

Corrosion Inhibition of mild steel by alcoholic extract of

Artocarpus heterophyllus in acidic media

Vipin Kumpawat*, Urvija Garg, Lalitkumar Bansal**, Rajkiran

chauhan, S. P. Mathur and R. K. Tak

*Department of chemistry, Government College, Ajmer-305001-Rajasthan-INDIA.

E-Mail: vipinkb1979@gmail.com

**AFL Telecommunication, R&D center, Duncan, SC, U.S.

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Abstract

Corrosion inhibitors play a major role in the cost of effective control of corrosion. Because of the toxic nature and high cost of conventional chemical inhibitor, plant extracts are currently used as corrosion inhibitors. The present study has been undertaken to formulate environmentally acceptable inhibitors. Extracts of various plant parts consist of a mixture of flavonoids, alkaloids, carbohydrates and steroids. All these constituents are known for their inhibition of corrosion. The

inhibitive action of the alcoholic extracts of leaf, seed, fruit, bark and latex from

the *Artocarpus heterophyllus* plant towards hydrochloric and sulfuric acid corrosion of mild steel is tested by using mass loss and thermometric techniques. It was found that the extracts act as a good corrosion inhibitor for mild steel corrosion in all concentration of hydrochloric and sulfuric acid solution with the inhibitive efficiency up to 97.70%. It was found that the inhibition efficiency (η %) increases as the inhibitor concentration is increased. Inhibition Efficiency varies linearly with the immersion time and temperature. Maximum inhibition efficiency of 94.95% was obtained at 343K in 0.60% of inhibitor concentration of latex in 0.2N sulfuric acid solution. The adsorption of latex on mild steel surface was found to obey Langmuir adsorption isotherm. The inhibitive action of the extracts of *Artocarpus heterophyllus* was investigated using scanning electron microscopy.

Introduction

Corrosion is a process of deterioration or destruction and consequent loss of a solid metallic material, through an unwanted chemical or electrochemical attack by its environment, starting at its surface. Corrosion affects almost all metallic materials. Millions of dollars are lost each year because of corrosion. Dissolution of metal in aqueous media was a subject of interest as evidenced by a large number of reports in the literature [1-7]. In case of iron, oxide forms by oxidation

do not firmly adhere to the surface of the metal and flakes off easily causing

“pitting”. Extensive pitting eventually causes structural weakness and disintegration of the metal.

Mild steel, being an industrially important metal, it is widely used for mechanical and structural engineering purposes in bridge work, structural reactors, boilerplates, steam engine parts automobiles etc. In alkaline medium mild steel is fairly resistant to attack by alkali because of passiveness. However in acidic medium, the metal tends to corrode.

To prevent the metal from corrosion, corrosion inhibitors are used. Corrosion inhibitor is a substance which when added in a small quantities to the aqueous corrosive environment, effectively decreased the corrosion rate of a metal [8]. In some conventional chemical inhibitors like chromates, phosphates, borates, nitrites and silicates are present, which are hazardous, expensive and not environmental friendly. So there is an increased need for an environmental friendly, non toxic and low cost alternative for a corrosion inhibitor. It has been shown that natural products of plant origin contain different organic compounds e.g. alkaloids, tannins, pigments, organic and amino acids, and most are known to have inhibitive action towards corrosion [9-16]. Hence, the extract of naturally

occurring plant is a potential alternative to conventional corrosion inhibitor.

Various naturally occurring substances like *Datura- stramonium*[17] , *Henna* [18], *Prosopis juliflora* [19], *Fiaes religeosa* [20], *Ficus virens* [21], *Capparis deciduas* [22], *Annona squamosa*, *Ponamia glabra*, *ginger* [23], *garlic* [24], *Artocarpus heterophyllus* [25], *Acaccia senegal* [26] have been evaluated as a effective corrosion inhibitors.

Artocarpus heterophyllus is commonly known as Katahal, jackfruit. It has medicinal properties [27], antibacterial activity [28], and antioxidant property [29] and claimed to be an aphrodisiac [30]. The carbon prepared from jackfruit peel has earlier been used for the removal of malachite green dye [31] and its efficiency in removing metal ion like Cd (II) [32], Hg (II) [33], Cu (II) [34] and Rhodamine-B dye [35] from aqueous solution has also been reported. Generally the organic compounds having heteroatom O, N, S has higher basicity and thus assists corrosion inhibitor [36].

Latex of *Artocarpus heterophyllus* contains 82.6-86.4% resin and proteins [37] and bark contains 3.3% tannin. Seeds contain starch, calcium, iron, Vitamin B₁ and B₂. The seed powder was subjected to standard chemical tests as described by Farnsworth to determine the presence of alkaloids, flavanoids, phenols, steroids, oils, saponins, carbohydrates, starch, glucose, amino acids, and peptides [38]. It

contains many flavonoids like Artocapetin (5,2',4'-trihydroxy-7-methoxy flavone),

Artocarpanone (5,2',4' – trihydrox – 7 methoxy flavanone), Artocarpin and Isoartocarpin from heartwood. Cyanomaclurin, Dihydromorin, Artocarperin, mixture of Morin and Norartocarpetin, Artocarpin dimethyl ether, Dihydrocycloartocarpin, Artonin A and Artonin B from wood.

