Inhibition of corrosion of mild steel by mixed fatty acid thiosemicarbazides derived from non traditional oils

S.D. Toliwal*, Kalpesh Jadav

Department of Industrial Chemistry, Institute of Science and Technology for Advanced Studies and Research (ISTAR), Vallabh Vidyanagar 388-120, India
*Corresponding:Email: toliwalsd@yahoo.co.in

Abstract

Thiosemicarbazides of mixed fatty acid hydrazides from nontraditional oils (neem, rice bran and karanja) have been synthesized and evaluated as corrosion inhibitors for mild steel (MS) in hydrochloric acid (HCl) solution by weight loss method. Adsorption of all thiosemicarbazides on MS surface in acid solution obeyed Temkin's adsorption isotherm. Inhibition efficiency of these compounds increases with increase in concentration of the compound, and vary with solution temperature, immersion time and concentration of acid solution. Various thermodynamic parameters were also calculated to investigate the mechanism of corrosion inhibition.

Keywords: Corrosion inhibition; Mild steel; Nontraditional oils; Mixed fatty acid thiosemicarbazides

Introduction

Hydrazides are important starting materials for a wide range of derivatives used as pharmaceutical products, corrosion inhibitors (CIs) and surfactants. Several triazole derivatives obtainable from hydrazides exhibit corrosion inhibition [1], antibacterial [2] and insecticidal activities [3-4]. Corrosion inhibition in acid medium of mild steel (MS), which is extensively used as fabrication material in sugar, petrochemical, food, paper and textile industries, has been studied [5-7]. Organic compounds containing nitrogen (N), sulphur (S) and/or oxygen (O) atoms are widely used as CIs in acidic environments [8-15] in various industries. CIs derived from fatty acids constitute an important and potential class of inhibitors [16-18]. Corrosion inhibiting properties of modified oils [19-20] and fatty acid [21] in acidic media have been investigated and reported earlier.

However, little work has been reported on mixed fatty acid thiosemicarbazides as corrosion inhibitors in 1 N acidic solution. In continuation of work on the development of acid CIs based on fatty materials [22-32] the authors have studied the corrosion inhibiting behavior of fatty acid thiosemicarbazides, namely thiosemicarbazides of nontraditional oils like neem (AN_2), rice bran (AR_2) and karanja (AK_2), on corrosion of MS in HCl solutions with a view to explore their utilization in new field.

Up gradation and utilization of non-traditional oils has been the subject of various investigative studies [33-38].

Experimental

Material Preparation

Oils were procured from Mahavir oil industries Ltd, Mahemdavad. Physico-chemical analysis of neem, rice bran and karanja by standard BIS methods [39] gave, respectively : sp.gr$^{25\ 0C}$, 0.917, 0.918 and 0.921; acid value, 15.41,14.12 and 17.34; iodine value, 75.01,109.42 and 90.78; refractive index at 25 ^{0}C, 1.465, 1.462 and 1.458; and sponification value, 188.16,185.62 and 189.71. Fatty acid composition of oils (Table 1) was determined by gas liquid chromatography [40] (GLC) by Perkin Elmer Auto system XL gas chromatograph with flame ionization detector (FID). The capillary column BP-225 (moderate polar, 25m x 0.22mm x 0.25 microns) packed with 50% cynopropyl phenyl polysiloxane at 220^{0}C with nitrogen as carrier gas at flow rate 1 ml/min at an injector temperature of 250^{0}C. All other chemicals were of laboratory grade and were used without any modification.
MS coupons having composition in wt% (C, 0.084; Mn, 0.34; Si, 0.13; P, 0.037; S, 0.095 and remainder iron) with a hole (diam, 3mm) near upper edge have been used for corrosion inhibition study.

Preparation of methyl ester from oil [41]

Methyl ester from oils were prepared by acid catalyzed esterification method in which 100 gm oil was taken in 500 ml round bottom flask and 300 ml methanol and 1ml concentrated sulfuric acid were added. The contents were refluxed for 4 h on water bath. At the end of reaction, the excess methanol was distilled off and 50 ml distilled water was added. The contents were then transferred to a separating funnel and lower aqueous layer was withdrawn. The upper organic layer was washed 2-3 times with 1 % sodium carbonate solution to remove un-esterified fatty acids. The esters were purified by distillation under 4-5 mm Hg pressure.
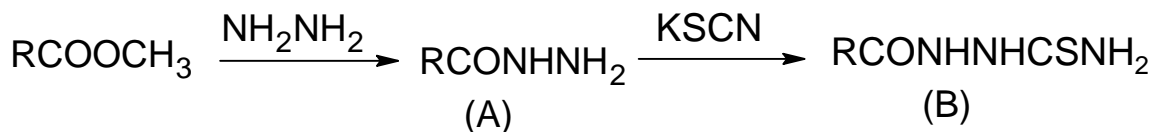
Preparation of mixed fatty acid hydrazides [42]

To a solution of fatty acid esters (0.1M) in ethanol (150 ml) hydrazine hydrate (95%, 0.2 M) was added. The reaction mixture was refluxed for 3 - 4 h. It was cooled, and the solid separated was collected, washed and recrystallised from ethanol.

Preparation of Thiosemicarbazide [43]

To a solution of a mixed fatty acid hydrazide (0.02 M) in methanol (50 ml) a solution of potassium thiocynate (0.03 M) and hydrochloric acid 3 ml was added with constant stirring. The mixture was immediately evaporated to dryness on a steam bath and heated for an additional hour with another 50 ml ethanol. The resulting solid was treated with water, and with little ethanol and recrystallised from ethanol.

The preparation of thiosemicarbazides of mixed fatty acid hydrazides, is schematically shown as under:

$$RCOOCH_3 \xrightarrow{NH_2NH_2} \underset{(A)}{RCONHNH_2} \xrightarrow{KSCN} \underset{(B)}{RCONHNHCSNH_2}$$

Scheme 1 Preparation of Fatty thiosemicarbazides of mixed fatty hydrazides

R- Fatty alkyl chain; **A-** Fatty acid hydrazides; **B-** Fatty Thiosemicarbazides

Characterization of thiosemicarbazides

Infrared (IR) spectra of all thiosemicarbazides were recorded by FTIR- 8201 PC (Shimadzu) infrared spectrophotometer in KBr.

