Investigation of *Ageratum Conyzoides* Aqueous Extract as Inhibitor for Hydrochloric Acid Corrosion of SX 316 Steel

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Abstract

The inhibitive effect of the extract of Ageratum conyzoides on corrosion of SX 316 steel in HCl solution was determined using weight loss measurement and galvanostatic polarisation techniques. It was found that the presence of the plant extract reduces markedly the corrosion of steel in acid solution and inhibition efficiency ranged between 94.39 ─ 99.15 %. The inhibition efficiency increases as the plant extract concentration was increased. The inhibitive effect of A. conyzoides extract (ACE) was discussed on the basis of adsorption of the components on the metal surface. Negative value of energy of adsorption indicates the spontaneity of the process.

Keywords*:*   Acid corrosion, natural product, inhibition, steel

1.   INTRODUCTION

Studies have shown that organic compounds containing N, S, and O show significant corrosion inhibition efficiency (Singh and Adeyemi, 1989; Adeyemi and Singh, 1992; Adeyemi, 2006). Many organic compounds have been tested and applied industrially as corrosion inhibitors). However, most of these compounds are not just expensive, but also toxic to living things (Raja and Sethuraman, 2008), but those that are non-toxic are presently gaining much attention than in the past. The present trend in the field of bio-degradable organic corrosion inhibitors has been focused on using cheap, easily available and effective molecule at low or zero environmental impact. It is therefore needless to point out the importance of cheap and safe corrosion inhibitors and this has prompted the recent research for green corrosion inhibitors.

The use of naturally occurring substances of plant origin to inhibit the corrosion of metals have been tested for various metals in acidic and alkaline environments by a number of workers (Adeyemi *et al*., 2006; Adeyemi and Olubomehin 2010; Adeyemi and Olubomehin 2010; Adeyemi *et al*., 2008; El-Etre, 1998, 2003, 2006; Okafor *et al*., 2005; Amoretti *et al*., 2004; Sethuraman *et al.*, 2005; Rajendran *et al.,* 2005).

The inhibitive properties of aqueous extract of Eucalyptus leaves on acid corrosion of mild steel and copper have been reported (Pravinar *et al.,* 1993). The inhibition efficiency was found to be concentration dependent and decreases with rise in temperature. The extract was a mixed type inhibitor as it inhibited both anodic and cathodic reactions but was predominantly cathodic

control. Aymen and Singh (1991) reported that the inhibitive action of pomegranate was primarily due to the presence of alkaloids in the plant extract. They suggested that the inhibitive action was due to formation of metal-additive complex on the metal surface.

Many workers (Martinez and Stern, 2001; Eddy and Ebenzo, 2008; Oguzie, 2008a) suggested that the corrosion inhibition of plant extracts on metallic material in corrosive media is due to the presence of some antioxidant compounds in the plants.

Ageratum conyzoides is an annual herb which grows to about 60 cm high and produces pretty pink flowers at the top of its hairy stems. It is generally considered a weed that is hard to control. *A. conyzoides* ranges from South Eastern North America, but the centre of origin is in Central America and the Caribbean. *Ageratum* is also found in tropical and sub-tropical regions of Africa and Brazil. *Ageratum* contains many bioactive compounds including flavonoids, alkaloids, cumarine, essential oils, chromenes, benzofurans, terpenoide and tannins (Gill *et al*., 1978) as shown below:
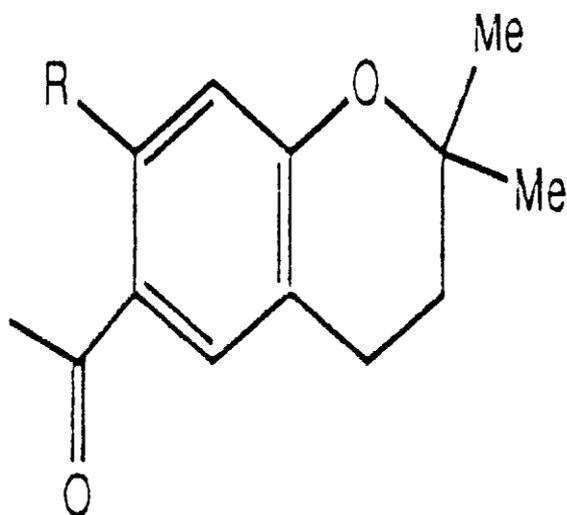
Alkaloid derivative

