (ΔG_{ads}), in 2M HCl was found to be -6.021 $kJmol^{-1}$while for 2M H_2SO_4 it was found to be -8.083 $kJmol^{-1}$ 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 [31].

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 AB 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.

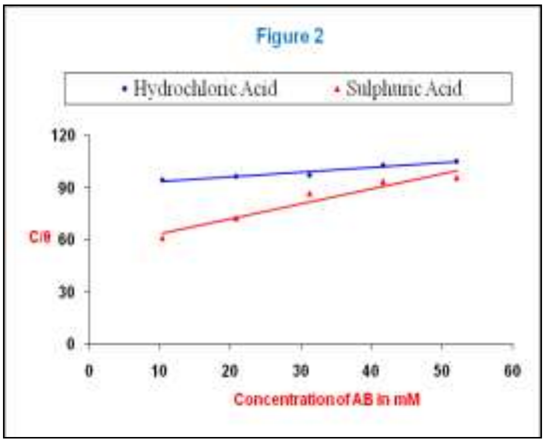


Figure 2- Langmuir isotherm for adsorption of AB on mild steel surface studied at various acid media (2M).

SEM Analysis:

The polished mild steel specimens were immersed in the acid solution (2M HCl and 2M H_2SO_4) and in the acids containing inhibitor Allamanda Blanchetti for 2 h, then the specimens were taken out, dried and observed under Scanning Electron Microscope (SEM).

The micrograph are shown in the Figure 3 & 4 shows polished specimen which was kept in the blank solution of 2M HCl and 2M H_2SO_4, which is associated with polishing scratches.

Figure 5 & 6 shows specimen which was kept in the 52.05 mM concentration of inhibitor solution with 2M HCl and 2M H_2SO_4 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.

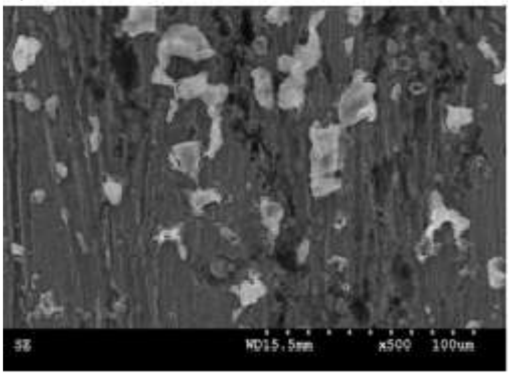


Figure 3 SEM images obtained for the mild steel surfaces immersed for 2 h in 2M HCl (blank acid solution)

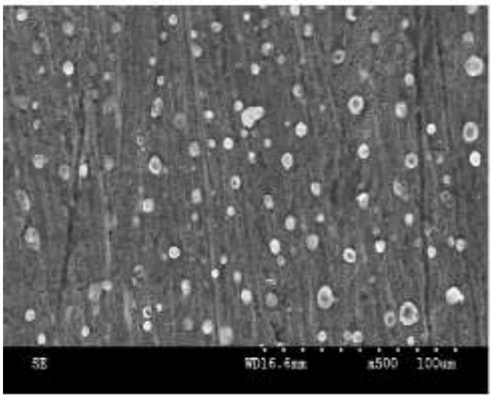


Figure 4 SEM images obtained for the mild steel surfaces immersed for 2 h in 2M H_2SO_4 (blank acid solution)

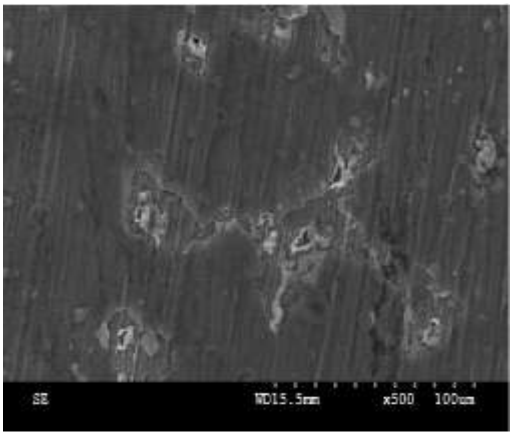


Figure 5 SEM images obtained for the mild steel surfaces immersed for 2 h in 2M HCl with 52.05mM (AB) inhibitor solution.