IR spectra of thiosemicarbazides of all three oils (Fig. 5, 6 and 7) showed characteristic bands at 2850 and 2906 cm^{-1} corresponds to C-H stretching of long alkyl chain. Absorption band at around 1746 cm^{-1} is due to C=O stretching. Absorption bands at 3320 cm^{-1} and 3220 cm^{-1} corresponds to N-H group stretching, which is typical for primary amine and amide. A strong band at 1160 cm^{-1} for C=S was observed. Additional characteristic absorption band at 1600-1630 cm^{-1} corresponding to C=O secondary amide and N-H stretching in primary amine was observed.

Weight loss studies [44]

MS coupons (3 x 1 x 0.05cm) were mechanically polished with different grade emery papers and degreased with acetone, washed thoroughly with conductivity water and finally dried in air. Coupons were weighed and suspended vertically in aerated unstirred 1 N HCl (150 ml) with and without inhibitor for 6 h. Coupons were removed from solution and cleaned by brushing under running tap water to remove corrosion products, dried and reweighed to determine weight loss. In each case, triplicate experiments were performed and inhibition efficiency (IE) value of weight loss determined. IE (%) was calculated as

$$IE = 100 \times (W_o - W_i)/W_o \qquad \ldots\ldots\ldots\ldots (1)$$

Where W_o and W_i are weight losses in uninhibited and inhibited corroding solutions respectively. Expression, $\theta=1-(W_i/W_o)$ was used to determine degree of surface coverage (θ). Corrosion rate in $mg/cm^2/h$ was also calculated.

Results and Discussion

Melting points for thiosemicarbazides are observed in the following order: $AN_2 > AR_2 > AK_2$ (Table 2). Found nitrogen contents for AN_2, AR_2 and AK_2 are quite close to theoretical. All these compounds inhibit corrosion of MS in 1 N HCl solution (Table 3) at all concentrations (100-500ppm). IE for all these compounds increased with increase in concentration (Fig.1). Increased inhibitive action with increase in concentration of inhibitor can be ascribed to blocking of active sites of metal surface [45].

All compounds (AN_2, AR_2 and AK_2) exhibited increase in IE (Fig. 2) with increase of immersion time (3 - 24 h). This shows persistency of adsorbed thiosemicarbazides over a longer test period.

From Fig.3, it is clear that IE decreases with increase in acid concentration up to 3 N HCL for all the thiosemicarbazides. Further increase in acid concentration up to 5 N HCL causes sharp decrease in IE for all the thiosemicarbazides. The decrease in IE on increasing acid concentration beyond 3 N is due to increased aggressiveness of the acid [46].

With increase in temperature (30 – 40 ^{o}C) a significant increase in IE has been observed for AN_2 but IE decreased for AR_2 and AK_2 from 40 ^{o}C onwards. Beyond 50 - 60°C, decrease in IE has been observed for all the three thiosemicarbazides, in this range. This may be attributed to decomposition of hydrophobic long chain at higher temperatures (Fig. 4).

Application of adsorption isotherm

In order to understand the mechanism of corrosion inhibition the adsorption behaviour of the organic adsorbate on the metal surface must be known. At any instant a fraction θ of the metal surface is covered by the inhibitor molecules and the uncovered fraction (1- θ) reacts with acid as it does in the absence of inhibitor. The surface coverage θ values are very useful in explaining the adsorption characteristics. The surface coverage increases thereby increasing the percentage inhibition. To examine the adsorption behaviour of the inhibitor, the data were fitted to the various isotherms. A plot of θ versus Log C was a straight line supporting the monolayer adsorption of the inhibitor (AN_2, AR_2 and AK_2) on the metal surface (Fig.8). The applicability of Temkin's adsorption isotherm verifies the assumption of monolayer adsorption on a uniform, homogeneous metal surface with an interaction in the adsorption layer [47].

Kinetic treatment of weight loss results with inhibitor

Activation energy, E_a (KJ/mol) at 303 and 313 K for 500 ppm concentration of inhibitor was calculated using Arrhenius equation

$$k = A\ e^{-Ea/RT} \qquad\qquad \text{................. (2)}$$

where k is specific first order rate constant (h^{-1}), A is Arrhenius frequency factor, R is universal gas constant (8.314 J/mol/K) and T is temperature in K. Taking natural logarithm of Eq. (2) and after rearrangement gives

$$E_a = [19.14\ T_1 T_2 (\log k_{313} - \log k_{303})] / 1000 (T_2 - T_1) \qquad \text{.................... (3)}$$

T_2 represents 313 K while T_1 represents 303 K with the corresponding rate constants k_{313} and k_{303}.

E_a value obtained for MS – HCl systems without inhibitors was 15.66 KJ/mol. AK_2 exhibited average E_a value of 50.14 KJ/mol, while AR_2 and AN_2 displayed only 48.64 KJ/mol, 20.4 KJ/mol respectively indicating AK_2 as a better inhibitor than AR_2 and AN_2 [48] (Table 5). MS is, therefore, expected to be more protected in AK_2 - HCl system and for longer period than in AR_2 - HCl and AN_2 - HCl system.

A low activation energy means a fast reaction and a high activation energy means a slow reaction [49]. A high activation energy corresponds to a reaction rate that is very sensitive to temperature. Conversely a small activation energy indicates a reaction rate that varies only slightly with temperature [50]. If a reaction has zero activation energy its rate is independent of temperature. In some case activation energy (E_a) is found negative which indicates that the rate decreases when temperature is raised and such a behaviour is a signal that the reaction has a complex mechanism.