Chromone

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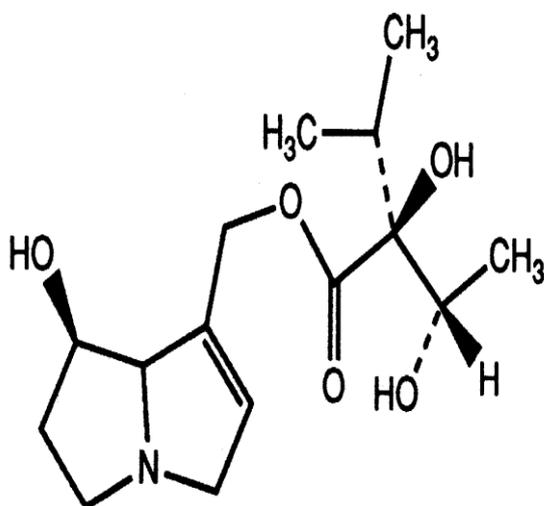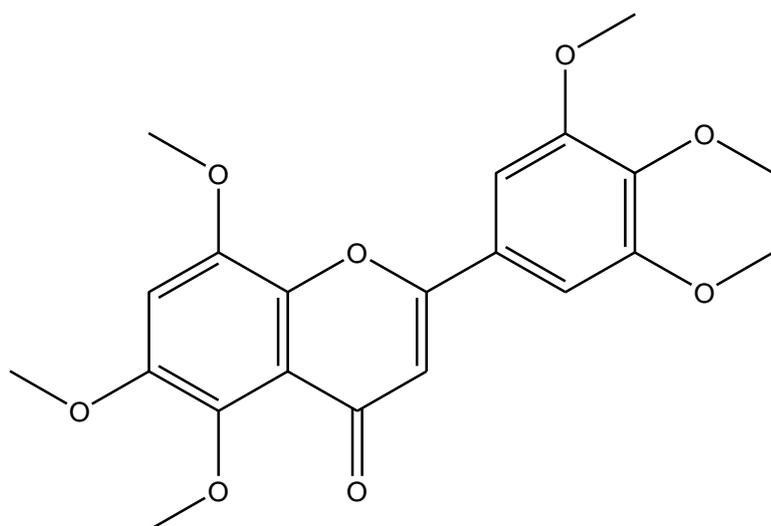
5,6,8,3',4',5' -hexamethoxyflavone

Green corrosion inhibitors are biodegradable and do not contain heavy metals or other toxic compounds. Efforts to find naturally occurring organic substances have been the focus of our research team (Adeyemi *et al.,* 2006; Adeyemi and Olubomehin 2010; Adeyemi and Olubomehin 2010; Adeyemi *et al*., 2008)

2. EXPERIMENTAL

2.1 Preparation of steel sample

The steel sample use for these studies was procured from Niger Dock Yard, Apapa, Lagos. It had a nominal percentage composition (C 0.0447; Si 0.037; P 0.017; S 0.013; Cu 0.054; Cr 0.049; Ni 0.057 and the rest Fe). All the steel samples were rectangular in shape and 3 x 3 x 3 cm in sizes. Each coupon was polished to smooth surface with various grades of emery papers up to 1200 grade and then washed with double distilled water. The washed coupons were then degreased with acetone and desiccated overnight before use. The coupons were weighed before and after immersion in test solutions.

2.2 Extraction of corrosion active ingredient from plant

Ageratum conyzoides was collected in and around Ago-Iwoye town-ship in Ijebu North, Ogun State, South Western Nigeria. 2 kg of A. conyzoides was taken and dried 30 ºC for 21 days in the laboratory, then ground and powdered. The powdered plant material was weighed at specific concentration of 50, 100, 150, 200 and 250 g respectively in 1000 mL of double-distilled water in a round bottomed flask and boiled under low and control heat for 2 days, cooled to room temperature and filtered. The stock solution was used to prepare different concentration of the extract.

