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A Comparative Study of Corrosion Inhibition Efficiencies of *Catharanthus Roseus* and *Murraya Koenigii* on Aluminium in Hydrochloric Acid Solution

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ABSTRACT

Leaf and stem extracts of *Catharanthus roseus* and *Murraya koenigii* were taken for the comparison of their corrosion inhibition efficiencies on Aluminium in hydrochloric acid solution. Weight loss and thermometric methods were employed for these investigations. 1M and 2M for weight loss and 1M and 2M concentrations of HCl solutions were taken for thermometric analysis. Inhibitor concentrations were taken 0.1%, 0.3%, 0.5% and 0.7% in these methods. Results show good agreement mutually and illustrate that the corrosion inhibition efficiency of leaf and stem extracts of *Catharanthus roseus* was more as compared to that of *Murraya koenigii*. Further, results revealed that corrosion inhibition efficiency increases with the increase in the concentration of the acid as well as those of inhibitors. Maximum efficiency was found for 2M concentration of HCl at 0.7% concentration of leaf extract of the *Catharanthus roseus* whereas minimum efficiency was found for 1M concentration of HCl at 0.1% concentration of stem extract of the *Murraya koenigii*.

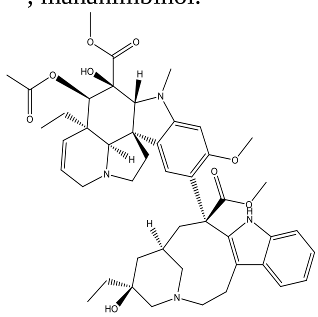
Introduction

The procedure of decaying or destruction and consequent loss of a solid metallic substance, by an unnecessary or inadvertent chemical or electrochemical assail by its surroundings, commencing from its surface is called corrosion. "Corrosion is the disintegration of an engineered material into its constituents due to chemical reactions with its surrounding"[1]Metals corrode because we use them in environment where they are chemically unstable. [2]

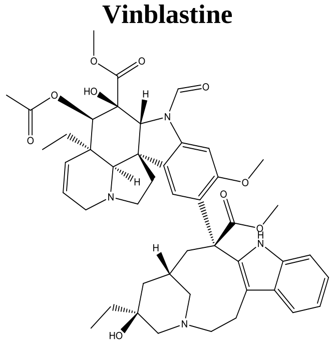
Aluminium has remarkable qualities[3-4] which are evident from its cosmopolitan uses. It also shows resistance to corrosion due to its oxide layer, which increases the life span of products made from aluminium. Furthermore, high conductivity, non-toxicity and easy recyclability are also some major characteristics of aluminium.

The naturally occurring plant products are ecofriendly, compatible, non polluting, less toxic, easily available, biodegradable and economic, so they can be used safely as corrosion inhibitors. A lot of investigations regarding the exploration of corrosion inhibition properties of various plant products like tannins, alkaloids, organic amino acids and organic dyes are being done in the whole world[5]. Some naturally occurring products like Gulmohar6, Opuntia[7], Neem[8], Trifla[9], Saunf[10], Holy Basil[11] etc have been studied as corrosion inhibitors. Many organic compounds having heteroatoms like O, N, S etc have been studied as corrosion combating agents[12-14] for metals like Al, Fe, Cu, Zn, Sn etc[15].

In the present investigation the comparative study of *Catharanthus roseus* and *Murraya koenigii* plant on the Al metal in HCl solution, extracts of leaves and stems of both plants were taken. The curiosity regarding *Catharanthus roseus* plant originates due to the fact that it has been found to contain more than 120 alkaloids. Various alkaloids extracted from this plant are already in clinical use *viz* vinblastine and vincristine that are used to fight cancer[16]. *Murraya koenigii* is an aromatic plant commonly known as "meetha neem". The whole plant is a rich source of carbazole alkaloids [17] like murrayazolinol [18], mahanimbinol.[19]