From the value of Q_A given in Table 5, it is assumed the inhibitor is adsorbed on the metal surface in the form of monolayer film, covering at any instant fraction θ, of the metal surface in a uniform random manner, then the heat of adsorption Q_A, of the inhibitor can be calculated with the help of the equation [51]:

$$Q_A = 2.303 \times (T_1 \times T_2/T_2 – T_1) [Log (Wo* – Wi*/Wi*) – Log (Wo – Wi/Wi)] \dots\dots\dots\dots\dots (4)$$

Where,
Wo* = weight losses in uninhibited acid and Wi* = weight losses in inhibited acid solutions and Wo = weight losses in uninhibited acid and Wi = weight losses in inhibited acid solutions by the inhibitor at Kelvin temperatures T_2 and T_1 respectively.

The values of the free energy ΔG^o less than -40 KJ/mol (-9.56 Kcal/mol) indicated that the tested mixed fatty acid thiosemicarbazides are physically adsorbed on the metal surface [52]. The low and negative value of ΔG^o indicates the spontaneous adsorption of inhibitor on the surface of mild steel [53]. It was also found that values of activation energy of the inhibited systems were lower than that of uninhibited system. Putilova [5] indicated that this type of inhibitor is effective at higher temperatures. The values of adsorption ΔG^o were calculated from the equation [50]:

$$\Delta G^o = 2.303 \times R \times T [Log\ C_{inh} – Log (Wo – Wi/Wi) – 1.75] \dots\dots\dots\dots\dots\dots (5)$$

Where, R = Constant (1.987), T= Temperature in Kelvin
C= Concentration of inhibitor in mole/L

The values of the entropy of activation ΔS^o indicates the system is entopic controlled. ΔS^o were calculated from the equation [51]:

$$\Delta S^o = \frac{QA – \Delta G}{T} \dots\dots\dots\dots\dots\dots\dots\dots (6)$$

Where, Q_A = Heat of adsorption, T= Temperature in Kelvin, ΔG^o = free energy.

Comparison of Corrosion Inhibition Behaviour of AN_2, AR_2 and AK_2

The prepared inhibition obeyed Temkin's adsorption isotherm [54] (Fig. 8). However, average E_a values for AN_2 (20.4 KJ/mol), AR_2 (48.64 KJ/mol) and AK_2 (50.14 KJ/mol) are within the range for physical adsorption, and less than 80 KJ/mol expected for chemisorption [55]. This observation suggests that initial adsorption exhibited by all inhibitors was probably physical where multi layer formation was obtained but as adsorption bonds became stronger with increase in temperature, inhibitors then exhibited chemical adsorption resulting in mono molecular layer formation and better protection for MS. AK_2 is more soluble in 1 N HCl than AN_2 and AR_2 and therefore is expected to be present at higher concentrations than AN_2 and AR_2 in the solution. Difference [56] in inhibitory properties of inhibitor is closely related to the difference in molecular structures and solubility.

Conclusion

➢ Thiosemicarbazides of neem, rice bran, and karanja showed good performance as corrosion inhibitors in hydrochloric acid media.

➢ All the thiosemicarbazides inhibit corrosion by adsorption mechanism and the adsorption of the compounds from acid solution follow adsorption isotherm.

➢ IE increases with increasing inhibitor concentration.

➢ Activation energy calculated in the absence and presence of inhibitor reveal the efficiency of the inhibitor. Higher values of thermodynamic activation function (E_a) for inhibited system than those in free acid solution indicate that all inhibitors are more effective at room temperature.

➢ The lower value of heat of adsorption (Q_A) for these inhibitors shows physical nature of adsorption and lower value of ΔG^o indicates that the inhibitor are physically adsorbed on the metal surface and negative value of ΔG^o indicates the spontaneous adsorption of inhibitor on the surface of mild steel.

➢ The entropy of activation ΔS^o in the absence and presence of the inhibitors are large and negative. This indicates that the activated complex in the rate determining step represents an association rather than dissociation.

➢ All the compounds examined acted as mixed inhibitors in HCl.

