ISSN 2455-4863 (Online) www.ijisset.org Volume: 4 Issue: 12 | 2018

A study of Anti corrosive effects of Schiff's Base and *Murraya koenigii* on mild steel in H_2SO_4 acid

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Abstract: *Extract of leaves of Murraya koenigii_and newly synthesized Schiff's Base (SB) were taken for studying the anti corrosive effects on mild steel in H_2SO_4 acid. Weight loss and Thermometric methods have been employed for the studies.1M and 2M H_2SO_4 solutions were taken for Weight loss and for Thermometric method, 2 M and 3 M concentrations of H_2SO_4 solutions were taken. Inhibitor concentrations were taken 0.1%, 0.3%, 0.5% and 0.7% in both methods .Both the methods are in good agreement with each other and show that the corrosion inhibition efficiency of leaf extract of Murraya koenigii was more than newly synthesized Schiff's Base. Further results show that corrosion inhibition efficiency increases with the increase in the concentration of the acid as well as those of inhibitors.*

Keywords: *Murraya koenigii, Schiff's Base (N-(4-Methylbenzal) 1-Naphthylamine), Weight Loss, Inhibitionefficiency, Corrosion Rate , Surface Coverage, Reaction number.*

1. INTRODUCTION

Corrosion is a destructive phenomenon which is chemical or electro chemical in nature.[1-2] Corrosion not only changes the physical and chemical properties of metals and alloys but it also decreases strength and other features which restricts the metal from its specific uses. Many organic compounds having heteroatoms like O, N, S etc have been studied as corrosion combating agents[3-5] for metals like Al, Fe, Cu, Zn, Sn etc[6]which are generally used in industries. These heteroatoms are found to have lone pair of electrons which adsorb on metal surface which results in inhibition of corrosion[7]. Effects of N and S containing organic compounds such as substituted Benzothiazoles and various organic S containing compounds on the corrosion of Iron and mild steel have been studied[8-11]. Mild steel is thoroughly used due to its properties like good strength, abundant availability and wide spectrum of uses. Corrosion of mild steel is very common and serious problem which causes considerable economic loss throughout the world. Although it is unavoidable but proper maintenance, good design, and proper inhibitors may control it. The role of alloying elements in the control of corrosion and application of film forming inhibitors are well known[12].

A large number of chemists are working to find out efficient as well as non harmful inhibitor against the corrosion of mild steel .The inhibition of mild steel corrosion by acids has been previously studied by various researchers using different organic compounds. Some natural occurring products[13-21] as well as some Schiffs's Bases[22-26] have also been studied earlier as corrosion inhibitors for mild steel and Aluminium in acid media of different concentrations. The best method found in protection against corrosion with regarding acidic medium is the use of natural as well as chemically synthesized inhibitors.

In the present investigation the non corrosive effects of newly synthesized ligand and extracts of leaves of *Murraya koenigii* have been studied for mild steel in sulphuric acid solutions.

2. BACKGROUND OR RELATED WORK

In recent years, sol-gel coatings doped with inhibitors show real promise. Although substantial research has been devoted to corrosion inhibition by plant extracts, reports on the detailed mechanisms of the adsorption process and identification of the active ingredient are still scarce. Development of computational modeling backed by wet experimental results would help to fill this void and help understand the mechanism of inhibitor action, their adsorption patterns, the inhibitor-metal surface interface and aid the development of designer inhibitors with an understanding of the time required for the release of self-healing inhibitors.

3. SCOPE OF RESEARCH

Many organic compounds having hetero atoms like O, N, S etc have been studied as corrosion combating agents for metals like Aluminium, Iron, Copper, Zinc, Tin etc which are generally used in industries. Also some naturally occurring products like Opuntia, Gulmohar, Neem, Trifla, Saunf *etc* have also been studied as corrosion inhibitors. The present study has its importance that some new ligands will be synthesized in the laboratory and some naturally occurring plants found in the nearby areas will be studied as corrosion combating agents. Simultaneously they will be studied for the same metal in same acidic media in same environmental conditions to know a comparative effectiveness of two combating agents.The importance of present study lies in the observation that two categories of corrosion combating agents are either equally effective or have advantages over each other costwise, effectiveness and ecologically.