In the present investigation, the inhibitive effects have been evaluated of alcoholic extract of leaf, seed, fruit, bark and latex from *Artocarpus heterophyllus* plant. In this work we used mass loss method and thermometric measurement to calculate the corrosion inhibition efficiency.

Experimental

Specimen preparation

Rectangular specimens of mild steel of dimensions 2.5 x 1.5 x 0.025 cm with a small hole of about 2 mm diameter near the upper edge were employed for the determination of mass loss measurements. The chemical composition of test specimens used was C=0.12%, Mg=0.10%, Si=0.14%, S=0.01% and Fe remainder. Specimens were cleaned by buffing to produce a mirror finish with the help of emery paper and were then degreased with acetone.

Test Solution preparation

The solution of 0.2, 0.5 and 1N hydrochloric acid and sulfuric acid were prepared using doubly distilled water. The extract of *Artocarpus heterophyllus* was obtained by dried, then finally powdered and extracted with ethanol. The solvent is distilled off and the residue treated with inorganic acids. Where the bases are extracted as their soluble salts. The free bases are liberated by the addition of any base and extracted with various solvents e.g. ether, chloroform, etc. The mixture of bases thus obtained is separated by various methods into the individual compounds.

Measurement

Mass Loss Method

In the mass loss experiments, a clean weighed mild steel coupon was immersed completely in a 50 ml beaker containing the test solution at room temperature with the aid of glass rod and hooks. Evaporation losses were made up with distilled water. The coupons were retrieved at 3 hour interval progressively for 24 hour immersed in different concentration of hydrochloric and sulfuric acid. After the test, specimens were cleaned with saturated solution of ammonium acetate. The differences in weight of the coupons were taken as the mass loss, which was used to calculate inhibition efficiency ($\eta\%$).

The percentage of inhibition efficiency ($\eta\%$) was calculated using eq. (1) [39].

$$\eta\% = \frac{\Delta M_u - \Delta M_i}{\Delta M_u} \times 100 \quad (1)$$

Where ΔM_u and ΔM_i are the mass loss of the metal in uninhibited acid and inhibited solution respectively.

The Corrosion Rate in mmpy (mille miles per year) can be calculated using eq. (2) [40].

$$\text{Corrosion Rate} = \frac{\text{Mass Loss} \times 87.6}{\text{Area} \times \text{Time} \times \text{Density}} \quad (2)$$

Where mass loss is expressed in mg, Area is expressed in square cm of metal surface exposed, Time is expressed in hour of exposure, and metal density is expressed in gm/cm^3 .

The value of Corrosion Current (i) can be calculated using eq. (3) [41].

$$i = \frac{\text{CR} \times F}{N} \quad (3)$$

Where i is the corrosion current, CR is corrosion rate, F is feradey's constant which is equal to 96500 and N is the number of electron.

Thermometric method

Inhibition efficiencies were also determined by using a thermometric technique. This involved the immersion of single specimen measuring 2.5 x 1.5 x 0.025 cm in a reaction chamber containing 50ml of solution at an initial temperature of $25 \pm 0.1^\circ \text{C}$. Temperature changes were measured at interval of 5 min. using a thermometer with a precision of 0.1°C . the temperature increased slowly at first, then rapidly and attained a maximum value before falling. The maximum temperature was recorded.

The percentage inhibition efficiencies ($\eta\%$) were calculated using eq. (4) [42].

$$\eta\% = \frac{\text{RN free} - \text{RN Ix}}{\text{RN free}} \times 100 \quad (4)$$

Where RN free and RN i are the reaction number in the absence and presence of inhibitors respectively and RN ($\text{K} \cdot \text{min}^{-1}$) is defined using eq. (5).

$$\text{RN} = \frac{T_m - T_o}{t} \quad (5)$$

Where T_m and T_o are the maximum and initial temperatures respectively and t is the time required to reach the maximum temperature.

Surface analysis by SEM

The surface morphology of mild steel specimens in 1 N sulfuric acid in the absence and presence of the extract of *Artocarpus heterophyllus* was studied using scanning electron microscope model number Hitachi SU 1500.

Result and discussion

Mass Loss study

All the inhibitors reduced the corrosion rate to a significant extent. The maximum efficiency of inhibitor was obtained in lowest acid concentration (i.e. 0.2 N) in sulfuric acid. The inhibitors have shown efficiencies in the range from 71.26% to maximum of 97.70% for latex, the corrosion is substantially reduced in the case of 0.60% extract of leaf, seed, fruit, bark and latex in 0.2 N sulfuric acid solutions. The effect of inhibition was also monitored with time; it was observed that the mass loss decreased gradually up to 24 h in both acid solutions. The maximum efficiency of inhibitor was obtained in the lowest acid concentration (i.e. 0.2N) in hydrochloric and sulfuric acid (Table-1).