References

1. Quraishi, M.A.; Jamal, Danish.; J Am Oil Chem Soc, 77, 1107-1111 (2000).
2. Mir, I.; Siddiqui. M.T.; Comrie. A.; Tetrahedron, 26, 5235-5238 (1970).
3. Lieberman, D.; Rist, N.; Grumbach. F.; Bull Soc Chim France, 1440-1445 (1954).
4. Sengupta A K, Garg M.; Chandra U.; J Ind Chem Soc, 56, 1230-1234 (1974).
5. Putilova, I.N.; Balezin, S.A.; and Barannik, U.P.; "Metallic Corrosion Inhibitors" Pergamon Press, New York, 1960, 31.
6. Damaskins, B.B.; "Adsorption for Organic Compounds on Electrodes" Plenum Press, New York, 1971, 221.
7. Chaudhary, R.S.; Tyagi, D.K.; Kumar, A.; J Sci Indu Res, 66, 835-840 (2007).
8. Achouri, M.El.; Infante, M.R.; Lzquierdo, F.; Kertit, S.; Gouttoya, H.M.; Ncirir, B.; Corr Sci, 43, 19-35 (2001).
9. Chebabem, D.; Ait Chikh, Z.; Hajjaji, N.; Srhiri, A., Zucchi, F.; Corr Sci, 49 309-320 (1993).
10. Hajjaji, N.; Rico, I.; Srhiri, A.; Lattes, A.; Soufiaoui, M.; Ben Bachir, A.; Corr Sci, 49, 326-334 (1993).
11. Bastidas, J.M.; Polo, J.L.; Cano, E.; J Appl Electrochem, 30, 1173-1177 (2000).
12. Hamner, N.E.; "in Corrosion Inhibitors", edited by Nathan, C.C.; Nace Houston, Taxas, USA, 1973, 1.
13. Larabi, L.; Harek, Y.; Benali, O.; Ggalein, S.; Prog Org Coatings, 57, 170-176 (2006).
14. Raman, A.; Labine, P.; Rev Corr Inhib Sci Tech NACE Int Houston, 2, 1 (1996).
15. Abd-El-Nabey, B.A.; Khmis, E.; Ramadan, M.S.; El-Gindy, A.; Corrosion, 52, 671-667 (1996).
16. Badran, B.M.; Abdel Fattah, A.A.; Abdul Azim, A.A.; Corr Sci, 22, 513-523 (1982).
17. Badran, B.M.; Abdel Fattah, A.A.; Abdul Azim, A.A.; Corr Sci, 22, 525-532 (1982).
18. Hanna, F.; Sherbini, G.M.; Brakat, Y.; Brit Corros J, 24, 269-272 (1989).
19. Badran, B.M.; Abdel Fattah, A.A.; Abdul Azim, A.A.; Corros. Sci, 22, 513 (1982).
20. Badran, B.M.; Abdel Fattah, A.A.; Abdul Azim, A.A.; Corros. Sci, 22, 525 (1982).
21. Hanna, F.; Sherbeni, G.M.; Brakat, Y.; Br. Corros. J, 24, 269 (1989).
22. Quraishi, M.A.; Jamal, D.; Corrosion, 56, 156 (2000).
23. M.A. Quraishi, Jamal, D.; Corrosion, 56, 983 (2000).
24. Quraishi, M.A.; Jamal, D.; Saeed,\M.T.; J. Am. Oil Chem. Soc, 77,265 (2000).
25. Quraishi, M.A.; Jamal, D.; J. Am. Oil Chem. Soc, 77,1107 (2000).
26. Ajmal, M.; Jamal, D.; Quraishi, M.A.; Anti-Corros. Methods Mater, 47,77 (2000).
27. Quraishi, M.A.; Jamal, D.; Anti-Corros. Methods Mater, 47, 233 (2000).
28. Quraishi, M.A.; Jamal, D.; J Am Oil Chem Soc, 77, 1107-1111 (2000).
29. Quraishi, M.A.; Saxena, N.; Jamal, D.; Indian J Chem Technol, 11,220-224 (2005).
30. Toliwal, S.D.; Jadav, Kalpesh.; J Sci Indu Res, 68(3), 235 (2009).
31. Toliwal, S.D.; Jadav, Kalpesh.; Ind J Chem Tech, 16 (1),32 (2009).
32. Toliwal, S.D.; Jadav, Kalpesh.; Patel, Kalpen.; J Ind Council of Chem, 25(1), 37 (2008).
33. Raval, D.A.; Toliwal, S.D.; J Oil Tech Assoc India, 26,27-29 (1994).
34. Toliwal, S.D.; Khotpal, R.R.; J Oil Tech Assoc India, 31,119-121 (1999).
35. Toliwal, S.D.; Dighe, A.K.; J Sci Ind Res, 59, 808-813 (2000).
36. Parmar, R.J, Toliwal, S.D.; J Sci Ind Res, 60,876-882 (2001) 876-882.
37. Parmar, R.J.; Toliwal, S.D.; Khotpal, R.R.; Paint India, 54, 51-60 (2004).
38. Toliwal, S.D.; Jadav, Kalpesh.; Patel, Kalpen.; J Ind Council of Chem, 25(2),126 (2008).
39. BIS: 548, Part –I, 'Methods of sampling and tests for oils and fats' Bureau of Indian Standards, New Delhi, 1964, 29.

40.   BIS: 548, Part – III, 'Analysis of gas liquid Chromatography' Bureau of Indian Standards, New Delhi, 1976, 6.
41.   BIS: 548, Part – III, 'Methods of sampling and test for oils and fats' Bureau of Indian Standards, New Delhi, 1976, 6.
42.   Daulatabad, C.D.; Mirajkar, A.M.; J Oil Tech Assn of India, 20, 9 (1988).
43.   Boots, S.G. Cheng, C.C.; J Heterocycl Chem, 4, 272 (1967).
44.   Champion, F.A.; "Corrosion Testing Procedures" Champman and Hall, London, 1952, 187.
45.   Nagarajan, Prabavathi.; Sulochana, N.; J Ind Council Chem, 23, 51 (2006).
46.   Quraishi, M.A.; Rawat, J.; Ajmal, M.; Corrosion, 54,99 (1996).
47.   Stoyanova, A.E.; Sokkolova, E.I.; Raicheva, S.N.; Corros Sci, 39,1595 (1997).
48.   Talati, J.D.; Daraji, J.M.; J Indian Chem Soc, 68, 67 (1991).
49.   Lavine, I.N, "Physical Chemistry" McGraw-Hill, New York,1988, 539.
50.   Atkins, P.W.; "The Elements of Physical Chemistry" Oxford University Press, Oxford, 1996,282.
51.   Abdel, A.M.S.; Saiyed, A.El.; Trans SAEST, 16, 197 (1981).
52.   Brinic, S.; Grubac, Z.; Babic, R.; Metikos Hukovic, M.; 8th Eur Sump Corros Inhib Ferrara, Italy, 1, 197 (1995).
53.   Gomma, G.K.; Wahdan.; M.H.; Indian J Chem Technol, 2, 107 (1995).
54.   Rehim, S.A.; Ibrahim, M.A.M .; Khalid, K.F.; Mater Chem Phys, 70, 268-273 (2001).
55.   Ita, B.I.; J Nig Environ Soc, 1,113 (2003).
56.   Ita, B.I.; Offiong, O.E.; Abakedi , O.U.; Alobi, N.O.; J Sci and Indu Res, 66,919 (2007).