2.3 Weight loss method

The desiccated coupons were immersed in 250 mL 10, 20, 30, 40 and 50 ppm solutions of plant extract as well as blank solution (0.5 M HCl) at 30°C for 3, 6, 9, 12, 15 hours. They were then

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retrieved washed in 20 % NaOH solution containing 100 g/L Zn dust and rinsed in deionized water and cleaned. The weight loss of each steel sample was then determined. From the weight loss data the inhibition efficiency (IE %) and corrosion rate (CR) were calculated using Equations 1, 2 and 3 respectively

$$IE\% = 1 - \frac{W2}{W1} \times 100 \qquad \qquad 1$$

$$CR\ (gh - 1cm - 2)\ = \frac{\Delta W}{AT} \qquad \qquad 2$$

$$\Theta\ =\ 1 - \frac{W2}{W1} \qquad \qquad 3$$

where w_1 and w_2 are weight loss in the absence and presence of plant extract respectively. A is the area of the coupons in cm^2, and T the immersion time in hours respectively and

$$\Delta W = w_1 - w_2 \qquad \qquad 4$$

The weight loss data and the inhibition efficiency, surface coverage (θ) and corrosion rate are shown in Table 1.

Table 1: Corrosion parameter of steel after immersion in the presence and absence of inhibitor at 30ºC for all hours of experiment

CONCENTRATION	TIME OF IMMERSION (HRS)	WEIGHT LOSS (g)	INHIBITION EFFICIENCY % I.E	SURFACE COVERAGE (Ө)	CORROSION RATE (mm/yr)
Blank(0.5 M HCl)	3	0.0535	-	-	0.1463
10 ppm		0.0030	94.39	0.944	0.0082
20 ppm		0.0018	96.64	0.966	0.0049
30 ppm		0.0015	97.19	0.972	0.0041
40 ppm		0.0009	98.32	0.983	0.0025
50 ppm		0.0006	98.57	0.986	0.0016
Blank(0.5M HCl)	6	0.1299	-	-	0.1803
10 ppm		0.0049	96.22	0.9622	0.0068
20 ppm		0.0037	97.15	0.972	0.0051
30 ppm		0.0030	97.60	0.977	0.0042
40 ppm		0.0017	98.69	0.987	0.0024
50 ppm		0.0011	99.15	0.992	0.0015
Blank(0.5M HCl)	9	0.2129	-	-	0.1821
10 ppm		0.0125	94.13	0.941	0.0097
20 ppm		0.0055	97.42	0.974	0.0043
30 ppm		0.0040	98.12	0.981	0.0031
40 ppm		0.0033	98.45	0.985	0.0026
50 ppm		0.0021	99.01	0.990	0.0016
Blank(0.5M HCl)	12	0.2712	-	-	0.1868
10 ppm		0.0138	94.91	0.949	0.0053
20 ppm		0.0073	97.13	0.971	0.0028
30 ppm		0.0064	97.64	0.976	0.0025
40 ppm		0.0054	98.00	0.980	0.0021
50 ppm		0.0048	98.23	0.982	0.0019
Blank(0.5M HCl)	15	0.3411	-	-	0.1982
10 ppm		0.0168	95.07	0.951	0.0098
20 ppm		0.0097	97.16	0.972	0.0056
30 ppm		0.0093	97.27	0.973	0.0054
40 ppm		0.0076	97.77	0.978	0.0044
50 ppm		0.0069	97.97	0.980	0.0040

2.4   Galvanostatic Studies

The potentiostatic studies were carried out in a 5-neck electrochemical cell. A platinum wire gauze was used as a counter electrode, and the reference electrode was a saturated calomel electrode. The latter was connected through a lugging capillary to the electrochemical cell. Before each experiment, the steel working electrode was mechanically polished with various grades of silicon carbide papers up to 1200 grade, washed with double distilled water, degreased with acetone and desiccated before usage.