Vinblastine



Vincristine

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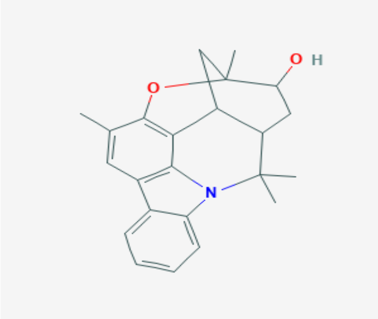
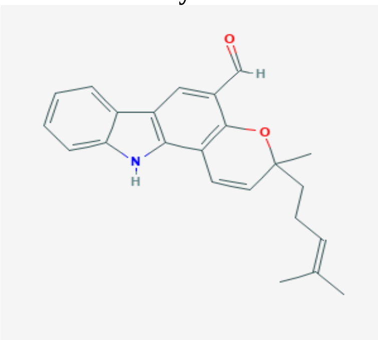


Murrayazolinol



Mahanimbinol

Experimental

Square shaped specimens of aluminium having dimension 2.5cm x 2.5cm x 0.05cm containing a small hole of about 0.02cm diameter near the upper edge were taken. The specimens were cut out from a single sheet of uniform thickness. Each specimen was washed with acetone and dried. The solutions of HCl were prepared using double distilled water. All chemicals used were of analytical reagent grade. Tests were carried out in 1M and 2M concentration of HCl 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.

The percentage inhibition efficiency η% was calculated as[20]:-

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

Where ,

W_u is the weight loss in uninhibited solution and

W_i is the weight loss in inhibited solution

Corrosion rate in $\left(\frac{mm}{yr}\right)$ can be calculated by following equation[21]:–

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

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 .

The degree of surface coverage (θ) can be calculated as[22]

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

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[23]:-

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

Where ,

RN_u is the reaction number in uninhibited solution,

RN_i is the reaction number in inhibited solution

Reaction Number (RN) can be calculated in terms of temperature as [24]–

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

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

Result and Discussion

Weight loss (ΔW), percentage inhibition efficiencies (η%), corrosion rate and surface coverage (θ) for 1M and 2M concentrations of HCl with different concentrations of 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 *Catharanthus roseus* leaf extract (99.31%) at its 0.7% concentration with 2M HCl solution whose corresponding corrosion rate (mm/yr) and surface coverage are also shown in Table 1 whereas the minimum efficiency was found (61.31%) for the stem extracts of *Murraya koenigii* at its 0.1% concentration with 1M HCL solution.

The relative order of inhibition efficiency for the leaf and stem extracts of both the plants can be shown in the following manner:

M K stem < M K leaf < C R stem < C R leaf

Fig. 1.2 (a) and Fig. 1.2 (b) shows the variation of *log* [θ/(1-θ)] and *log* C in 1M and 2M HCl respectively. According to Langmuir adsorption isotherm[25]:

log [θ/(1-θ)] = *log* A + *log* C-(Q/2.303 RT)

where,

θ = Surface coverage,

A = temperature dependent constant,

C = Bulk concentration of inhibitor (Mole/L),

Q = Heat liberated in reaction

A straight line should be obtained, when log [θ/ (1-θ)] is plotted against log C with unit gradients but deviation occurred in graphs. This is due to the deviation of kind of adsorption of inhibitor on the surface of metal. Langmuir assumed that adsorption is unimolecular but in fact adsorption is not strictly unimolecular due to interactions between inhibitor and surface molecules.

It is observed that corrosion rate of aluminium decreases with the increase in the concentration of inhibitors whereas corrosion rate increases with the increase in the strength of HCl solutions as the surface coverage i.e. the surface of the specimen covered by the inhibitor by chemisorption increases with the increase in the concentration of inhibitor.

Table 1 also shows the variation of inhibition efficiency, corrosion rate and surface coverage with various concentrations of inhibitors in 2M HCl solution also. Similar trends of these parameters are shown in 2M HCl as shown in 1M HCl solution.

