Adansonia Digitata (Baobab) Plant Fruit Pulp And Seed Extracts As Green And Eco-Friendly Corrosion Inhibitor For Mild Steel In HCLSOLUTION

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Abstract:

The corrosion inhibition of mild steel in 0.5M HCl solution by the methanolic extracts of adansoniadigitata (baobab) fruit pulp (ADPE) and seeds (ADSE) was studied by gravimetric, potentiodynamic polarisation and SEM methods. The weight loss and polarisation studies reveal that the corrosion inhibition efficiency increases with increase in the concentrations of inhibitors ADSE and ADPE in acidic medium. ADSE exhibited high corrosion inhibitor efficiency (91.12%) for mild steel compared with that of pericarp extract (ADPE) which is possibly due to specific interaction between functional groups containing heteroatoms like nitrogen, sulfur, oxygen having free lone pair of electrons, and the metal surface. Tafel plots show that baobab fruit extracts act as efficient mixed-type corrosion inhibitors.The decrease in corrosion rate with increasing inhibitor concentration suggests that the inhibitor molecules act by adsorption on the metal surface.The SEM images confirmed severe surface deterioration of mild steel exposed to HCl solution in the absence of inhibitors. The ADSE exhibited high efficiency as green and eco-friendly corrosion inhibitor for mild steel in acidic medium due to the adsorption of flavonoids, phytosterols, amino acids and other phytoconstituents.

Keywords: Mild steel,Green inhibitor, Adansonia digitata, Acid corrosion, SEM.

1. Introduction

The Mild steel (MS) has wide spread applications in chemical and allied industries due to its low cost, ease of fabrication and good tensile strength in addition to its other desirable properties. MS corrosion has been a serious problem of global concern since many decades with the enhancement of its application in various fields such as automobiles, aviation, agriculture, building construction, power plants, oil and gas industry.

The MS corrosion in acidic media has gained significance in the recent past, due to increased industrial applications of mild steel in acidic solutions such as acid pickling, acid descaling, industrial cleaning and oil well acidizing [1]. Degradation of mild steel during service conditions has created limitation in industries. Therefore the protection of mild steel from corrosion is of paramount significance.

The corrosion damage of MS on exposure to acidic environment and consequent environmental pollution can be retarded considerably by the use of corrosion inhibitors [2]. The corrosion inhibition method of protecting mild steel has gained much importance recently among all the other protection methods for economical and practical reasons [3]. The use of inhibitors has been well documented as an effective method of protecting metallic materials from corrosion [4]. Synthetic organic inhibitors have shown efficiency in corrosion inhibition, but they have high cost of production, toxicity, and non-biodegradability properties which stimulates search for green corrosion inhibitors [5].

Green corrosion inhibitors are biodegradable and do not contain heavy metals or other toxic compounds. In recent times there has been serious search for better green corrosion inhibitors for MS so that the environment is protected. A large number of researchers have explored the natural plant extracts as effective corrosion inhibitors such as, Hunteriaumbellata [6], Ligulariafisheri [7], African perquetina [8], Nicotianatabacum [9], Psidiumguajava [10], Aquilariacrassna [11], Aloe Barbadensis [12], Adenopusbreviflorus [13], Musa paradisica [14], Hibiscus sabdariffa [15], etc.

The phytochemical investigation of Adansonia digitata (baobab) fruit seed and pulp revealed the presence of organic components such as flavonoids, terpenoids, phytosterols, amino acids, carbohydrates, lipids, vitamins and minerals. Methanol extract of the pulp of the fruits of Adansonia digitata contain catechin and various epicatechins [16] while the seed oil contains the compounds such as campesterol, cholesterol, isofucosterol, ß-sitosterol, stigmasterol and tocopheroll [17]. The presence of theses effective organic compounds in baobab fruit, which contain N, O heteroatoms,-OH group and n electrons in their structures is connected to corrosion inhibition. However, this baobab fruit pulp and seed extracts have not yet been investigated for their corrosion inhibition properties.

The present work was aimed to investigate the efficiency of methanolic extracts of Adansonia digitata fruit pulp and seedsas green and eco-friendly corrosion inhibitors for MSin 0.5M HCl solution by gravimetric, polaristaion and SEM techniques.

