International Journal of Engineering Technology and Management Sciences[IJETMS]

Website: ijetms.in Issue:1, Volume No.3, January-2019

Application of Expired Karthika Shampoo as Corrosion Inhibitor for Aluminum (Al) in 3 M HCl Solution

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Abstract

The efficiency of Expired Karthika shampoo as a corrosion inhibitor for aluminum corrosion in 3 M HCl solution has been examined through gasometric, atomic absorption spectroscopy, Tafel plot and impedance spectroscopy techniques. Addition of non-toxic compound (inhibitor) reduces the aluminum corrosion rate values. Gasometric results show that, amount of hydrogen gas evolved is reduced in the presence of expired Karthika shampoo. Results obtained show that, the protection rate reached 95. 121 % at 0.0 4 g/L of expired Karthika shampoo. The atomic absorption spectroscopy (AAS) data reveal that, the dissolved aluminum amount is decreased in the presence of expired Karthika shampoo and 95.464 % is the maximum protection efficiency obtained from the AAS technique. The Tafel plots showed that, expired Karthika shampoo greatly reduces both anodic and cathodic reactions and act as mixed type corrosion inhibitor. AC impedance and scanning electron microscopy (SEM) and energy dispersive x-ray spectroscopic analysis (EDX) observations complement the results of gasometric, atomic absorption and Tafel plot results.

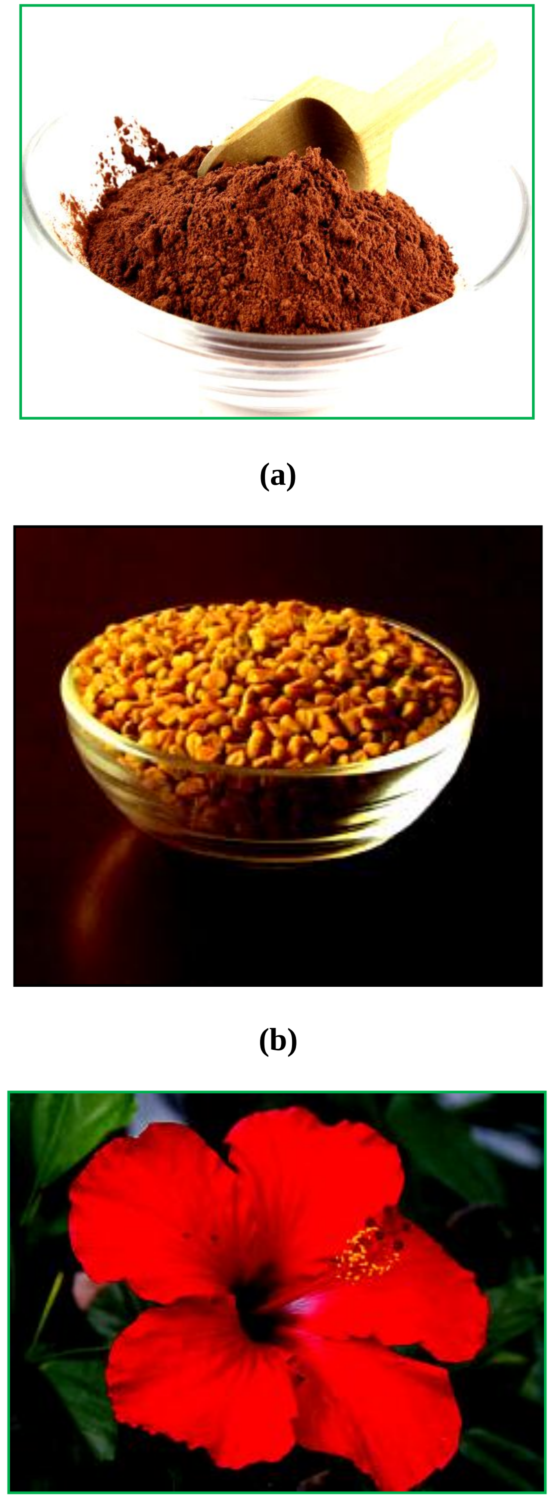
Keywords- Atomic absorption spectroscopy, Expired Karthika shampoo, Gasometric, Impedance**,** Tafel plot

1. INTRODUCTION

Aluminum is being used in both engineering and construction industries because of its workability and low cost. Several processes in industries like removal of rust, cleaning of boilers, ore processing, petroleum processing, recovery of ion exchangers, acid descaling, and oil well acidizing and steel pickling operations involve hydrochloric acid [1-3]. The use of hydrochloric acid causes severe damage to the aluminum due to the overall aggressive nature of hydrochloric acid solutions. The losses consequently persistence due to the corrosion of aluminum by several chemical industries around the globe quantity to many Indian rupees annually. The corrosion inhibitors generally accustomed to preventing the attack of hydrochloric acid on aluminum. Throughout in last few decades, some inhibitors are synthesized and used in the several industrial operations [4-7]. But, most significant drawback associated with majority of those corrosion inhibitors is that they are pricy and non-eco friendly nature. Hence, study of inexpensive and latest non toxic corrosion inhibitor is very much significant to overcome this problem. Due to negative environmental effects of synthetic corrosion inhibitors, the corrosion scientist's attention focused on the investigating the zero or less toxic and cheaper corrosion inhibitors. Since, majority synthetic compounds are not cost effective and they are toxic, the successful use of plant extract compounds as zero or less toxic corrosion inhibitors was pursued [8-10].