4. PROPOSED METHODOLOGY AND DISCUSSION

Square shaped specimens of mild steel having dimension2.5cm x 2.5cm x 0.05cm containing a small hole of about 0.02cm diameter near the upper edge were taken. The approximate chemical composition of the specimen was 99.9% Fe,0.14%Si,0.12% C,0.4%Mg and 0.04%S.The specimens were cut out from a single sheet of uniform thickness. Each specimen was washed with acetone and dried. The solutions of H_2SO_4 were prepared using double distilled water. All chemicals used were of analytical reagent grade. Tests were carried out in 1M and 2M concentration of H_2SO_4 solution. The test solutions were prepared by taking 0.1%, 0.3%. 0.5% and 0.7% inhibitor concentrations in alcohol. One specimen in each beaker containing 50ml test solution was suspended with a glass hook of 'V' shape and left exposed to air. After sufficient exposure the test specimens were cleaned with running water and then weighed again.

4.1 The percentage inhibition efficiency η% was calculated as[27]:-

$$\eta\ \% = \frac{(\Delta W_u - \Delta W_i)}{\Delta W_u} \times 100$$

Where ,

W_u is the weight loss in uninhibited solution and

W_i is the weight loss in inhibited solution

4.2 Corrosion rate in $\left(\frac{mm}{yr}\right)$ can be calculated by following equation[28]:–

$$\text{Corrosion Rate}\left(\frac{mm}{yr}\right) = \frac{87.6\ \Delta W}{DAT}$$

Where,ΔW is weight loss in mg, D is the metal density in $g.cm^{-3}$, A is the exposed area in cm^2 , T is the time of exposure in hours .

4.3 The degree of surface coverage (θ) can be calculated as

$$\text{Surface Coverage}(\theta) = \frac{\Delta W_u - \Delta W_i}{\Delta W_u}$$

ΔWu= Weight loss of specimen in uninhibited solution.

ΔWi= Weight loss of specimen in inhibited solution.

Inhibition efficiencies were also determined by another technique,*i.e.* thermometric method. This method involved, the immersion of single specimen of same dimensions as were used in weight loss method in a thermal insulating reaction chamber having 50ml of test solution at an initial temperature (Ti). Temperature changes were measured at regular intervals using a thermometer with a precision of 0.1.The temperature increase was slow initially and then rapid and finally reached to maximum(Tm) and then started to decrease. The percentage inhibition efficiency η% was calculated as[29]:-

$$\eta\% = \frac{(RN_u - RN_i)}{RN_u} \times 100$$

Where ,

RN_u is the reaction number in uninhibited solution,

RN_i is the reaction number in inhibited solution

4.4 Reaction Number (RN) can be calculated in terms of temperature as [30]–

$$\text{Reaction Number}(RN) = \frac{(T_m - T_i)}{t}$$

where,

T_m is the maximum temperature of the test solution,

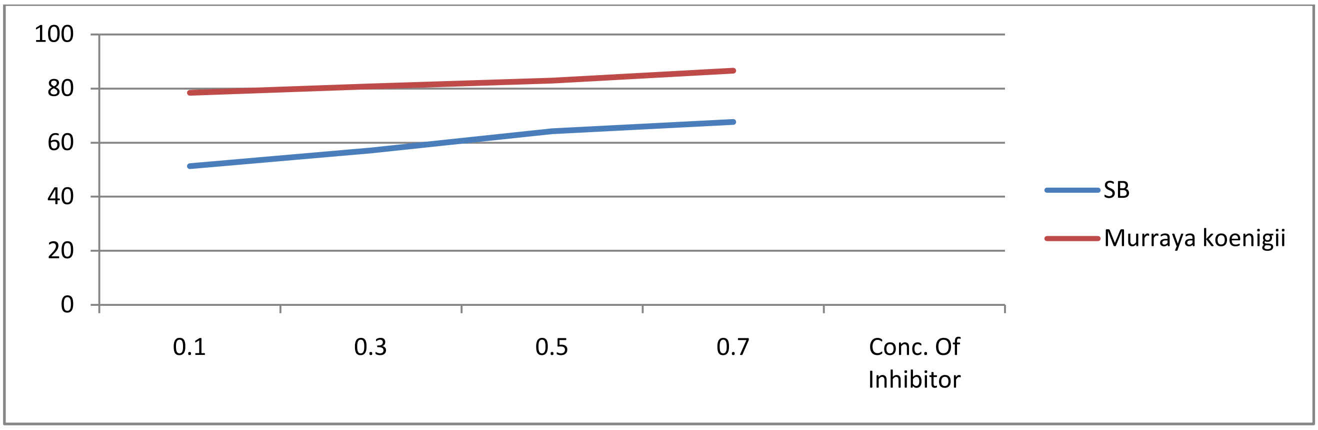
T_i is the initial temperature of the test solution and