Thermometric study

The values of Inhibitor efficiencies were also determined by the thermometric method for mild steel in 5N hydrochloric acid and 5N sulfuric acid solution. Inhibitor efficiencies were recorded with various inhibitor concentrations. Results obtained are in good agreement with those from mass loss experiment. The variation of the reaction number with inhibitor concentration, presented graphically in (Fig. 2-3), which shows that reaction number decreases with increasing inhibitor concentration and the value of Reaction number is greater in sulfuric acid in comparison to hydrochloric acid solution.

Generally, the adsorption of organic molecules on metallic surfaces involves oxygen, nitrogen and sulfur atoms and in case of plant extracts of *Artocarpus heterophyllus* hydroxyl group of steroids, flavonoids and ascorbic acid (Fig. 1), nitrogen of alkaloid and oxygen atom may be responsible for the adsorption.

Organic inhibitors having active portions are generally C-H chain or rings with positively charged amine nitrogen groups at one end. In acid and water, the terminal primary, secondary and tertiary amine group takes additional hydrogen that gives them a net positive or cationic charge. The polar amine group is adsorbed on the metal and the hydrocarbon portion forms an oily water repellant

surface film. The molecular shape (dissymmetry) helps these materials act as surfactant and can stabilize emulsion of oil and water. Organic corrosion inhibitors [43-44] may function by (a) chemisorptions of the molecule on a metallic surface, (b) complexing of the molecule with the metal ion, which remains in a solid state, (c) neutralizing the corrodent and (d) adsorbing the corrodent. They offered large coverage due to the long hydrocarbon chain and by the presence of oh groups. Being hydrophilic in nature, the OH groups counteracted the effects of chain length and ensured higher solubility.

The process may block active sides, hence may decrease the corrosion rate. The OH- group present in the flavonoids which is present in latex of *Artocarpus heterophyllus* has a positive inductive effect, which increases the electron density at the nitrogen atom of protein. This explains the higher inhibition efficiencies have shown by latex for 0.60% concentration. Adsorption plays an important role in the inhibition of metallic corrosion by organic inhibitors.

Impact of immersion time

The results are obtained by mass loss method for various exposure times for mild steel specimens immersed in 0.2N sulfuric acid for different concentration of latex are presented in Table (2) and Fig (4). It is found that the latex has a good

property to inhibit the corrosion of mild steel for 0.2 N sulfuric acid, even when

the exposure time is large. It is observed that the inhibition efficiency increases with the increase in time. This indicates that the latex of *Artocarpus heterophyllus* in 0.2N sulfuric acid is stable for maximum at 24 hours. This may be due to stability of adsorbed molecule on mild steel surface.

Effect of temperature

The samples were exposed in acidic media at specific temperature (303K, 313K, 323K, 333K and 343K). It is illustrated that the maximum inhibition efficiency was 94.95% at an optimum concentration of 0.60% in 0.2N sulfuric acid at 343K Table (3), Fig. (5). The enhancement of IE at higher temperature may be due to Higher activation energy available for adsorption at higher temperatures and enhancement in the surface coverage at higher temperature by the inhibitor molecule on mild steel surface.

Artocarpus heterophyllus has various types of flavonoid and ascorbic acid which is shown in Fig. (1), maybe responsible for the corrosion inhibition.

Adsorption Isotherm

The corrosion inhibition with the help of inhibitors involves the adsorption of the inhibitor on the surface of the metal is the phenomenon of interaction between

the metal surface and indicator. Many investigators have used the Langmuir

adsorption isotherm to study inhibitors characteristics, assuming that the inhibitors absorbed on the metal surface decreases the surface area available for the cathodic and anodic reactions to take place.

Langmuir adsorption isotherm

$$\text{Log } [\theta / 1 - \theta] = \text{Log } A + \text{Log } C - (\theta / 2.3 R T) \quad (6)$$

Where θ is the surface coverage, A is a temperature independent constant and C is the concentration of the inhibitor. A Straight line was obtained on plotting $\log [\theta / 1 - \theta]$ vs. $\log C$ Fig (6), suggesting that the adsorption of the compounds from sulfuric acid on mild steel surface follows Langmuir adsorption isotherm.

SEM

The SEM study shows that the surface changes in the specimen. Fig. 7 depicts the view of pure mild steel sample. Fig. 8 is in 1N sulfuric acid after the exposure of the specimen for about 1 hour, where as fig. 9 in sulfuric acid with inhibitor for the same time. Fig. 8 shows immense roughness which indicates the metal surface has been adversely affected in 1N sulfuric acid. In case of fig.3 in the presence of inhibitor, corrosion is almost inhibited, shows almost plan surface.

Summary

It is anticipated that the proposed investigation on natural products as corrosion inhibitors may be useful for preventing the losses caused due to corrosion. The importance of the proposed study lies in the fact that the natural products proposed to be utilized as corrosion inhibitors are readily and very cheaply available. Moreover this applicability is valid for a variety of metals and corrosive media. To observe the influence of influence of various parameters like inhibitor concentration or acid concentration, corrosion inhibition efficiency (η %) of the compounds has been calculated by mass loss measurements and thermometric method.