The electrode with 2 x 2 cm^2 exposable area was polarised and attained its open corrosion potential (OCP) after about 120 minutes when cathodic and anodic polarization curves were recorded at a sweep rate of 0.45 mVs^{-1}. The anodic and cathodic Tafel slopes (b_a and b_c) and values of the corrosion current density (i) with and without plant extract (0.5 M HCl) were calculated using a non-interactive method for determining corrosion parameters from sequence of polarization data. The inhibition efficiency (%IE) was calculated according to the equation

$$\%IE = (\frac{i_o-i}{i_o}) \times 100 \qquad\qquad 5$$

where i_o and i are corrosion current densities in the absence and presence of the plant extract, respectively. Table 2 presents data on weight loss, inhibition efficiency, surface coverage and corrosion rate at 50°C.

Table 2: Corrosion parameter of steel after immersion in the presence and absence of inhibitor at 50°C for all hours of experiment

CONCENTRATION	TIME OF IMMERSION (HRS)	WEIGHT LOSS (g)	INHIBITION EFFICIENCY % I.E	SURFACE COVERAGE (Θ)	CORROSION RATE (mm/yr)
Blank(0.5M HCl)	3	0.1296	-	-	0.3657
10 ppm		0.0540	58.3333	0.5833	0.1524
20 ppm		0.0265	79.5524	0.7955	0.0649
30 ppm		0.0141	89.1204	0.8912	0.0202
40 ppm		0.0075	94.2130	0.9421	0.0194
50 ppm		0.0024	98.1481	0.9815	0.0070
Blank(0.5M HCl)	6	0.1494	-	-	0.1803
10 ppm		0.0801	46.3855	0.4639	0.1130
20 ppm		0.0661	55.7564	0.5576	0.0810
30 ppm		0.0515	65.5288	0.6553	0.0369
40 ppm		0.0220	85.2744	0.8527	0.0285
50 ppm		0.0170	88.6212	0.8862	0.0247
Blank(0.5M HCl)	9	0.1735	-	-	0.0828
10 ppm		0.1341	22.7090	0.2271	0.1321
20 ppm		0.0990	42.9395	0.4294	0.0809
30 ppm		0.0785	54.7550	0.5476	0.0375
40 ppm		0.0350	79.8270	0.7983	0.0308
50 ppm		0.0184	89.3948	0.8939	0.0179
Blank(0.5M HCl)	12	0.1988	-	-	0.1285
10 ppm		0.1881	5.3823	0.0538	0.1390
20 ppm		0.1319	33.6519	0.3365	0.0806
30 ppm		0.0515	65.5288	0.6553	0.0369
40 ppm		0.0425	78.6217	0.7862	0.0275
50 ppm		0.0344	82.6962	0.8270	0.0123

Blank(0.5M HCl)	15	0.2112	-	-	0.1230
10 ppm		0.2006	5.0189	0.0502	0.1186
20 ppm		0.1648	21.9697	0.2197	0.0808
30 ppm		0.1595	24.4792	0.2448	0.0457
40 ppm		0.0675	68.0398	0.6804	0.0350
50 ppm		0.0504	76.1364	0.7614	0.0293

The apparent activation energy (ΔE_A) evaluated from Arrhenius equation

$$k = A.e - E_A/_{RT} \qquad\qquad 6$$

and other corrosion parameters are shown in Table 3.

**Table 3: Electrochemical Parameters and Inhibition efficiency at different temperature and concentrations**

Concentrations	293 K			303 K			313 K			323 K			333 K		
	E_{corr} (mV)	b_c	I (%)	E_{corr} (mV)	bc	I (%)	E_{corr} (mV)	b_c (mV)	I (%)	E_{corr} (mV)	b_c (mV)	I (%)	E_{corr} (mV)	b_c (mV)	I (%)
0.5M HCl	-480	128	-	-470	135	-	-490	140	-	-470	160	-	-485	195	-
10 ppm	-480	125	50	-480	130	52	-480	140	55	-475	150	60	-470	160	68
20 ppm	-480	125	70	-460	130	74	-490	130	76	-480	155	75	-480	160	80
30 ppm	-490	125	90	-500	125	93	-500	130	94	-500	140	93	-500	150	93
40 ppm	-500	120	95	-510	125	96	-520	125	97	-505	135	96	-510	140	98
50 ppm	-520	125	95	-510	120	97	-520	125	97	-530	140	97	-535	135	98