Table 2 shows inhibition efficiencies determined by the other method implemented i.e. thermometric method. 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 *Catharanthus roseus*. The maximum efficiency is 85.66% in 2M HCl at 0.7% concentration. It means both methods have unanimity with each other regarding the results. 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 *Catharanthus roseus* leaf and stem extracts are more efficient than *Murraya koenigii* leaf and stem extracts. It may be due to the fact that in the *Catharanthus roseus* plant may have more hetero atoms than *Murraya koenigii* plant.

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 *Catharanthus roseus* 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 inhibition efficiency also increases with increasing concentration of acid which is due to the fact that inhibitor is basic in nature which is more dissociated in more acidic conditions and thus get more adsorbed on the surface of metal. The leaf and stem extracts of *Catharanthus roseus* plant is more efficient than the leaf and stem extracts of *Murraya koenigii*. It may be due to the presence of more hetero atoms in the leaf and stem extracts of *Catharanthus roseus* plant, which are the centres of more electron density which covers the active sites of metal.

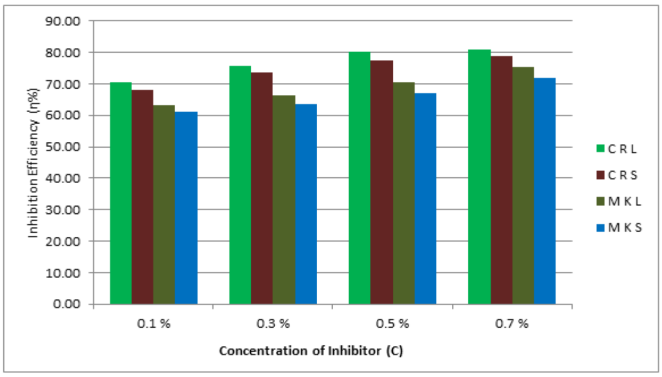


Fig-1.1(a). Variation of inhibition efficiency with concentration of inhibitor for Aluminium in 1 M HCl solution.

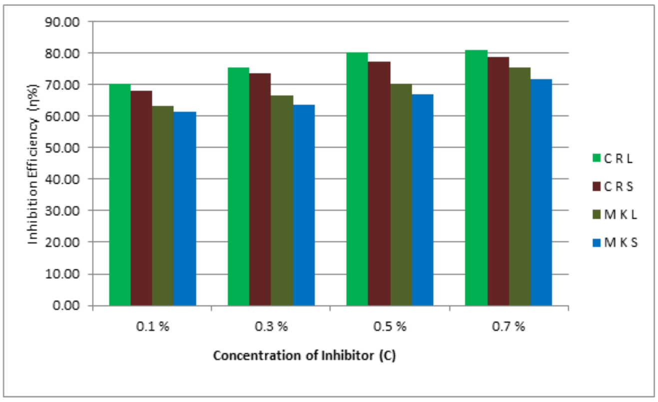


Fig-1.1(b). Variation of inhibition efficiency with concentration of inhibitor for Aluminium in 2 M HCl solution.

Table 1

Weight Loss (Δw), Inhibition Efficiency (η %), Corrosion Rate and Surface Coverage (θ) data for Aluminium in HCl Solution with given Inhibitors