2. Experimental

2.l Materials and sample preparation

The MS plate of grade JIS G 3132 having the composition(wt.%) of C (0.18), Si (0.35), Mn (0.60), P (0.040), S (0.040), Cr (0.14) and remaining Fe,was used to prepare the coupons for this study. The MS coupons of dimension 76.2 mm x 22.23 mm x 3.18 mm with a hole drilled 6 mm from one side were used for weight loss measurements and for electrochemical studies the square rod of the same material with dimension 10 mm ×10 mm ×30mm coated with epoxy resin to give an exposed area of 1cm^2 was used. For surface studies by Scanning Electron Microscopy (SEM), the MS coupons of dimension 30 mm × 30 mm × 3 mm were used. Prior to each experiment, the coupons were mechanically polished with emery papers of grades 600, 800 and 1000, rinsed in distilled water, degreased in acetone, air dried stored in desiccators. The corrosive medium was prepared by diluting analytical grade sulphuric acid with distilled water to get 0.5M HCl solution.

2.2. Preparation of plant fruit extracts

Dry baobab (*Adansonia digitata*) fruits were collected from the villages around the University of Dodoma. The baobab fruits, pulp and seeds are shown in Figure 1.



(a) (b) (c)

Figure 1: Baobab fruits (a) pulp (b) and seeds (c)

The fruit pulp was separated from the seeds by manual grinding and sieving to remove the fibres. The collected powder was allowed to dry at room temperature and then stored in airtight polythene bags. 500 g each of dried pulp powder and seeds powder were each extractedseparately with 2.5 L of 80 % (V/V) aqueous methanol for 24 h at room temperature. Selection of the solvent was based on efficiency of extraction. After double filtration, first with clean textile then with Whatman filter papers to remove the residues, the extract were concentrated using warm air evaporator to get the crude extracts. Adansonia digitata pulp extract (ADPE) and Adansonia digitata seeds extract (ADSE) were stored in glass bottles for corrosion studies.

2.3. Gravimetric method

Gravimetric (weight loss) experiments were carried out as described by ASTM practice standard G-31. The weighed MS coupons (76.2 mm x 22.23 mm x 3.18 mm) were immersed in 200ml of 0.5M

HCl acid solutions containing different concentrations of ADSE and ADPE inhibitors for immersion periods of 24h, 48h and 72h at room temperature. After the experiments, the coupons were removed from the corrosive acid solution and immersed in 70°C mixtures of 200 g/L of NaOH and 20g/L of Zinc metal dust and left for the period of 45 minutes to remove the corrosion product from the surface of MS coupons. From the hot solution, coupons were then cleaned with brush in running tap water and rinsed with distilled water, cleaned in acetone, dried and reweighed. The mean of weight loss values of two identical coupons was used to calculate the surface coverage (0), percentage inhibition efficiency (%IE) and corrosion rate (CR) in millimetres per year (mmpy) using the following formula;

$$\text{surface coverage } (0) = \frac{w_0 - w_1}{w_o} \quad (1)$$

$$\text{Inhibition efficiency (\% IE)} = \frac{w_0 - w_1}{w_o} \times 100 \quad (2)$$

$$\text{Corrosion rate } (q) = \frac{87.6W}{qAt} \quad (3)$$

Where:

w_o = Average weight loss without inhibitor

w_1 = Average weight loss with inhibitor

w = Weight loss (mg)

q = Density (gm/cm^3) = 7.86 gm/cm^3(for mild steel)

A = Area of the mild steel coupon (cm^2)

t = Time (h)

2.4. Electrochemical measurements

The Electrochemical measurements were carried out using Autolabpotentiostat/galvanostat model Aut50665 and the data was collected with NOVA 1.11 software. All experiments were conducted at room temperature using 200 ml of 0.5 M HCl with different concentration of ADSE and ADPE inhibitors. Each experiment was repeated at least three times to check the reproducibility and the good reproducible results were reported. The Tafel curves were extrapolated to obtain corrosion current densities (i_{corr}), corrosion potential and corrosion rate. The inhibition efficiency was calculated from the measured i_{corr} values using the following formulas;

$$\text{Inhibition effeciency (\%IE)} = \frac{i^0_{corr} - i^1_{corr}}{i^0_{corr}} \times 100 \quad (4)$$

i^0_{corr} = Corrosion current density without in hibitor

i^1_{corr} = Corrosion current density with in hibitor

2.4. Surface analysis

Surface of polished mild steel coupons immersed in 0.5M HCl for 3 hours in the presence and absence of inhibitor were immediately examined using scanning electron microscope (SEM) COXEM MODEL CX200.