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3.   RESULTS AND DISCUSSION

3.1   Weight Loss Studies

The corrosion parameters- weight loss, % IE, surface coverage, corrosion rate (CR) obtained from the weight loss studies are shown in Table 1. The data obtained from electrochemical studies are presented in Table 2. From Table 1 it is evident that the presence of plant extract reduced metal dissolution. The weight loss and the inhibition efficiency are concentration dependent. The inhibition efficiency (% IE) increased as the concentration of the plant extract was increased. The weight loss however decreased as the concentration of plant extract increased. The plots of weight loss against concentration are shown in Figure 1 while Figure 2 presents a representative of the variation of inhibition efficiency with concentration. Similar plots were obtained for higher temperatures. The corrosion rate and inhibition efficiency increased with increased concentration of the inhibitor. This observation is in good agreement with the works of others (Martinez and Stern, 2001; Eddy and Ebenzo, 2008; Oguzie, 2008a).

It is pertinent to note that the inhibition efficiency was equally time dependent because it decreased as the immersion time was increased from 6 hour to 15 hour. There is however no general gradation on the effect of time on the inhibition efficiency. The inhibition efficiency is highest at 3 hour where it varies from 58.33 – 98.15 % at lower temperature.
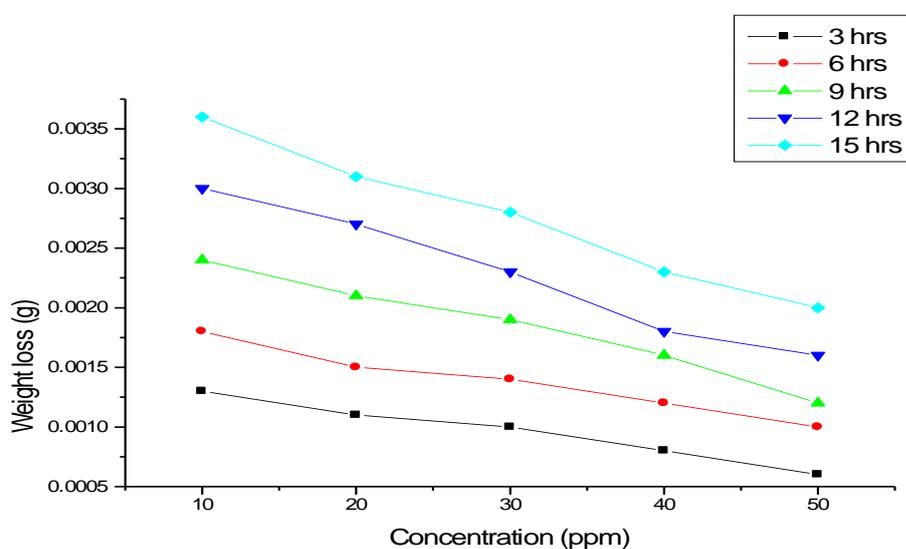
Fig. 1: variation of weight loss with concentration at different time intervals
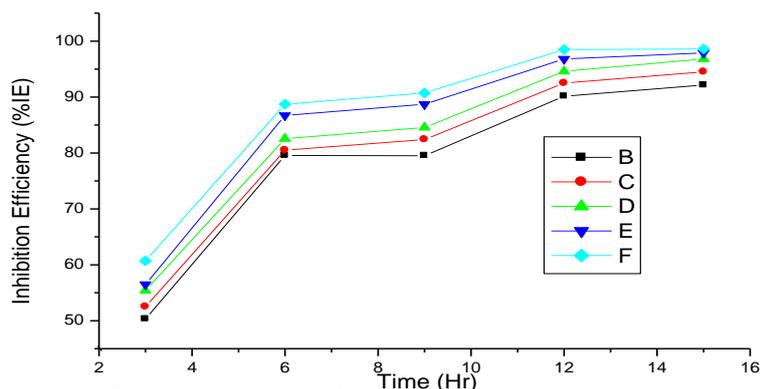
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Fig.2: Variation of inhibition efficiency with immersion time
(B 10; C 20; D 30; E 40; F 50 ppm)