Area of specimen: - 6.25 cm^2

Conc. Of inhibitor	**1M HCl (8 Hours 15 Minutes)**					**2M HCl (30 Minutes)**				
%	**Δw (mg)**	**Inhibition Efficiency (η%)**	**Corrosion Rate(mm/yr)**	**Surface Coverage (θ)**	$log\left(\frac{\theta}{1-\theta}\right)$	**Δw(mg)**	**Inhibition Efficiency (η%)**	**Corrosion Rate(mm/yr)**	**Surface Coverage (θ)**	$log\left(\frac{\theta}{1-\theta}\right)$
Uninhibited	305.0		200.86			362.6		3940.00		
***Catharanthus roseus* Leaf**										
0.1	90.0	70.49	59.27	0.70	0.3782	8.3	97.71	90.19	0.98	1.6303
0.3	74.4	75.61	49.00	0.76	0.4913	5.4	98.51	58.68	0.99	1.8205
0.5	60.0	80.33	39.51	0.80	0.6110	3.5	99.03	38.03	0.99	2.0111
0.7	58.2	80.92	38.33	0.81	0.6274	2.5	99.31	27.16	0.99	2.1585
***Catharanthus roseus* Stem**										
0.1	97.0	68.20	63.88	0.68	0.3313	25.0	93.11	271.65	0.93	1.1305
0.3	80.0	73.77	52.68	0.74	0.4491	14.8	95.92	160.82	0.96	1.3711
0.5	69.0	77.38	45.44	0.77	0.5341	7.0	98.07	76.06	0.98	1.7059
0.7	64.1	78.98	42.21	0.79	0.5750	5.0	98.62	54.33	0.99	1.8544
***Murraya koenigii* Leaf**										
0.1	112.2	63.21	73.89	0.63	0.2351	35.0	90.35	380.31	0.90	0.9713
0.3	102.3	66.46	67.37	0.66	0.2970	25.0	93.11	271.65	0.93	1.1305
0.5	90.0	70.49	59.27	0.70	0.3782	12.3	96.61	133.65	0.97	1.4545
0.7	75.0	75.41	49.39	0.75	0.4867	10.0	97.24	108.66	0.97	1.5473
***Murraya koenigii* Stem**										
0.1	118.0	61.31	77.71	0.61	0.2000	43.0	88.14	467.24	0.88	0.8711
0.3	111.0	63.61	73.10	0.64	0.2425	40.0	88.97	434.64	0.89	0.9066
0.5	101.0	66.89	66.51	0.67	0.3053	39.0	89.24	423.77	0.89	0.9189
0.7	86.2	71.74	56.77	0.72	0.4045	28.0	92.28	304.25	0.92	1.0774

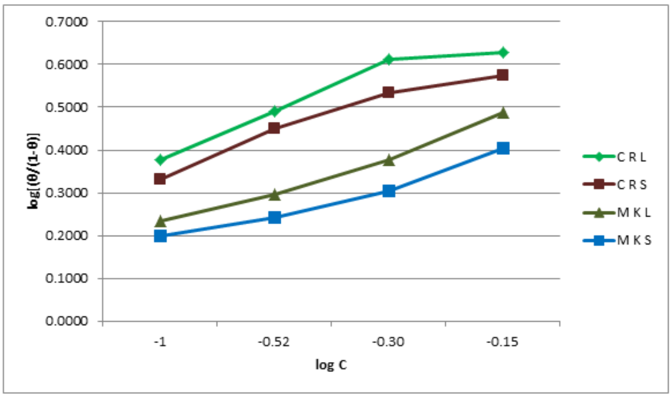


Fig-1.2(a) Langmuir adsorption isotherm for Aluminium in 1 M HCl solution

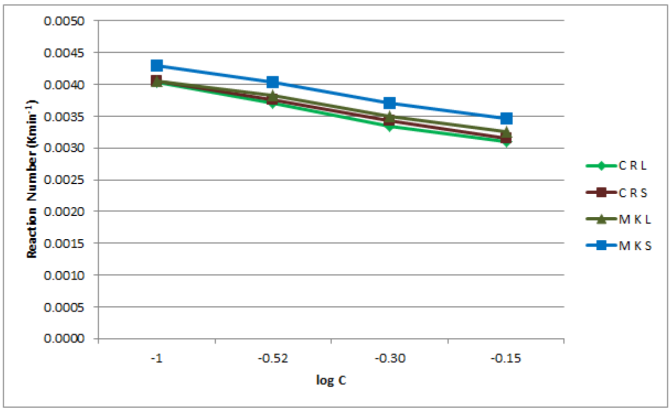


Fig-2.1 Variation of Reaction Number ($Kmin^{-1}$) with log of inhibitor concentration for Aluminium in 1 M HCl solution