t is the time in minutes to attain maximum temperature

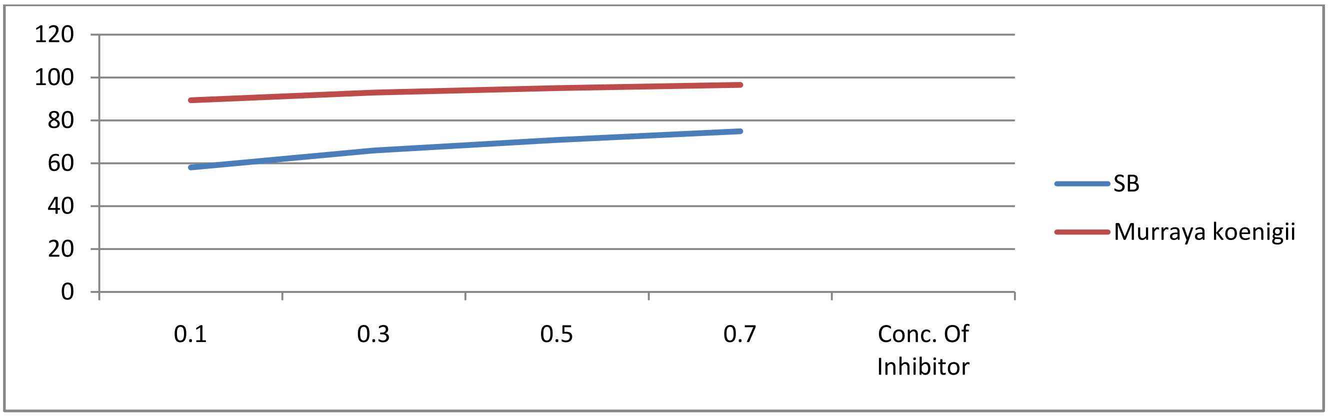
Table 1: *Weight Loss (Δw), Inhibition Efficiency (η%), Corrosion Rate and Surface Coverage(θ) data for Mild Steel in H_2SO_4 Solution with given Inhibitors*

Area of specimen :- 6.25 cm^2

Conc. Of inhibitor	1M H_2SO_4 (24 Hours)					2M H_2SO_4 (18 Hours)				
%	Δw (mg)	Inhibition Efficiency (η%)	Corrosion Rate(mm/yr)	Surface Coverage (θ)	$\log(\frac{\theta}{1-\theta})$	Δw(mg)	Inhibition Efficiency (η%)	Corrosion Rate(mm/yr)	Surface Coverage (θ)	$\log(\frac{\theta}{1-\theta})$
Uninhibited	380		31.48			755		83.41		
Murraya koenigii										
0.1	82	78.42	6.79	0.7842	0.5603	81	89.27	8.94	0.8927	0.9201
0.3	73	80.78	6.04	0.8078	0.6235	54	92.84	5.96	0.9284	1.1128
0.5	65	82.89	5.38	0.8289	0.6852	38	94.96	4.19	0.9496	1.2751
0.7	51	86.57	4.22	0.8657	0.8092	26	96.55	2.87	0.9655	1.4469
SB										
0.1	185	51.31	15.32	0.5131	0.0227	317	58.01	35.02	0.5801	0.1403
0.3	163	57.10	13.50	0.5710	0.1241	257	65.96	28.39	0.6596	0.2872
0.5	136	64.21	11.26	0.6421	0.2538	220	70.86	24.30	0.7086	0.3859
0.7	123	67.63	10.19	0.6763	0.3199	190	74.83	20.99	0.7483	0.4731



Graph between Conc. of Inhibitor (X Axis) and Inhibition Efficiency (η%) (Y Axis) for 1M H_2SO_4 Conc.