The extracts of *Artocarpus heterophyllus* is found to be an effective inhibitor in acid media giving up to 93.75% in hydrochloric acid and 97.70% in sulfuric acid solution. This can be safely used without any hydrogen damage, toxic effects and pollution. Mass loss and thermometric method has shown that the inhibition efficiency of all inhibitors increases with increase in inhibitor concentration.

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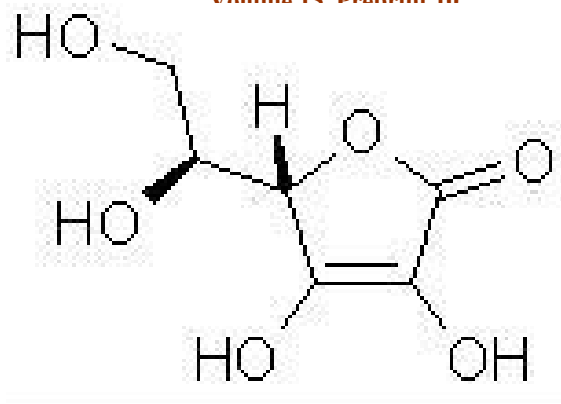


Fig. 1. Structure of Ascorbic acid

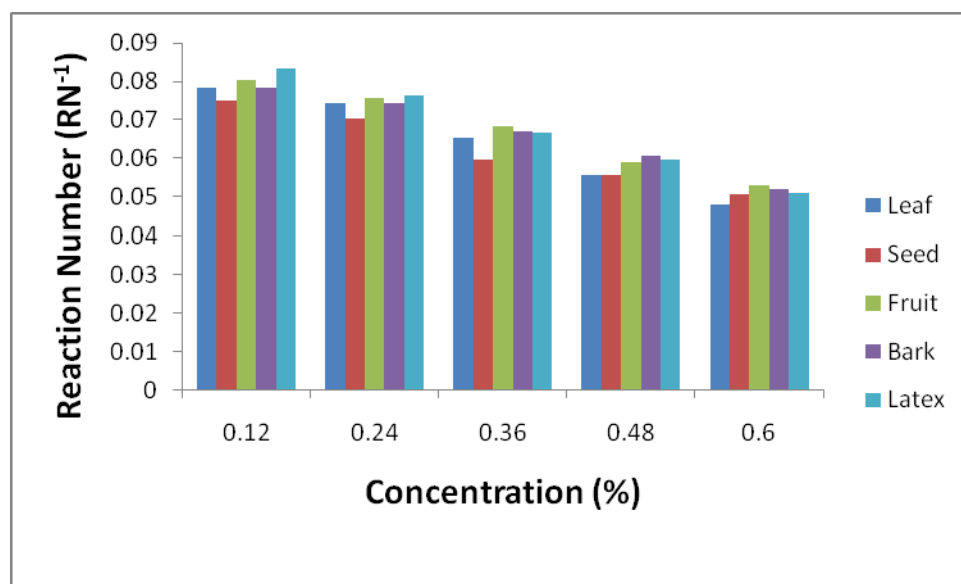


Fig. 2. Variation of reaction number vs. concentration with all inhibitors in 5N hydrochloric acid solution in mild steel

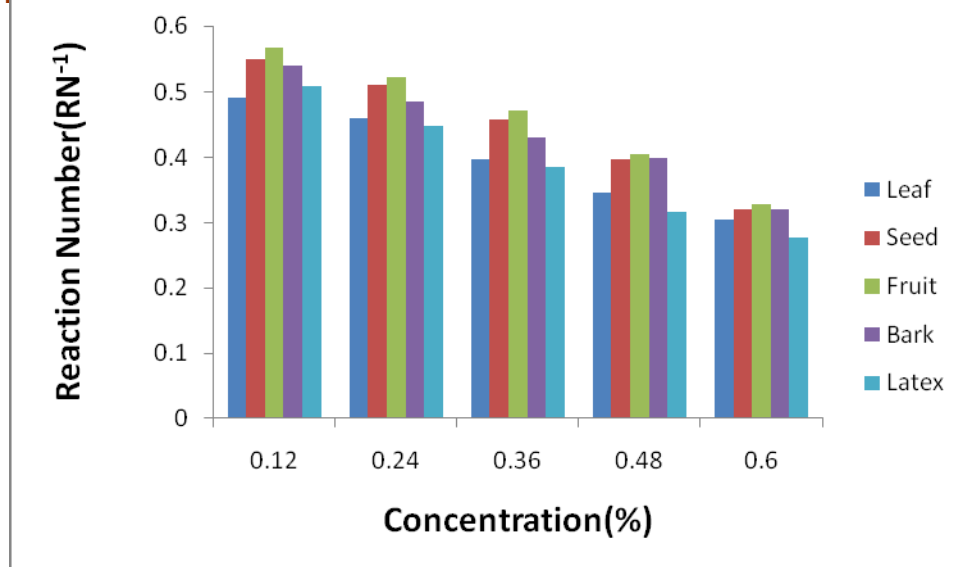


Fig. 3. Variation of reaction number vs. concentration with all inhibitors in 5N sulfuric acid solution in mild steel