3. Results andDiscussion

3.1. Gravimetric Measurements

The corrosion in hibition behavior of different concentrations of the extracts (300,600 and 600 ppm) on MS in 0.5 M HCl was studied for various immersion periods of 24, 48 and 72 hours using weight loss method. The corrosion rate, surface coverage, and inhibition efficiency were calculate dusing equations(1), (2), and (3)and the data obtaine daregiven in Table 1. It is clear from the results that the inhibition efficiency (% IE) increases with increase in concentration of inhibitors.

This show sthe depend enceofin hibiting effect of phyto constituents of fruit extract.Whent he inhibitor molecules accumulate on the surface of mild steel, they reduces the interaction between mild steel surface and aggressive medium by increasing in coverage of mild steel surface leading to a compact and coherent film on the surface of mild steel [18]. The effec to f inhibit or efficiency on the inhibitor concentrations is shown in Figure 2. Increasing the concentration of inhibitor from 300 to 900 ppm, increases % IE from 73.36% to 77.57% for ADPE and 87.85% to 91.12% for ADSE.ADSE exhibited high corrosion inhibitor efficiency (74.5%) for mildsteel.

Table1: The gravimetric parameters for MSin 0.5 MHClin the presence and absence of inhibitors with different concentrations at various immersion periods

Inhibitor	Exposure time (h)	Conc. of inhibitorin ppm	W_1 (g)	Surface coverage	Inhibition Efficiency	Corrosion rate (mmpy) E^{-3}
ADSE	24	Blank	0.642			7.53
		300	0.078	0.8785	87.85	0.90
		600	0.066	0.8972	89.72	0.75
		900	0.057	0.9112	91.12	0.66
	48	Blank	0.911			5.26
		300	0.172	0.8112	81.12	0.92
		600	0.135	0.8518	85.18	0.77
		900	0.118	0.8705	87.05	0.69
	72	Blank	1.092			4.23
		300	0.380	0.6520	65.20	1.49
		600	0.327	0.7005	70.05	1.30
		900	0.311	0.7152	71.52	1.22
ADPE	24	Blank	0.642			7.53
		300	0.171	0.7336	73.36	2.02
		600	0.163	0.7461	74.61	1.92
		900	0.144	0.7757	77.57	1.68
	48	Blank	0.911			5.26
		300	0.378	0.5851	58.51	2.13
		600	0.344	0.6224	62.24	2.07
		900	0.313	0.6564	65.64	1.85
	72	Blank	1.092			4.23
		300	0.556	0.4908	49.08	2.17
		600	0.511	0.5321	53.21	1.94
		900	0.408	0.6264	62.64	1.57