3.2   Electrochemical Studies

From the electrochemical studies (Table 3) and Figure 6, the plant extract decreased the cathodic processes by a larger extent and the anodic processes by a much less extent. From the polarization plots, the corrosion potential shifts to more negative values on the introduction of the organic inhibitors in the corroding medium. A similar effect was observed in the presence of plant extract (not shown). This behaviour confirms the predominating effect of inhibitors on the cathodic process.

The corrosion current (i_{corr}) increased with rise in temperature in both uninhibited and inhibited solutions. Conversely, however, the cathodic rate decreases as the inhibitor concentration increases. The results presented in Table 2 showed that inhibitor efficiency (% IE) increases both with increase in inhibitor concentration and with increase in temperature. The latter effect is probably due to the characteristics of the cathodic process of hydrogen evolution reaction in acid solution. Fig. 6 is a representative polarization curve of SX 316 steel in 0.5 M HCl. Similar plots (not shown) were obtained for the presence of plant extracts.

A careful inspection of the phytochemicals present in *Ageratum conyzoides* shows the presence of bondable hetero atoms which can form coordinate bonds with metal atoms. Organic inhibitors generally have hetero atoms. O, N, and S are found to have higher basicity and electron density and thus act as corrosion inhibitor (Singh and Adeyemi 1987, Adeyemi and Singh 1993). The hetero atoms are believed to be the active centres for the process of adsorption on the metal surface. Thus the presence of these atoms in the principal constituents shown above could probably be responsible for corrosion inhibition by the plant extract. But synergism could not also be ruled out. Umoren*, et al*., (2008) showed that the inhibitive properties of exudate gums of *Pachylobus edulis* and *Raphiahookeri* were due to the presence of phytochemical constituents of these plants. The exudate has been reported to contain tannin, oligosaccharides, polysaccharides and proteins. Thus it could be assumed that the extract of *A. conyzoides* established its inhibitive action via adsorption of these phytochemical component molecules on the metal surface. This adsorption process creates a barrier between the metal and the corrosive medium leading to inhibition of corrosion. Consequently inhibition efficiency increases as the fraction of metal surface area covered by the adsorbed molecules increased. The latter in turn increased as the plant extract increased.