Volume 12, Preprint 35   **submitted 22 July 2009**

Table 1 Fatty acid composition of oils

Fatty acid	Amount (%) in		
	Neem oil	Rice bran oil	Karanja oil
Palmitic	16.96	18.50	10.95
Stearic	16.39	2.50	6.57
Oleic	49.31	43.00	57.30
Linoleic	13.95	32.00	17.74
Linolenic	1.85	2.20	2.85
Arachidic	1.54	1.80	4.59

Table 2 Analysis of thiosemicarbazides of mixed fatty acid hydrazides

Sample	Molecular weight	Melting point ^{0}C	% Yield	Nitrogen Content (%)	
				Calculated	Found
AN_2	355.58	88	78	11.83	9.94
AR_2	355.58	84	76	11.83	12.53
AK_2	355.58	81	73	11.83	10.23

Table 3 Effect of AN$_2$, AR$_2$ and AK$_2$ on rate of corrosion of mild steel at 30± 1°C for 6 h

Inhibitor conc.	Weight loss (mg)			Inhibition efficiency(I.E) %			Corrosion rate (CR) mg/cm^2/h			Surface Coverage (θ)		
	AN$_2$	AR$_2$	AK$_2$	AN$_2$	AR$_2$	AK$_2$	AN$_2$	AR$_2$	AK$_2$	AN$_2$	AR$_2$	AK$_2$
HCL	49.1	49.1	49.1	---	---	---	1.2786	1.2786	1.2786	---	---	---
100	18.3	33.8	23.6	62.73	31.16	51.93	0.4766	0.8802	0.6146	0.6273	0.3116	0.5193
200	10.8	23.5	13.2	78.00	52.14	73.12	0.2812	0.6120	0.3437	0.7800	0.5214	0.7311
300	3.4	14.3	4.8	93.08	70.88	90.22	0.0885	0.3724	0.1250	0.9308	0.7088	0.9022
400	2.2	12.8	2.8	95.52	73.93	94.30	0.0573	0.3333	0.0729	0.9552	0.7393	0.9429
500	1.8	1.2	1.1	96.33	97.56	97.76	0.0469	0.0313	0.0286	0.9633	0.9756	0.9775

Table 4 Adsorption isotherm data for adsorption of AN$_2$, AR$_2$ and AK$_2$ in 1 N HCl on the surface of mild steel

Inhibitor conc. (ppm)	Log C (ppm)			θ			Log (θ)			θ/1- θ			Log (θ/1- θ)		
	AN$_2$	AR$_2$	AK$_2$	AN$_2$	AR$_2$	AK$_2$	AN$_2$	AR$_2$	AK$_2$	AN$_2$	AR$_2$	AK$_2$	AN$_2$	AR$_2$	AK$_2$
100	2.0000	2.0000	2.0000	0.6273	0.3116	0.5193	-0.2025	-0.5064	-0.2846	1.6831	0.4526	1.0803	0.2261	-0.3440	0.0335
200	2.3010	2.3010	2.3010	0.7800	0.5214	0.7311	-0.1079	-0.2828	-0.1360	3.5455	1.0894	2.7188	0.5497	0.0372	0.4344
300	2.4771	2.4771	2.4771	0.9308	0.7088	0.9022	-0.0311	-0.1495	-0.0447	13.4510	2.4341	9.2249	1.1288	0.3863	0.9650
400	2.6021	2.6021	2.6021	0.9552	0.7393	0.9429	-0.0199	-0.1312	-0.0255	21.3210	2.8358	16.5131	1.3288	0.4527	1.2178
500	2.6990	2.6990	2.6990	0.9633	0.9756	0.9775	-0.0162	-0.0107	-0.0099	26.2480	39.984	43.4444	1.4191	1.6019	1.6379

Table 5 Thermodynamic parameters for mild steel in 1N HCl in absence and presence of inhibitors of 500 ppm concentration

Inhibitor	Ea, KJ/mol	Q_A, KJ/mol	ΔG^o, KJ/mol		ΔS^o, J/mol	
			303 ^{o}K	313 ^{o}K	303 ^{o}K	313 ^{o}K
Blank	15.66	---	---	---	---	---
AN$_2$	20.4	-3.72	-40.27	-41.36	109.04	109
AR$_2$	48.64	-19.04	-41.6	-41.72	11.254	11.28
AK$_2$	50.14	-18.41	-41.37	-41.48	16.964	16.77

Temp = 30± 1°C
Acids strength = 1 N HCl
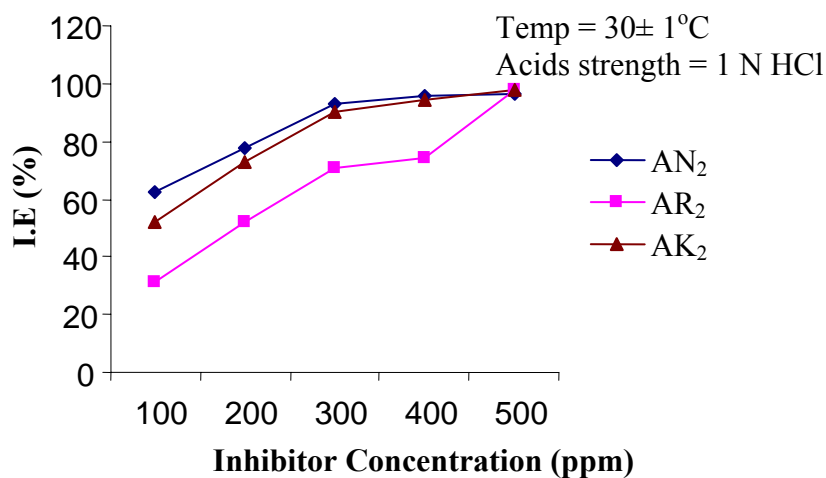
Fig 1 Variation of inhibition efficiency with inhibitor concentration for
100 – 500ppm concentration of inhibitors.