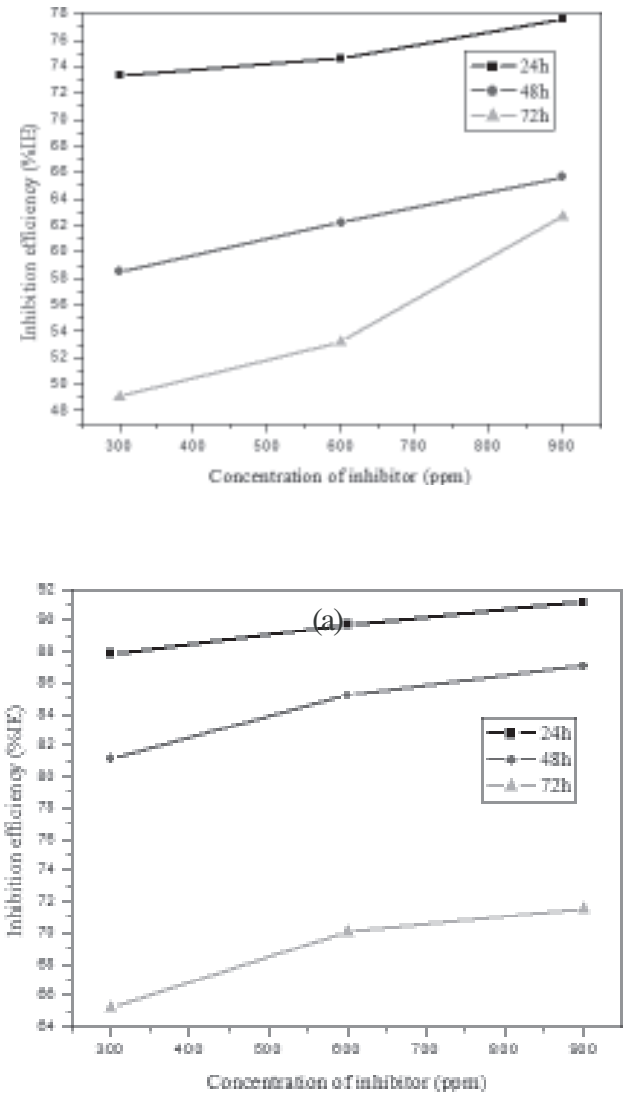


Figure 2: Inhibition efficiency plots against concentration of inhibitor ADPE(a) and ADSE (b) for MS corrosion in 0.5MHCl.

The degree of protection increases with the increasing surface coverage by adsorbed molecules [19]. Inhibition efficiency decreases with immersion time in ADPE and increase with immersion ime in ADSE. For ADSE this effect may be due to the formation of insolublefilm/corrosion producton the mild steel surface which lowers the interaction of the mild steel with the aggressive medium [20]. The decrease in corrosion rate with increasing inhibitor concentration suggests that the inhibitor molecules act by adsorption on the metal surface. Consequently the increase of the inhibitor efficiency was attributed to the increase in surface coverage by extract molecules[21].

3.2. Potentiodynamic Polarisation Measurements

Corrosion inhibition is achieved by altering the anodic process, cathodic process, or both, which result in the decreasing the rate of the corrosion process [22]. Potentiodynamic polarization parameters for the corrosion inhibition of mild steel in 0.5M HCl in the presence and absence of inhibitor are given in the Table 2. The corrosion current density i_{corr} values decreases markedly with increasing extract concentration from 175.94 to 32.86 A/cm^2 for ADPE, similarly for ADPE, i_{corr} decreases from 175.94to 19.58 A/cm^2. Tafel constants b_a and b_c markedly altered in presence of extract.

Polarization (Tafel) curves for MS in 0.5 MHCl solution at room temperature in the absence and presence of different concentrations of inhibitors are given in Figure3. From the figure it is obvious that the two extract salter the electrochemical process sesonmild steel by reducing the anodic reaction rates by reducing the corrosion current densities on both sides of the polarization curves. It can be concluded from Tafelslopes that the green inhibitor follows

mixed type inhibition mode as the shift in E_{corr} values for blank and inhibitor is less than 85 mV.Itis also seen form the plots that no significant change occurred for cathodic curves when compared with anodic curves which confirms that the inhibitor is more of anodic nature. It is also seen form the plots that no significant change occurred for cathodic curves when compared with anodic curves which confirms that the inhibitor is more of anodic nature.

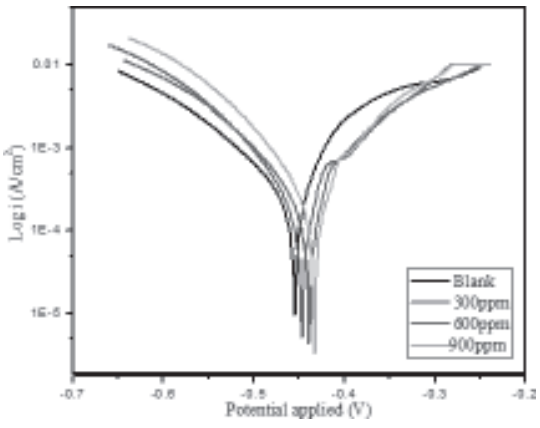
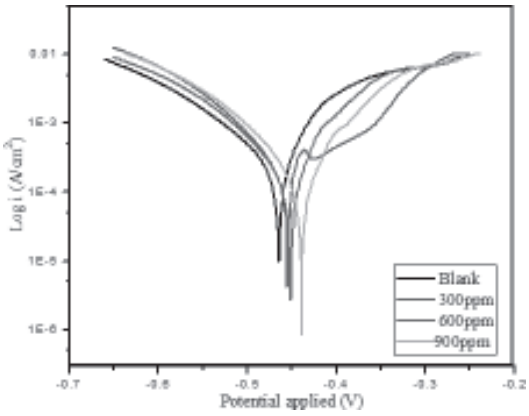