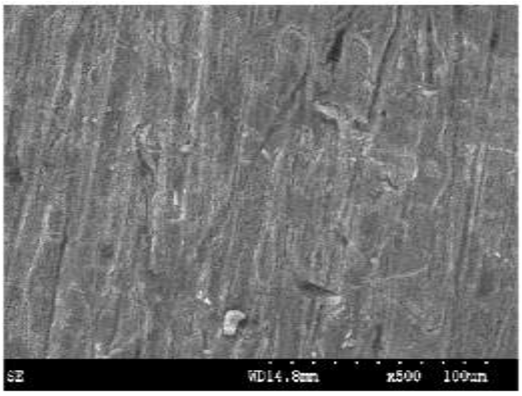


Figure 6 SEM images obtained for the mild steel surfaces immersed for 2 h in 2M H2SO4 with 52.05mM (AB) inhibitor solution.

FT-IR Studies:

The FT-IR analyses of metal surface (scraped corrosion product) can be useful for predicting whether organic inhibitors are adsorbed or not adsorbed on the metal surface [32]. 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 H2SO4 solution containing inhibitor. Figure 7.1(a) shows the FT-IR spectrum of the Allamanda Blanchetti (Flower).

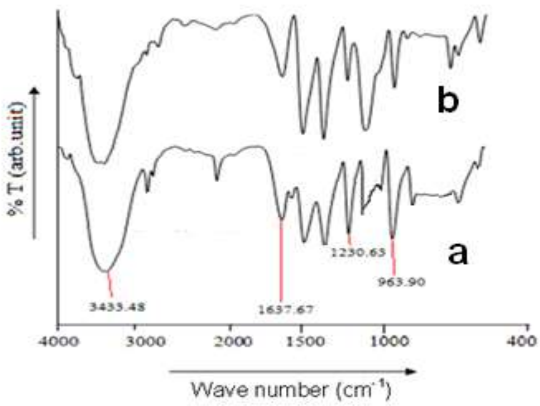


Figure 7.1 IR spectrum of the corrosion product showing adsorption in the presence of aqueous extract of Allamanda Blanchetti.

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 7.1 (b) is similar to Figure 7.1 (a) which indicates that the scarped corrosion product contains Allamanda Blanchetti. 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. Conclusions

The present study leads to the following conclusion in controlling the corrosion of mild steel by Allamanda Blanchetti (AB) in 2M HCl and 2M H_2SO_4.

Allamanda Blanchetti (AB) was found to be effective inhibitor in the acidic medium giving inhibition efficiency upto 49.49 % in 2M HCl and 54.41 % in 2M H_2SO_4 respectively.

The inhibition efficiency increased with increase in concentration of inhibitors for 10.41 mM to 52.05 mM at 2 h at room temperature.

From the comparative studies of weight loss method, it was concluded that the inhibitor efficiency is better in 2M H_2SO_4 than 2M HCl.

The adsorption of the compound investigated follows the Langmuir isotherm and the adsorption is physical in nature.

The FT-IR results also reveal the adsorption of inhibitor molecule on the metal surface and blocking the active sites.

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Table 1. Corrosion parameters in absence and presence of Allamanda Blanchetti 2M HCl and 2M H_2SO_4.

Inhibitor	Conc. of inhibitor (mM)	Corrosion Rate (mm/y)		Inhibitor Efficiency (%)	
		2M HCl	2M H_2SO_4	2M HCl	2M H_2SO_4
Allamanda Balanchetti	Blank	44.3572	70.7709	---	---
	10.41	39.4534	58.7343	11.05	17.00
	20.82	34.7725	50.4870	21.60	28.66
	31.23	30.0916	45.2488	32.16	36.06
	41.64	26.4137	39.2305	40.45	44.56
	52.05	22.4015	32.7664	49.49	54.41