Inhibitors concentration = 500ppm
Acid = 1 N HCl
Temp = 30± 1°C
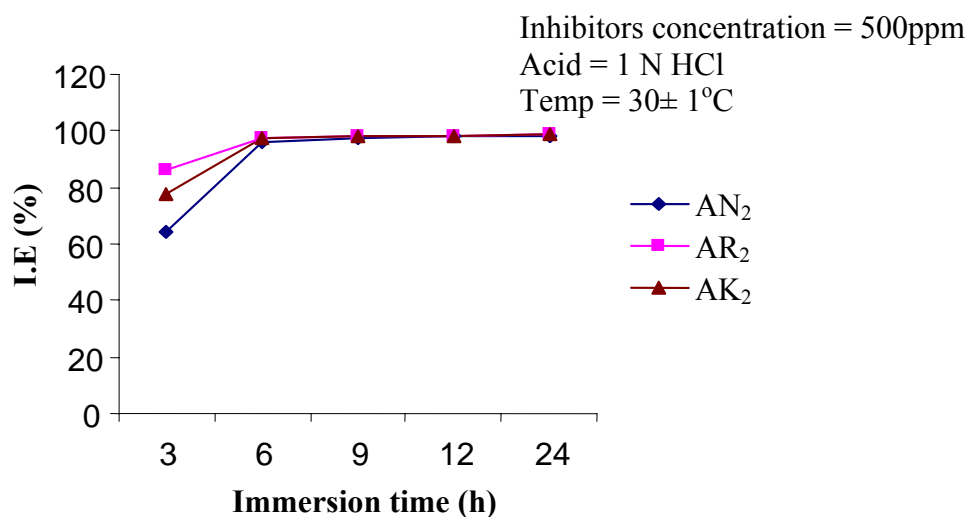
Fig 2   Variation of inhibition efficiency with immersion time in 1 N HCl for
500ppm concentration of inhibitors.
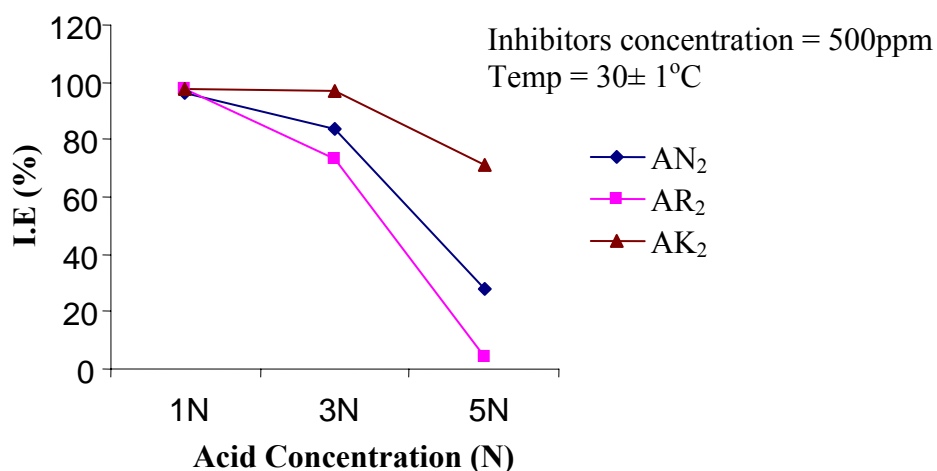
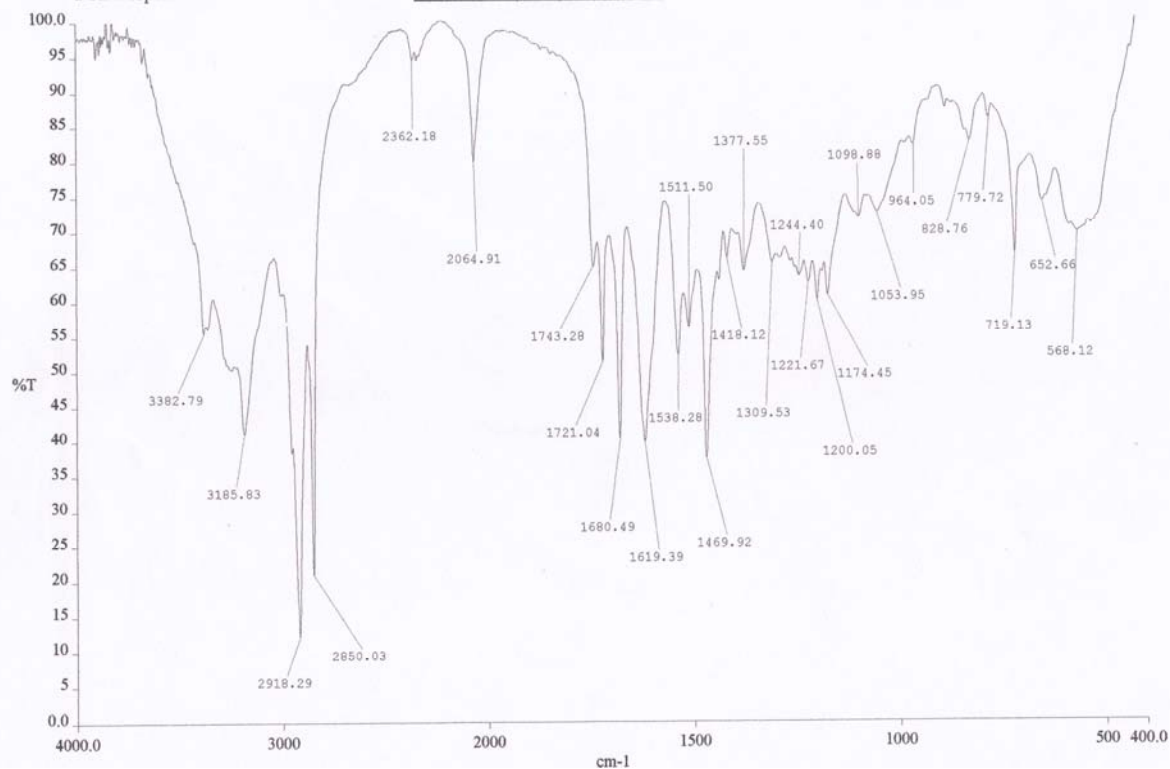**Fig 3** Variation of inhibition efficiency with acid concentration for 500ppm concentration of inhibitors.
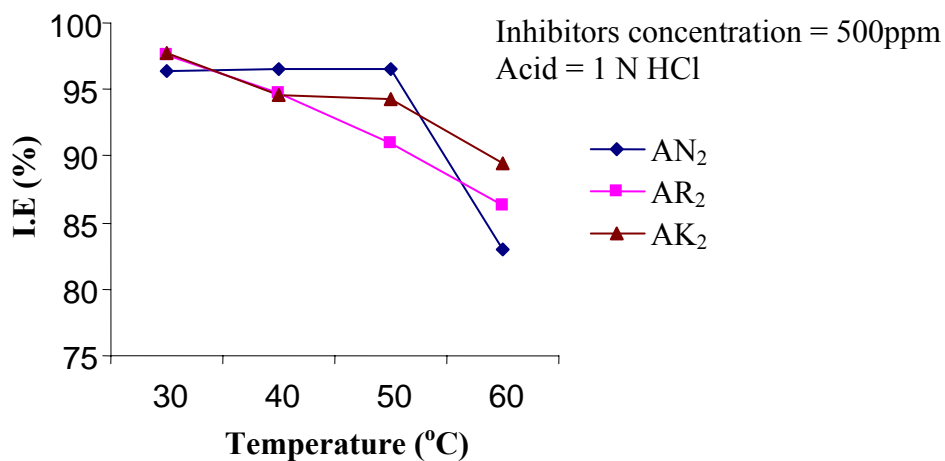
Fig 4 Variation of inhibition efficiency with solution temperature in 1 N HCl for 500ppm concentration of inhibitors.