Therefore, exploration of eco-friendly, biodegradable and cheap inhibitors are getting more interest [11-16]. Many papers published on Al corrosion in HCl environment [17-20]. But still work is needed to fill the practical gap. Hence, in this study, expired Karthika shampoo selected because, it is waste material and it is not fit for the consumers. The main chemical composition of expired Karthika shampoo [**Figure 1**] is succinic acid, arabinose, rhamnose, nicotine, calyctomine, ascorbic acid, glucose, lactone, acacic acid, spinasterol, citric acid, lupeol, tartaric acid, oxalic acid, spinasterone, hexacosanol, flavonoids, lipids, coumarin, and amino acids. These are electron rich groups. The use of this expired Karthika shampoo is expected to achieve concurrently the environmental and economic goals.

The corrosion inhibition property of expired Karthika shampoo was examined through the gasometric, atomic absorption spectroscopy, Tafel plot, impedance, SEM and EDX studies.



(a)

(b)

(c)

Fig. 1: Main constituents of expired Karthika shampoo, a) Shikakai powder b) Fenugreek, c) Hibiscus.

2. EXPERIMENTAL SECTIONS

The chemical composition of Al used in the present investigation are shown in the **Table I**. The hydrochloric acid solutions were prepared by analytical grade of HCl by diluting the de-ionized water. Gasometric studies were performed on the 100 ml of 3 M HCl solution without and with different amounts of expired Karthika shampoo. The following equation was used to evaluate the corrosion inhibition protection property of expired Karthika shampoo,

$$\text{Inhibition efficiency} = \frac{V_a - V_p}{V_a},$$

where, V_a= Amount of H_2 gas liberated in unprotected solution, and V_p= Amount of H_2 gas liberated in the protected solution.

Gasometric method is based on the principle of dissolution reaction in aqueous environment which is characterized by the gas evolution on the electrode surface. The detail procedure and apparatus used for this method is similar to literature [21-23]. The gasometric technique records the evolution of volume of hydrogen gas in the reaction system. 99 % of Al was used in the test with 100 ml of 3 M HCl solution at four different amounts of inhibitor. 100 ml of 3 M HCl solution was submerged in the reaction vessel which is connected to burette with delivery tube. The volume of air (initial) was recorded in the burette. After that, Al metal piece was submerged in the 3 M HCl solution and vessel is closed. The differences in the volume of gas were recorded. For each time, the experiment was performed with new Al metal pieces. The experiment performed three times and average values are recorded.

Table I Al pieces chemical composition

Element	Fe	Si	Tl	Zn	Mn
wt%	0.6	0.3-0.7	0.1	0.2	0.3
Element	Cr	Mg	Cu	Al	
wt%	0.2	0.4-0.9	0.1	Remainder (96.9-97.8%)	

The Tafel plots and impedance spectroscopy were performed by using the CHI instrument. Before performing the experiment, the Al electrode is submerged in the 3 M HCl solution for about one hour. The electrochemical Tafel plot and impedance spectroscopy test was carried out after the stabilization period of aluminum metal in the 3 M HCl solution by using the three electrode system (Pt= counter cell, saturated calomel= reference electrode and Al= working electrode). The electrochemical studies (both Tafel plot and impedance) were recorded by using the

CHI6086D instrument at 60 ± 1^{o} C with the help of ultra-circulating thermostat. Tafel plots generated at a scan rate of 0.01 V/s with electrode potential ± 250 mV. Nyquist curves obtained at an amplitude of 0.01 V in the frequency range 10^{5} to 1 Hz. ZSimpwin 3.20 program was employed for fitting the data.

The values of corrosion current density obtained from the potentiodynamic polarization technique were used in the determination of inhibition efficiency with the help of following equation;

$$\text{Inhibition efficiency} = \left[1 - \frac{i'_{corr}}{i_{corr}}\right] \times 100$$

Where, i'_{corr} = Protected Al corrosion current density and i_{corr} = Unprotected Al corrosion current density value.