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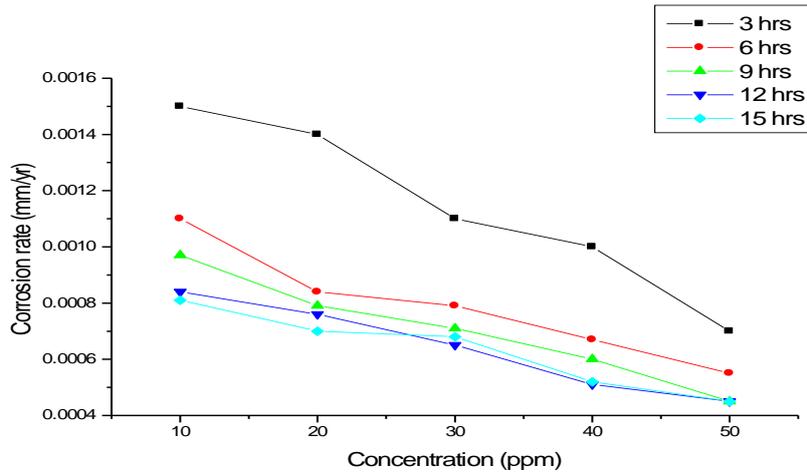
Fig. 3: variation of corrosion rate with concentration at different time intervals
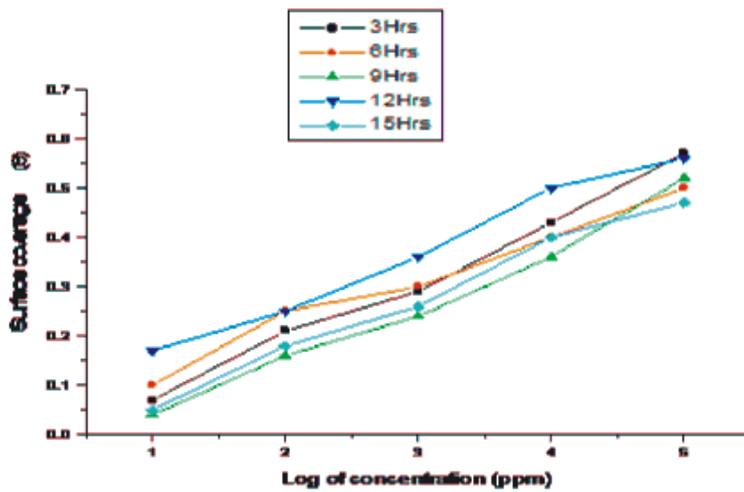
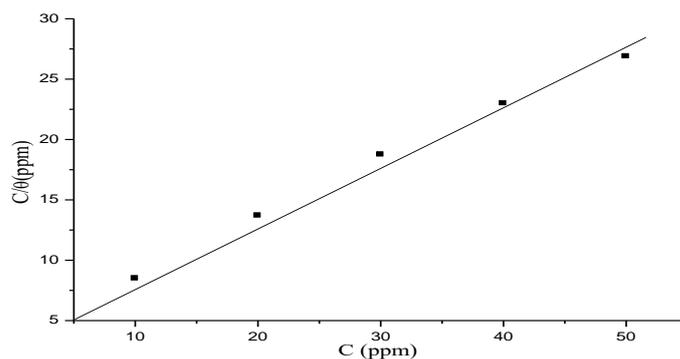**Fig. 4: Variation of surface coverage with log of concentration at different time intervals**

Fig. 5: Langmuir adsroption isotherm plots for SX316 steel in 0.5 M H₂SO₄
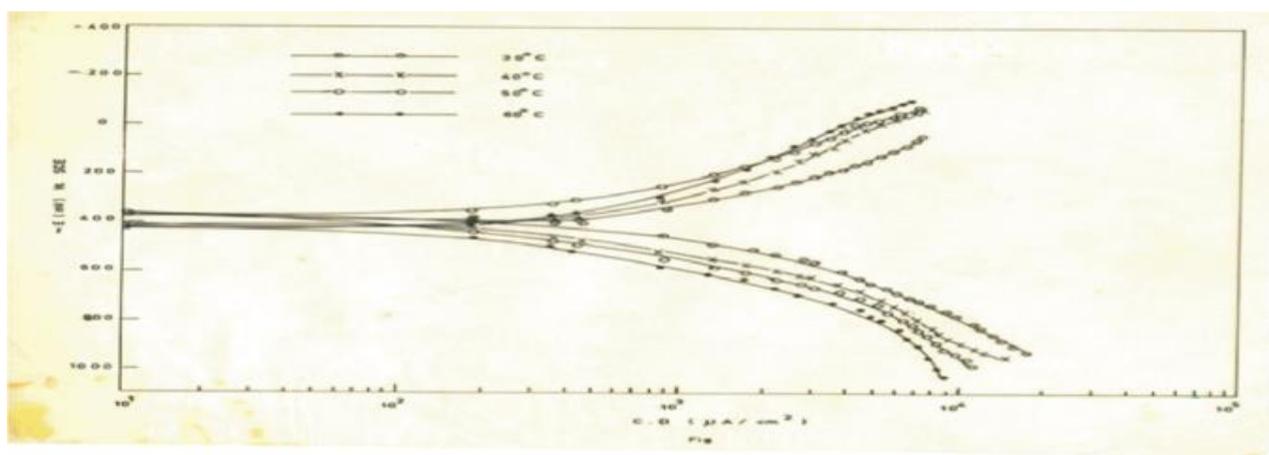

Fig. 6: Polarisation curves related to 3 hr electrode immersion

In this study, Langmuir adsorption isotherm was found to be suitable for the experimental findings and has been used to describe the adsorption characteristic of this inhibitor.