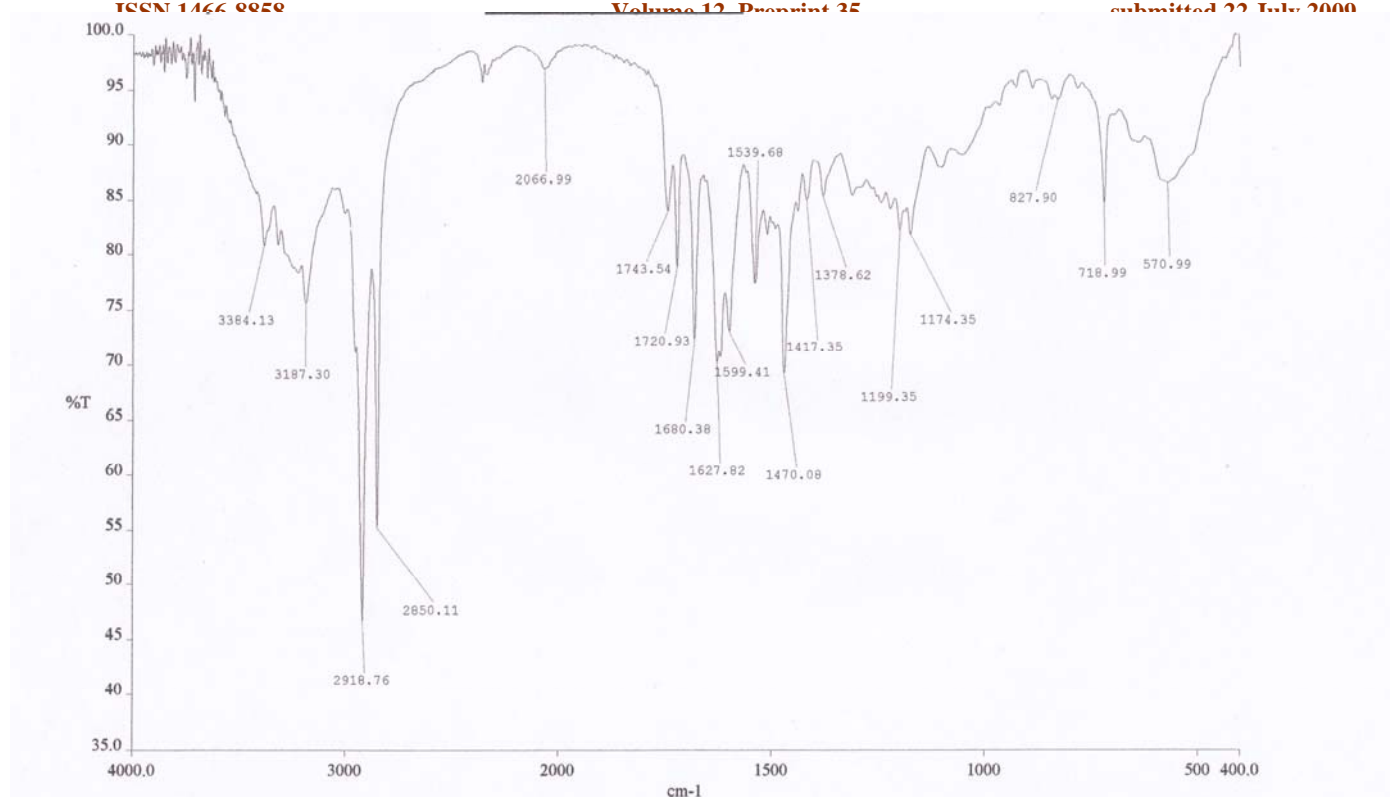**Fig 5** IR spectrum of AN$_2$ of neem oil
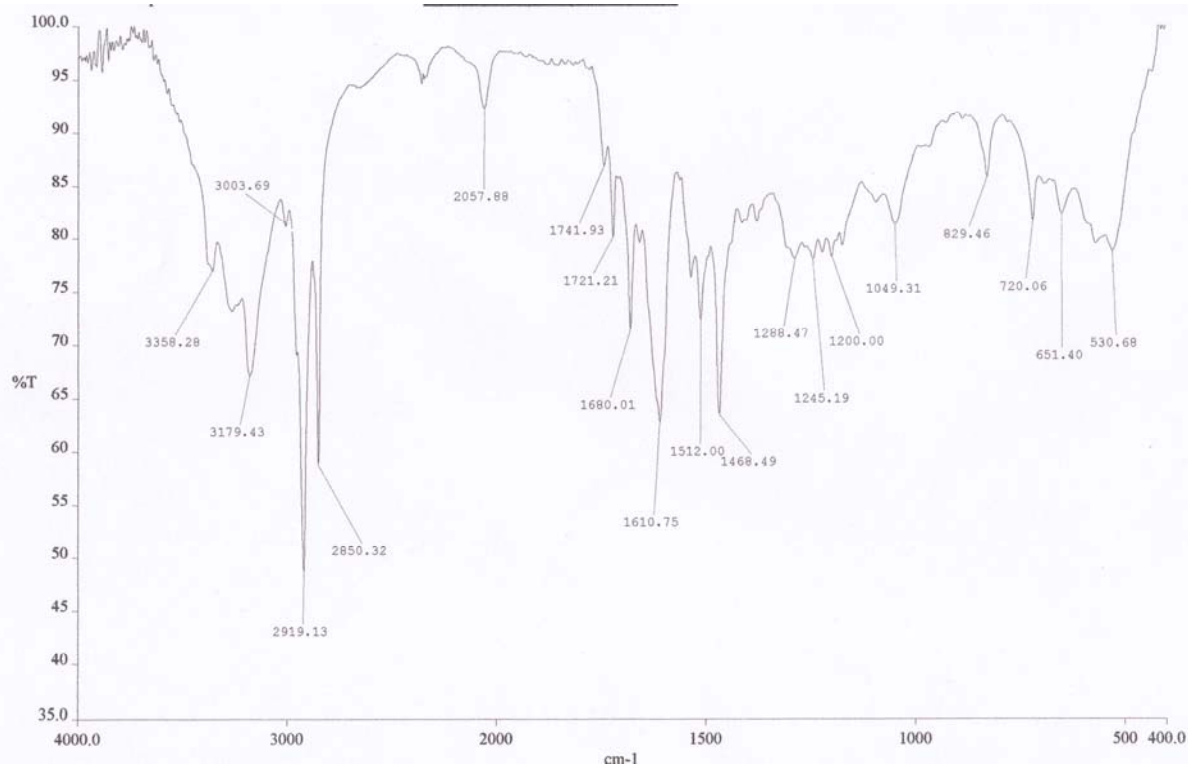
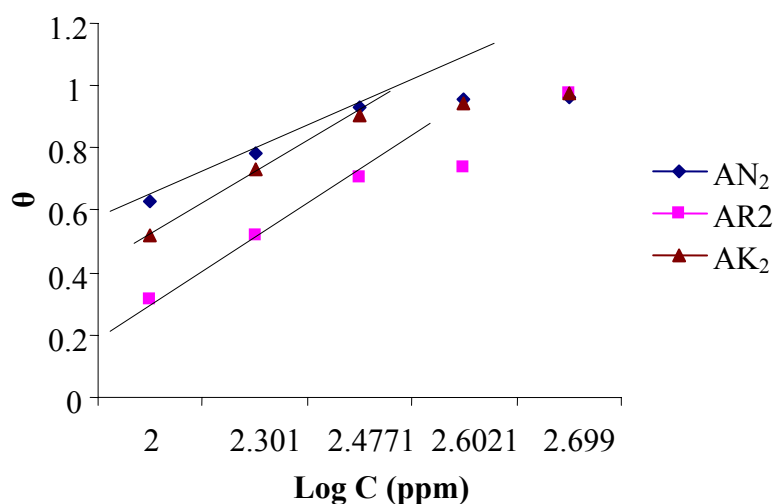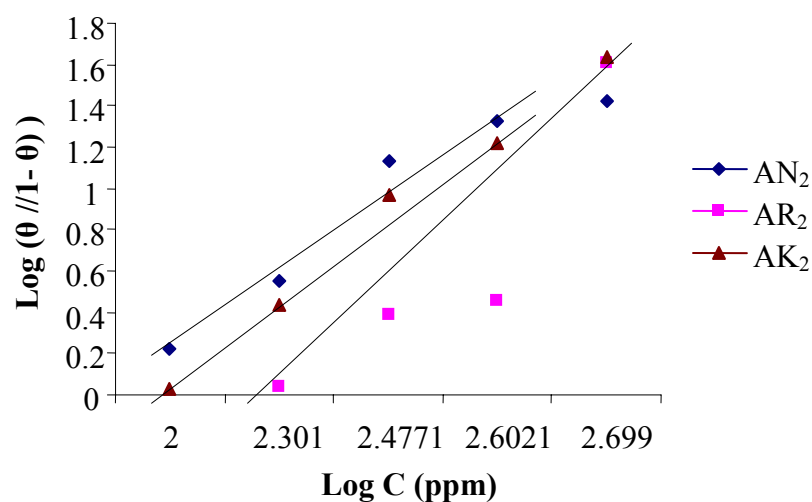**Fig 6** IR spectrum of AR$_2$ of rice bran oil