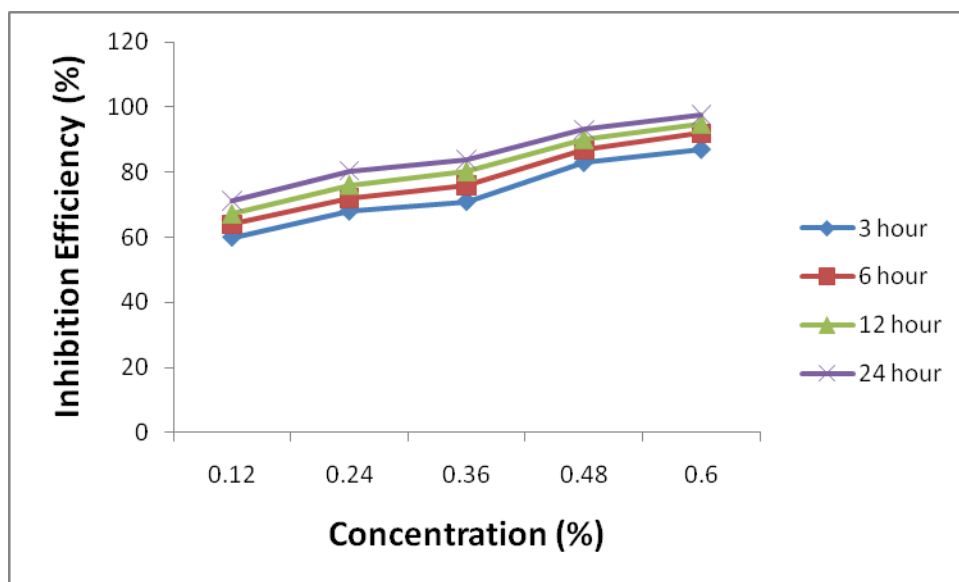


Fig. 4. Inhibitor concentration as a function of inhibitor efficiency

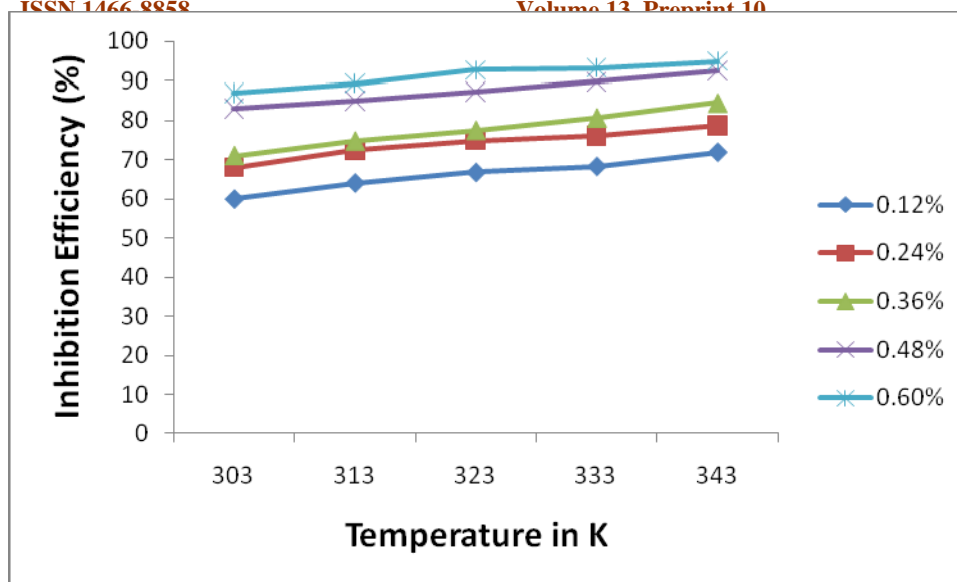


Fig. 5. Influence of temperature as a function of IE and concentration

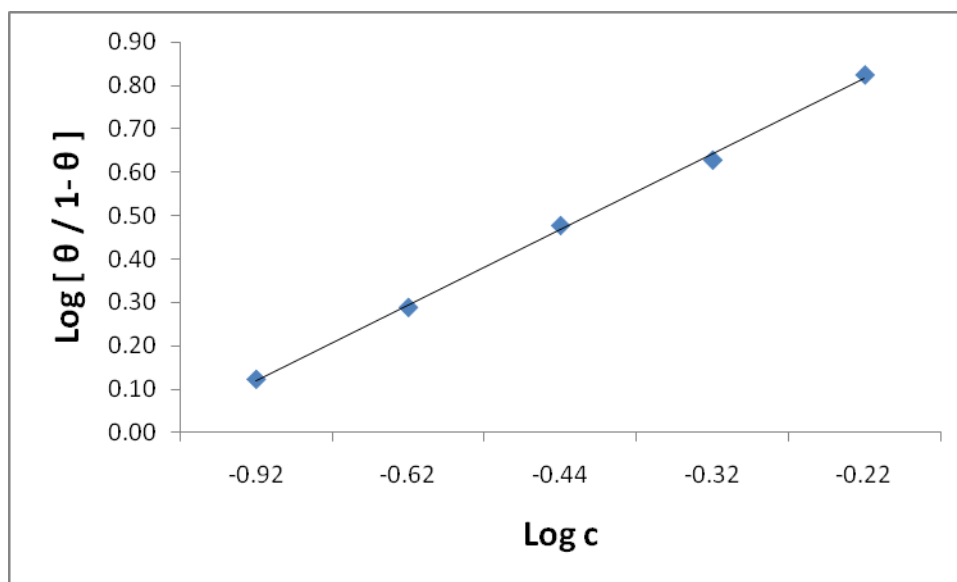


Fig. 6. Langmuir adsorption isotherm plot for the adsorption of extract of leaf in 0.2N sulfuric acid on the surface of mild steel at the room temperature (24h).



Fig. 7. SEM image of sample of mild steel without immersion.