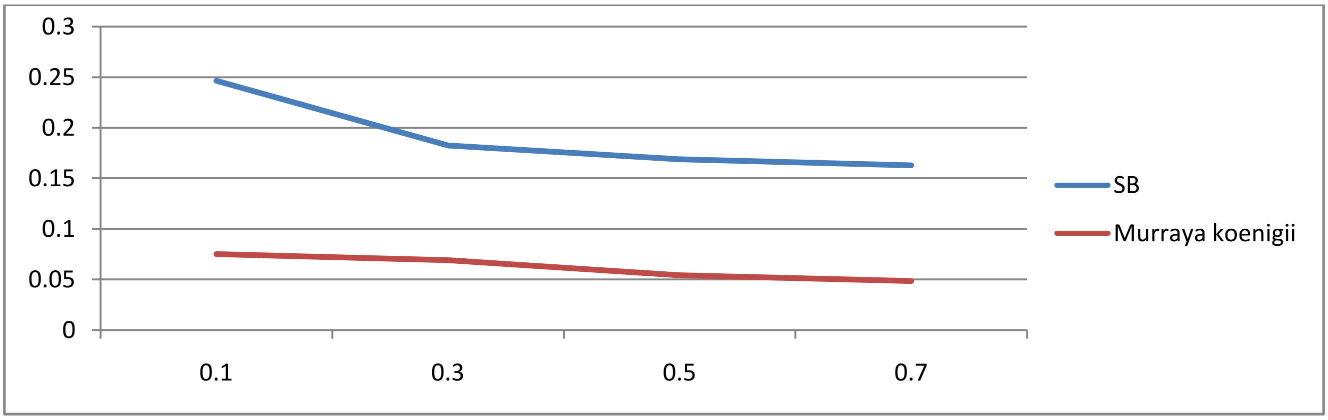


Graph between Conc. of Inhibitor (X Axis) and Inhibition Efficiency (η%) (Y Axis) for 2M H_2SO_4 Conc.

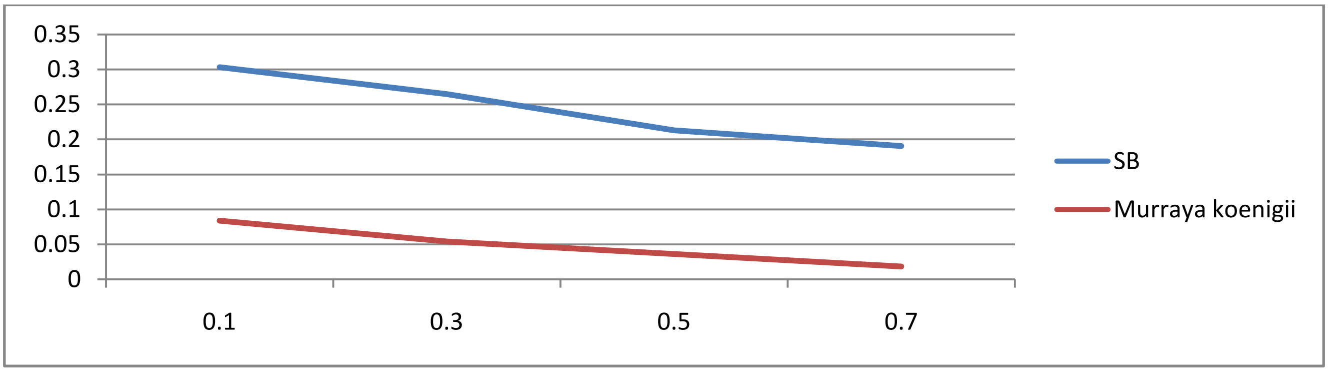
Table 2: Reaction Number (RN)and Inhibition Efficiency (η%) data for Mild Steel in H_2SO_4 Solution with given Inhibitors