The charge transfer resistance (R_{ct}) obtained from an R(QR(QR)) **[Figure 2**] electrical circuit was used in the determination of inhibition efficiency of the zero or less toxic corrosion inhibitor,

$$\text{Corrosion inhibition efficiency} = \frac{R_{ct\,(inh)} - R_{ct}}{R_{ct\,(inh)}} \times 100$$

Where, R_{ct} = Unprotected Al charge transfer resistance value and $R_{ct\,(inh)}$ = Protected Al charge transfer resistance value.

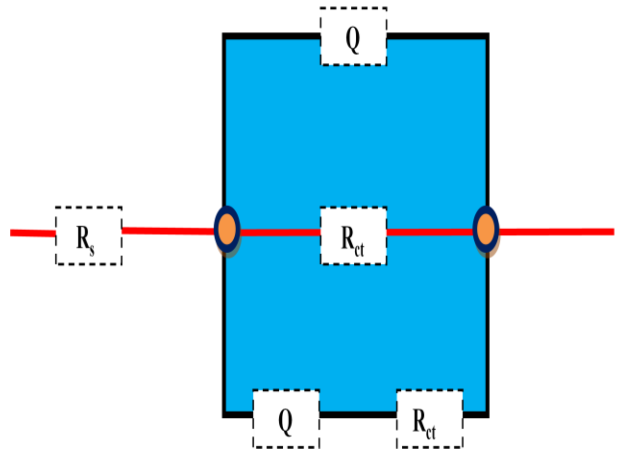


Fig. 2: R(QR(QR)) model. Where, R_{ct} = charge transfer resistance R_{s}= resistance of electrolyte in bulk, and Q constant phase element

Atomic absorption studies (model G8- 908) were employed in order to evaluate the amount of dissolved aluminum in the 3 M HCl solution containing different amounts of expired Karthika shampoo with an immersion period of one hour. The protection efficiency of the inhibitor was calculated by the following equation,

$$\text{Protection efficiency} = \frac{B-A}{B} \times 100,$$

Where, B= Amount of Al dissolved in the absence of inhibitor and A= amount of Al dissolved in the presence of the inhibitor.

Morphological studies

Surface topography of Al samples after the gasometric test was examined through SEM and EDX technique (with a contact time of one hour).

3. RESULTS AND DISCUSSION

3.1 Gasometrical studies

The geometric studies were performed on the surface of Al in the 3 M HCl solution (100 ml) without and with expired Karthika shampoo of different amounts at an immersion period of 1, 2, 3, 4, 5 and 10 hour period. The results of gasometric are shown in the **Table II** and **Figure 3**. The amount of hydrogen gas evolved on the Al surface in the 3 M HCl solution without and with of expired Karthika shampoo was determined. In all cases, an enhancement in the concentration of expired Karthika shampoo leads to the decrease the amount of evolution of hydrogen gas on the Al surface. This indicates that, the presence of expired Karthika shampoo blocks the corrosion of aluminum in the 3 M HCl solution, which shows that, inhibition of aluminum corrosion in the presence of expired Karthika shampoo takes place by adsorption at active aluminum sites. The maximum protection efficiency was observed at one hour immersion period. On the other hand, an increase in the exposure period from 1 to 10 hours resulted in a decrease in the protection rate and increase in the aluminum corrosion rate. This is probably due to the desorption of non-toxic corrosion inhibitor from the surface of aluminum for longer immersion period. As a result, amount of hydrogen gas evolution increases with an increase in the immersion period. Therefore, lower protection rate values were observed after one hour immersion time.

Table II Gasometric results

Concentration (g/L)	Immersion period	Volume of hydrogen gas evolved in ml	Protection efficiency (in percentage)
Blank	1	20.5	
0.01		4.0	80.487
0.02		3.1	84.878
0.03		2.3	88.780
0.04		1.0	95.121
Blank	2	25.1	
0.01		5.1	79.681
0.02		4.5	82.071
0.03		4.0	84.063
0.04		2.5	90.039
Blank	3	30.6	
0.01		7.0	77.124
0.02		6.5	78.758
0.03		6.0	80.392
0.04		4.5	85.294
Blank	4	37.2	

0.01		9.0	75.806
0.02		8.8	76.344
0.03		8.0	78.494
0.04		7.0	81.182
Blank	5	42.1	
0.01		11	73.871
0.02		10.5	75.059
0.03		10.0	76.247
0.04		9.5	77.434
Blank	10	47.8	
0.01		13.0	72.803
0.02		12.5	73.849
0.03		12.0	74.895
0.04		11.0	76.987