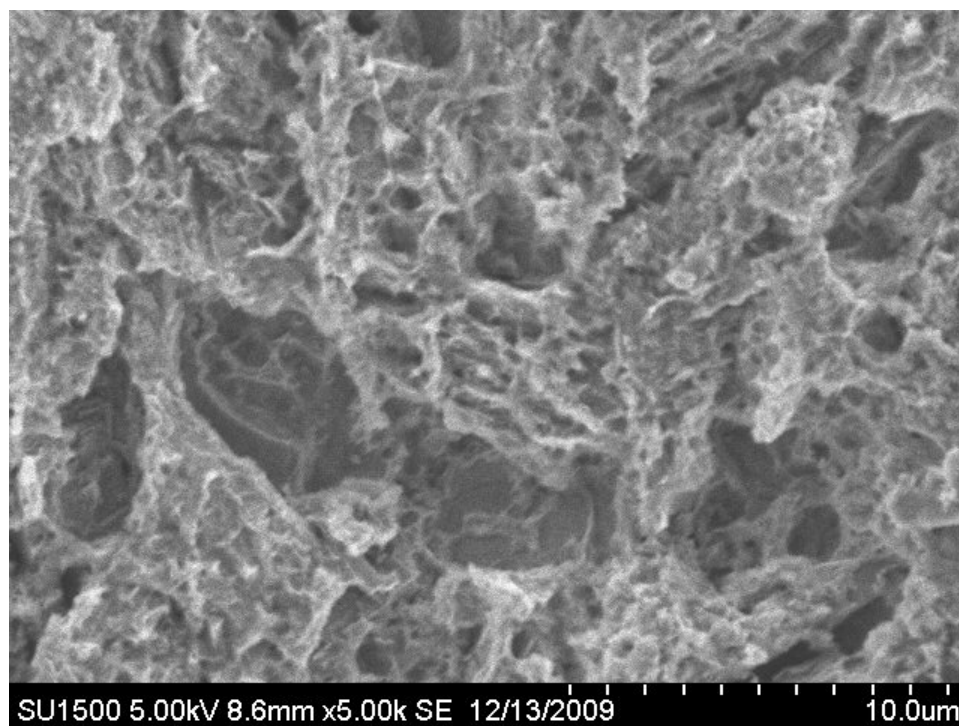


Fig.8. SEM image of sample of mild steel after immersion in acid solution

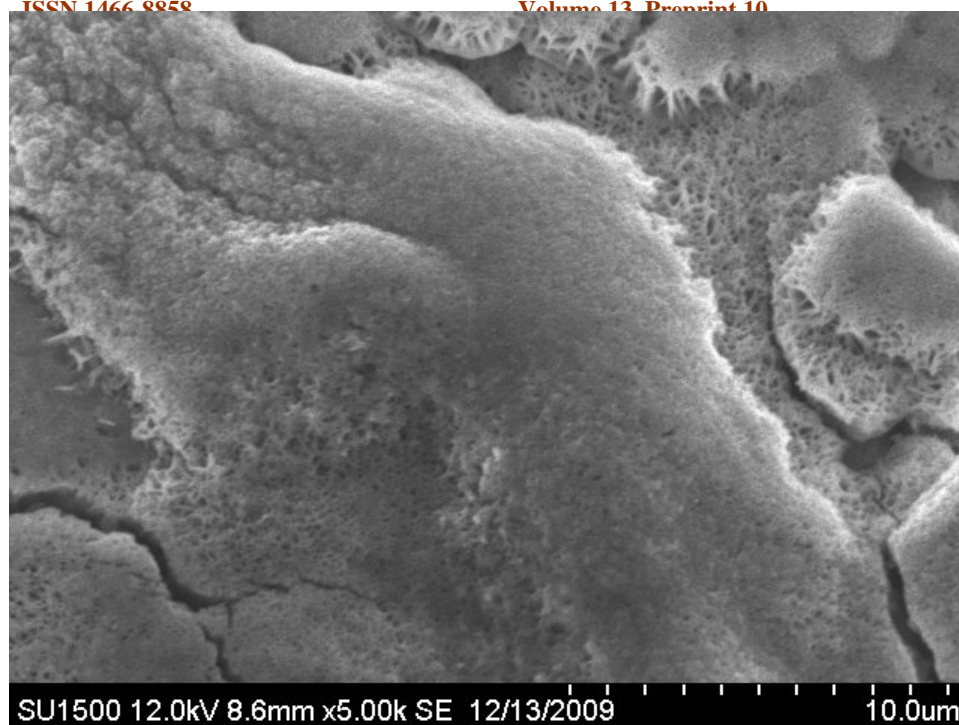


Fig. 9. SEM image of sample of mild steel after immersion in Inhibitor solution

Table 1:-Comparison of hydrochloric acid vs. sulfuric acid for mild steel with different concentration of inhibitor of *Artocarpus heterophyllus*.

Hydrochloric acid				Sulfuric acid			
Conc. (%)	0.2 N (24h)	0.5 N (24h)	1 N (24h)		0.2 N (24h)	0.5 N (24h)	1 N (24h)
Leaf							
0.12	56.25	51.67	47.83		66.67	64.17	60.99
0.24	65.63	65.00	59.78		75.86	73.33	70.21
0.36	75.00	70.00	64.13		82.76	80.00	75.89
0.48	81.25	76.67	70.65		89.66	86.67	83.69
0.60	93.75	90.00	83.70		96.55	91.67	88.65
Seed							
0.12	53.13	48.33	43.48		68.97	65.83	63.12
0.24	65.63	61.67	56.52		77.01	73.33	68.79
0.36	78.13	73.33	68.48		83.91	80.00	78.01
0.48	84.38	81.67	75.00		93.10	88.33	83.69
0.60	90.63	86.67	81.52		95.40	90.83	87.94
Fruit							
0.12	56.25	51.67	45.65		70.11	65.00	60.99
0.24	68.75	65.00	59.78		75.86	71.67	68.09
0.36	75.00	71.67	66.30		83.91	80.00	78.01
0.48	84.38	80.00	75.00		90.80	86.67	85.11
0.60	90.63	85.00	80.43		94.25	90.00	87.23