Langmuir adsorption isotherm is expressed in Equation 5

$$C/_\theta = \frac{1}{k} + C \qquad\qquad 7$$

where k is the equilibrium constant of adsorption and C is the inhibitor concentration. Thus a plot of C/θ versus $log\ C$ (Figure 7) must be a linear and indeed it is linear over a range of temperature. The heat of adsorption obtained in the presence and absence of inhibitor is presented in Table 4.

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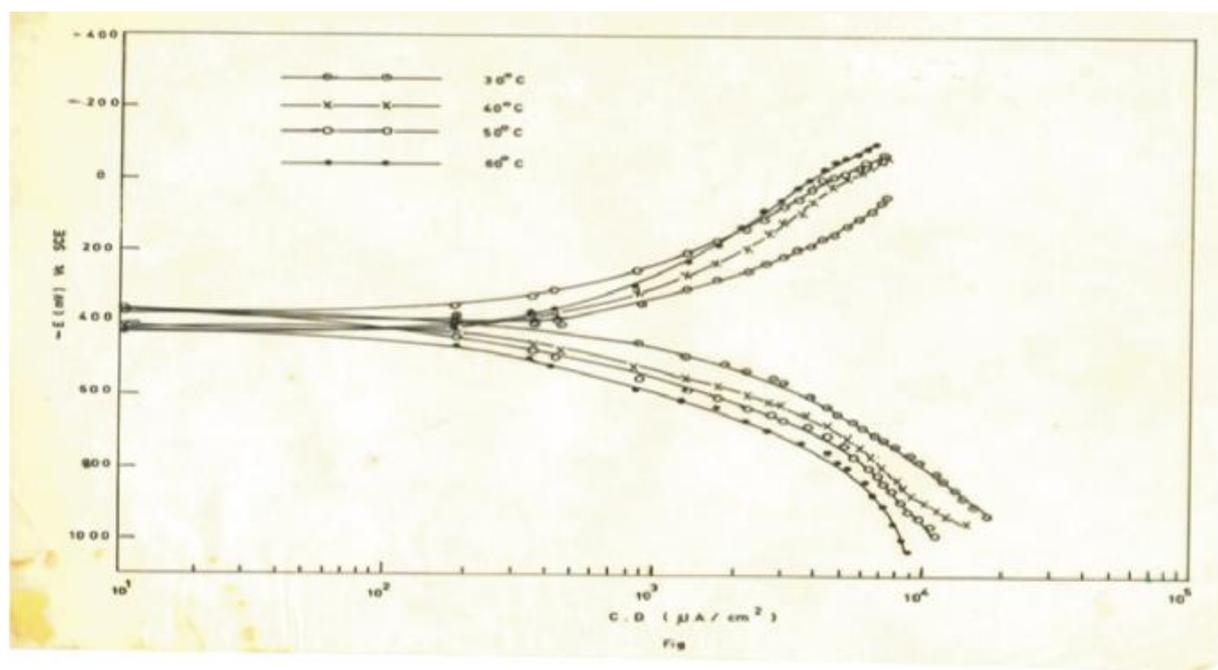
Fig. 7: Polarization curves of SX 316 steel in 0.5 M HCl at different temperatures

TABLE 4:   The Heat of absorption and activation energies

Compound	Heat of Adsorption KJ/mol at 10 ppm	Activation Energy EA kj/mol
0.5 M HCl	-	25.52
Plant Extract	51.19	18.24

It is assumed that the inhibitor molecule upon adsorption forms adsorption complex probably of the type [Metal-Inhibitor]$_{ads}$ on the metal surface. The presence of this complex on the metal surface reduces metal dissolution by blocking the active sites on the metal surface and corrosion is consequently inhibited.

4.   CONCLUSION

The plant extract reduces markedly the corrosion of steel in acid solution. The inhibition efficiency increases as the plant extract concentration is increased. The negative value of energy of adsorption indicates the spontaneity of the process. The phytochemical compounds are adsorbed through the hetero-atoms in their molecules on the metal surface.

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