Table2: Potentio dynamic polarization parameters for the corrosion inhibition of mild steelin 0.5 HCl in the presence and absence of inhibitor

Inhibitor	Conc. of inhibitor (ppm)	-Ecor (mV)	icorr (A/cm^2)	b_a(mV /de c)	b_c(mV/ dec)	Inhibition efficiency (%)	Corrosionrate (mm/year)
ADPE	Blank	456.60	175.94	44.83	81.199		2.044
	300	443.78	46.35	78.435	44.940	73.655	1.956
	600	445.83	38.38	32.012	48.855	78.182	1.095
	900	449.44	32.86	27.78	35.206	81.326	0.915
ADSE	Blank	456.60	175.94	44.83	81.199		2.044
	300	430.71	64.04	35.639	58.865	63.601	1.481
	600	449.38	27.48	28.94	49.630	84.377	0.891
	900	457.23	19.58	32.729	35.846	88.872	0.688



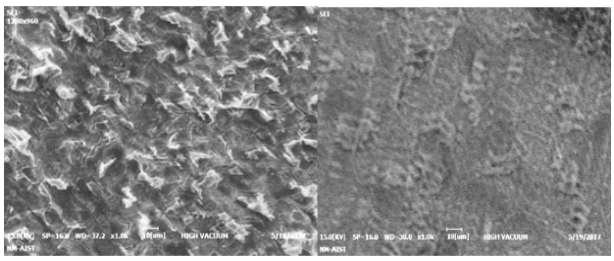
(b)

Figure 3: Tafel plots for MS corrosion in 0.5 M HCl solution with different concentrations of inhibitor ADPE (a) and ADSE(b).

The interaction between metal surface and lone pair of electrons of oxygen /nitrogen atoms of the extract decreases the anodic dissolution of mild steel due toadsorption.

3.3. SEManalysis

SEM images were recorded to know the surface deterioration before and after MS corrosion on exposure to the 0.5M HCl solution in the absence and presence of ADPE and ADSE inhibitors. The SEM images show that the mild steel was heavily corroded in 0.5M HClas shown in Figure 4 (a) without inhibitors where as in the presence of inhibitor ADSEas shown in 4 (b) the surface conditions were comparativelybetter.



(a) (b)

Figure 4: SEM images for mild steel surface after immersion in 0.5M HClwithout inhibitor ADSE (a) and with inhibitor (b).

This shows that the inhibitor molecules hinder the dissolution of mild steel byforming surface adsorbed layer and thereby reducing the corrosion rate. Metal surface was highly covered with the protective layer formed by the green inhibitor which prevents the metal from further attack of acid media[23].

4. Conclusions

The seeds(ADSE) and pulp(ADPE) extracts from baobab (Adansoniadigitata) fruits proved to be effective green and eco-friendly inhibitors for mild steel corrosion in 0.5M HCl medium. The gravimetric analysis revealed that both inhibitors ADSE and ADPE found to follow mixed type inhibition mode

even though anodic reaction influence was predominant.

The inhibitor efficiency of extracts was found increase with increase in inhibitor concentration. ADSE exhibited higher % IE compared to that of ADPE which could be attributed to the presence of higher percentage of active compounds in baobab seeds.

Potentiodynamic polaristaion plots revealed that the corrosion current density was least for higher concentration of inhibitors. Corrosion rate of MS was found to decrease with increase in extract concentrations. The surface analysis by SEM confirms the presence of protective film on MS surface in the presence of inhibitors. Both the inhibitors proved to be potential green an deco-friendly corrosion inhibitor for mild steelinacidic medium.

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