Bark							
0.12	59.38	51.67	46.74		68.97	65.00	61.70
0.24	65.63	60.00	56.52		78.16	74.17	65.25
0.36	78.13	73.33	68.48		85.06	83.33	77.30
0.48	84.38	80.00	76.09		90.80	88.33	82.27
0.60	90.63	86.67	80.43		93.10	90.83	87.94
Latex							
0.12	62.50	56.67	50.00		71.26	68.33	63.83
0.24	65.63	61.67	56.52		80.46	76.67	73.05
0.36	78.13	73.33	69.57		83.91	80.83	75.89
0.48	84.38	81.67	76.09		93.10	90.00	87.23
0.60	93.75	88.33	84.78		97.70	94.17	90.78

Table 2- Dependence of inhibition efficiency on concentration and exposure time for latex of *Artocarpus heterophyllus* in 0.2 N sulfuric acid in mild steel.

Conc. (%)	IE (%)	IE (%)	IE (%)	IE (%)
	3hr	6hr	12hr	24hr
0.12	60.00	63.98	67.19	71.26
0.24	68.03	72.03	76.04	80.46
0.36	71.00	76.06	80.21	83.91
0.48	82.97	86.92	90.10	93.10
0.60	86.99	91.95	94.79	97.70

Table 3- variation of inhibition efficiency at higher temperatures for latex of *Artocarpus heterophyllus* in 0.2N sulfuric acid

Conc (%)	303K	313K	323K	333K	343K
	IE (%)	IE (%)	IE (%)	IE (%)	IE (%)
0.12	60.00	64.12	66.83	68.36	71.99
0.24	68.03	72.56	74.91	76.05	78.76
0.36	71.00	74.78	77.54	80.71	84.51
0.48	82.97	85.01	87.2	89.76	92.56
0.60	86.99	89.38	92.71	93.31	94.95