Fig 7 IR spectrum of AK$_2$ of karanja oil
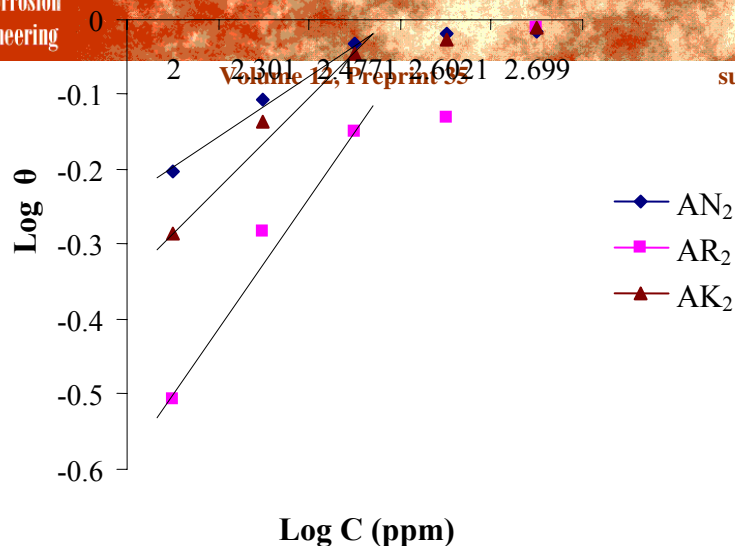
(a)

(b)

(c)

Fig 8 Adsorption isotherm plots for the adsorption of various inhibitors in 1 N HCl on the surface of mild steel (a) Freundlich adsorption isotherm (b) Temkin's adsorption isotherm (c) Langmuir's adsorption isotherm.