Temperature :- 303+0.1 K

	2M H_2SO_4 (21 Hours)		3M H_2SO_4 (18 Hours)	
Conc. Of inhibitor	Reaction Number ($Kmin^{-1}$)	Inhibition Efficiency (η%)	Reaction Number ($Kmin^{-1}$)	Inhibition Efficiency (η%)
Uninhibited	0.5549		0.7111	
Murraya koenigii				
0.1	0.0751	86.46	0.0838	88.21
0.3	0.0692	87.52	0.0539	92.42
0.5	0.0542	90.23	0.0362	94.90
0.7	0.0485	91.25	0.0183	97.42
SB				
0.1	0.2465	55.57	0.3030	57.38
0.3	0.1825	67.11	0.2648	62.76
0.5	0.1689	69.57	0.2129	70.06
0.7	0.1628	70.66	0.1906	73.19



Graph between Conc. of Inhibitor (X Axis) and Reaction Number($Kmin^{-1}$) (Y Axis) for 2M H_2SO_4 Conc.



Graph between Conc. of Inhibitor (X Axis) and Reaction Number($Kmin^{-1}$) (Y Axis) for 3M H_2SO_4 Conc.

5. EXPERIMENTAL RESULTS

Weight loss and percentage inhibition efficiencies (η%) for different concentrations of H_2SO_4 and inhibitors are shown in table 1.It is observed that percentage inhibition efficiency increases with the increase in the concentrations of the acid and also with the increase in the concentrations of inhibitors. Both the inhibitors show maximum inhibition efficiency at higher concentration of acid *i.e.* at 2M at their highest concentration *i.e.* at 0.7%.The maximum efficiency was shown by *Murraya koenigii* is (96.55%) corresponding corrosion rate (mm/yr) and surface coverage(θ) also shown in table 1. It is observed that corrosion rate of mild steel decreases with the increase in the concentrations of inhibitors whereas corrosion rate

ISSN 2455-4863 (Online) **www.ijisset.org** *Volume: 4 Issue: 12 | 2018*

increases with the increase in the strength of H_2SO_4 solutions. The values of surface coverage (θ) increases with the increase in the acid strength as well as with the increase in the concentration of inhibitors. Maximum surface coverage is observed at the highest concentration *i.e* 2M H_2SO_4at maximum concentration *i.e* (0.7%) of inhibitors. Inhibition efficiencies determined by thermometric method are shown in table 2. Since no significant changes in temperature were recorded for lower concentrations of acid so observations were taken at higher concentrations *i.e.* 2M and 3M. The results shown by thermometric method have the same trends as were observed in weight loss method. In thermometric method also the inhibition efficiency increases with the increase in the concentrations of both acid and inhibitors. Here also the best result is shown by leaves extract of *Murraya koenigii*. The maximum efficiency is 97.42% in 3MH_2SO_4 at 0.7% concentration. It means both methods have good agreement with each other. The variation of Reaction number (RN) with inhibitor concentration shows that the reaction number decreases with increasing concentration of inhibitors. Both the methods show that the naturally occurring plant is more efficient than chemically synthesized compound it may be due to the fact that in the naturally occurring plant may have more hetero atoms than chemically synthesized compound. The mechanism of corrosion inhibition by natural plant is very complicated but it may be supposed that it is basically based upon the phenomenon of chemisorption. It is supposed that alkaloids present in the extract of leaves of *Murraya koenigii* are basic in nature , they are adsorbed on the surface of metal in presence of acid and thus block the active sites on the surface, which are responsible for the corrosion of metal. More the adsorption, more will be the efficiency of the inhibitor and more the concentration of inhibitor more will be its adsorption on the surface of metal and more will be the surface coverage reducing exposed sites of metal for attack on metal. The leaves extract of *Murraya koenigii* plant is more efficient than the chemically synthesized Schiff's base. It may due to the presence of more hetero atoms in the leaves extract of *Murraya koenigii* plant, which are the centers of more electron density which covers the active sites of metal.

6. CONCLUSION

Thus above studies show that although both naturally occurring and chemically synthesized ligands act as anti corrosive agents for mild steel in H_2SO_4 acid but naturally occurring agents are more efficient than synthesized one and they are also more economical and eco friendly.

ACKNOWLEDGEMENT

Authors are highly grateful and thankful to Dr. Arun Sharma.

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