Reference

1. I. D. Vedonenko, M. M. Grantsianskii, Ukr. Khim Zh. 1962, 28, 991.
2. V. I. Ponomarenko, Y. V. Fedorov, Z. V. Pantilova, N. F. Kovalenko, Vopr. Khim Technol. 1981, 9, 64.
3. M. Amarnath, S. Gurmeet, K. R. kumar, Met. Corros. Proc, Int. Congr. Met. Corros. 8th . 1981, 2, 1239.
4. A. S. Fouda, M. M. El-Semongy, J. Indian Chem. Soc. 1982, 59, 89.
5. A. Baraka, M. E. Ibrahim, M. M. Al-Abdalah, Metallberflache. 1981, 35, 263.
6. T. P. Hoar, R. D. Holliday, J. Appl. Chem. 1953, 3, 502.
7. G. L. Makorei, V. R. Koroleva, I. N. Kumarkova, E. M. Norikova, Zashch Met. 1983, 19, 132.
8. J. N. Putilova, S.A.K. Balezin, U.P. Barannik, Pergmon Press, London. 1960.
9. H. Ashassi-Sorkhabi, D. Seifzadeh, Int. J. Electrochem. Sci. 2006, 1, 92.
10. A. A. Rahim, E. Rocca, J. Steinmetz, M.J. Kassim, R. Adnan, M. Sani Ibrahim, Corros. Sci. 2007, 49, 402.
11. E. E. Oguzie, Mater. Chem. Phys. 2006, 99, 441.
12. E. E. Oguzie, Corros. Sci. 2007, 49, 1527.
13. Z. Ghasemi, A. Tizpar, Appl. Surf. Sci. 2006, 252, 3667.

14. A. M. Abdel-Gaber, B. A. Abd-El-Nabey, I. M. Sidahmed, A. M. El-Zayady, M.

Saadawy, Corros. Sci. 2006, 48, 2765.

15. C. A. Loto, Corros. Prev. & Control. 2001, 48, 38.

16. A. Y. El-Etre, J. Colloid & Interface Sci. 2007, 314, 578.

17. G. S. Verma, Anthony, Prashant, S. P. Mathur, J. Electrochem Soc. India.
2002, 51, 173.

18. A. Chetouani, B. Hammouti, Bull. Electrochem. 2003, 19, 23.

19. R. Chowdhary, T. Jain, S. P. Mathur Bull. Electrochem. 2004, 20, 67.

20. T. Jain, R. Chowdhary, P. Arora, S. P. Mathur, Bull. Electrochem. 2005, 21,
23.

21. T. Jain, R. Chowdhary, S. P. Mathur, J. Electrochem Soc. India. 2004, 53, 33.

22. P. Arora, T. Jain, S. P. Mathur, Chemistry- An Indian J. 2005, 1, 766.

23. A. Bouyanzer, B. Hammouti, Bulletin Electrochem. 2004, 20, 63.

24. S. L. Priya, A. Chitra, S. Rajendran, K. Anuradha, J. Electrochem Soc. India.
2005, 54, 37.

25. V. Kumpawat, U. Garg, R. K. Tak, J. Indian Council Chemistry. 2009, 26, 82.

26. U. Garg, V. Kumpawat, R. K. Tak, Int. J. of Pure and Appl. Chem. 2009, 4 (in
press).

27. J. F. Morton, F. L. Miami, J. Morton, In: Fruit of warm climates; 1987, 58.

28.M. R. Khanm, A. D. Omoloso, M. Kihara, Fitoterapia. 2003, 74, 501.

29.F. N. Ko, Z. J. Cheng, C. N. Lin, C. M. Tang, Free Radical Biology and Medicine. 1998, 25, 160.

30.W. D. Premawathi, Artocarpus heterophyllus Lam. In Osuturu Visituru edited by Weragoda P B, part III, Depatment of Aurveda, Colombo, Sri Lanka. 1994.

31.I. B. Stephen, N. Sulochana, Indian J. Chem.Tech. 2002, 9, 201.

32.I. B. Stephen, N. Sulochana, Bioresource Technol. 2004, 49, 94.

33.I. B. Stephen, N. Sulochana in Proc 17th Int Conf Solid Waste Tecnol Manage, edited by R. L. Mersky (Widener University Philadelphia, PA). 2001, 802.

34.I. B. Stephen, N. Sulochana in Proc Symp Geoenvironment Reclam, edited by A. G. Paithankar, P. K. Jha, R. K. Agarwal (Oxford and I B H publishing Co Pvt. Ltd., New Delhi). 2000, 285.

35.I. B. Stephen, N. Sulochana, Indian J. Chem. Tech. 2006, 13, 17.

36.I. N. Putilova, S. A. Balizin, V. P. Barankik, Metallic Corro. Inhi. pergaman press, London. 1960.

37.Curr. Sci. 1965, 34, 212.

38.N. R. Franworth, J. Pharmaceut. Sci. 1996, 55, 225.

39.G. Trabanelli, V. Carassiti, Advance in Corrosion Science and Technology,

V.I. Eds-M. G. Fontana, R. W. Stachle, Plenum press, NY. 1976.

40.S. Laxmi, J. R. Chandra, V. Tainkili SEAST. 2004, 39, 127.

41.D. A. Jones, Principles of corro. 1996, 2, 34.

42.M. Stern, A. L. Gear, J. Electrochem. Soc. 1957, 104, 56.

43.O. L. Riggs, Jr. RL Every, Corrosion. 1962, 18, 262.

44.R. H. Hausler, Proc. Inti. Conf. on corrosion Inhibition, Texas, Dallas, 1983, 7,
16.