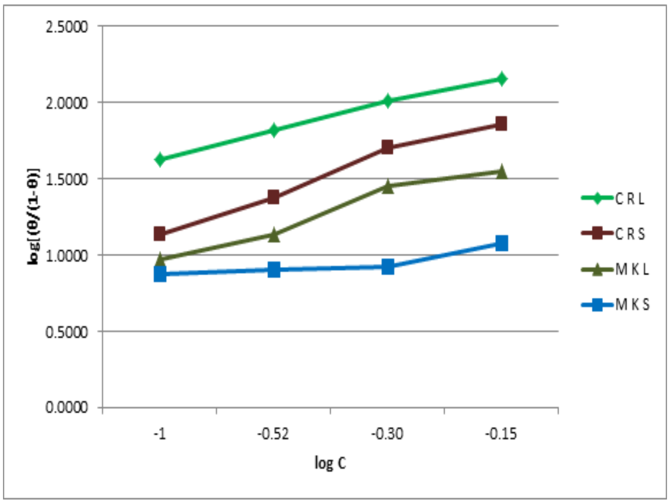


Fig-1.2(b) Langmuir adsorption isotherm for Aluminium in 2 M HCl solution

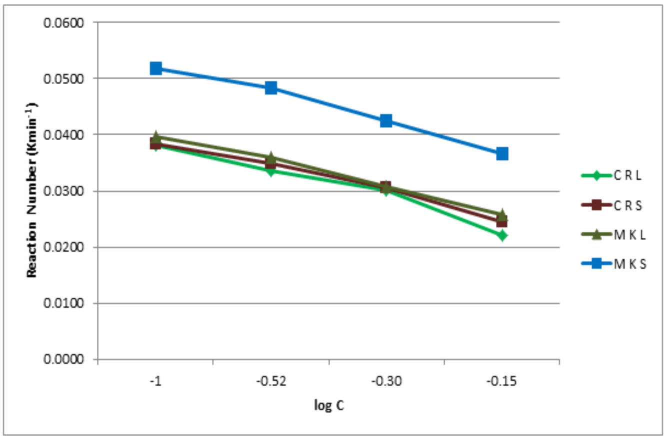


Fig-2.2 Variation of Reaction Number ($Kmin^{-1}$) with log of inhibitor concentration for Aluminium in 2 M HCl solution

Table 2

Reaction Number (RN)and Inhibition Efficiency (η%) data for Aluminium in HCl Solution with given Inhibitors

Temperature:-303+0.1 K Area of specimen :- 6.25 cm^2

	1M HCl (8 Hours 15 Minutes)		**2M HCl (30 Minutes)**	
Conc. Of inhibitor	**Reaction Number ($Kmin^{-1}$)**	**Inhibition Efficiency (η%)**	**Reaction Number ($Kmin^{-1}$)**	**Inhibition Efficiency (η%)**
Uninhibited	**0.0080**		**0.1536**	
***Catharanthus roseus* Leaf**				
0.1	0.0040	49.57	0.0382	75.16
0.3	0.0037	53.62	0.0336	78.12
0.5	0.0033	58.21	0.0302	80.33
0.7	0.0031	61.32	0.0220	85.66
***Catharanthus roseus* Stem**				
0.1	0.0040	49.45	0.0385	74.96
0.3	0.0038	53.12	0.0348	77.32
0.5	0.0034	57.16	0.0306	80.06
0.7	0.0032	60.56	0.0244	84.12
***Murraya koenigii* Leaf**				
0.1	0.0041	49.33	0.0397	74.16
0.3	0.0038	52.12	0.0361	76.51
0.5	0.0035	56.22	0.0308	79.95
0.7	0.0032	59.38	0.0258	83.22
***Murraya koenigii* Stem**				
0.1	0.0043	46.32	0.0517	66.32
0.3	0.0040	49.56	0.0484	68.52
0.5	0.0037	53.68	0.0425	72.36
0.7	0.0035	56.78	0.0366	76.14

Conclusions

From the above studies it can be concluded that although both *Catharanthus roseus* as well as Murraya koenigii act as corrosion combating agents for aluminium in HCl acid but *Catharanthus roseus* leaf and stem extracts are found to be more efficient than the leaf and stem extracts of *Murraya koenigii* ones.

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