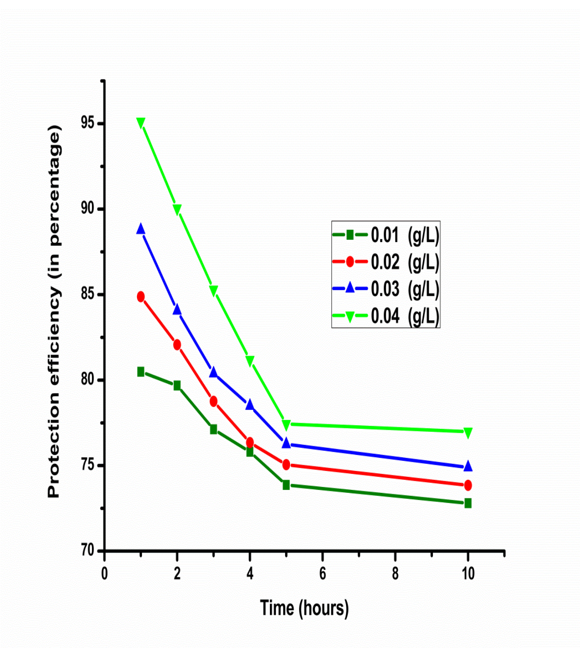


Fig. 3: Effect of contact time on protection efficiency of the inhibitor

3.2 Atomic Absorption Spectrophotometric (AAS) Studies

Atomic absorption spectroscopy was employed in order to estimate the amount of dissolved aluminum in the 3 M HCl solution containing four different types of expired Karthika shampoo. The results of AAS are shown in the **Figure 4** and **Table III.** The data about the AAS show that, the presence of the inhibitor (expired Karthika shampoo) decreases the amount of dissolved aluminum in the 3 M HCl solution. Introduction of expired Karthika shampoo to the 3 M HCl solution creates a protective layer on the Al surface. This is a clear hint of corrosion protection property of aluminum from the 3 M HCl solution. Hence, protection efficiency values increase with an increase in the amount of expired Karthika shampoo.

Table III AAS results

Concentration (g/L)	Amount of aluminum dissolved in 3 M HCl solution	Protection efficiency (in percentage)
Blank	18.3×10^{-3}	
0.01	1×10^{-3}	94.535
0.02	9.3×10^{-4}	94.918
0.03	8.7×10^{-4}	95.245
0.04	8.3×10^{-4}	95.464

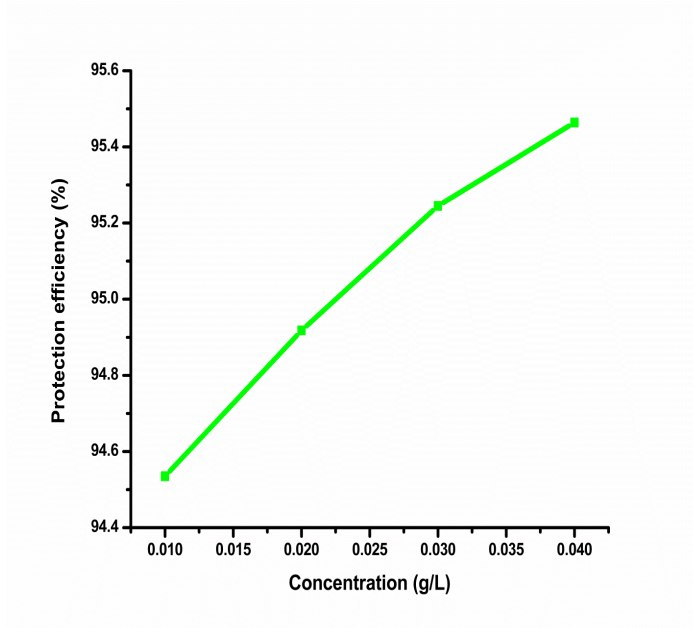


Fig. 4: Variation of protection efficiency with different amounts of inhibitor

3.3 Tafel studies

The effect of different amounts of expired Karthika shampoo on the Al surface corrosion rate in 3 M HCl solution at 60 ^{o} C has been evaluated by Tafel plot studies. The Tafel curves are shown in the **Figure 5.** The electrochemical parameters corrosion current density, cathodic and anodic Tafel slope and corrosion potential (E_{corr}) values are shown in the **Table IV**. The resulted table shows that, the expired Karthika shampoo is capable to decrease the corrosion current density values. The inhibitor expired Karthika shampoo exhibits the positive effect on the Al corrosion process in the 3 M HCl solution process. The efficiency values considerably increases with the inhibitor concentration. The inhibitor expired Karthika shampoo adsorbs on the surface of Al and consequently slows the aluminum disintegration process by hindering the active aluminum sites. **Table IV** shows that, presence of inhibitor expired Karthika shampoo in the 3 M HCl solution equally affects on the both cathodic and anodic Tafel slope values. Further, no much variation in the corrosion potential values. This behavior supports the mixed corrosion inhibition property of expired Karthika shampoo for Al in 3 M HCl solution.

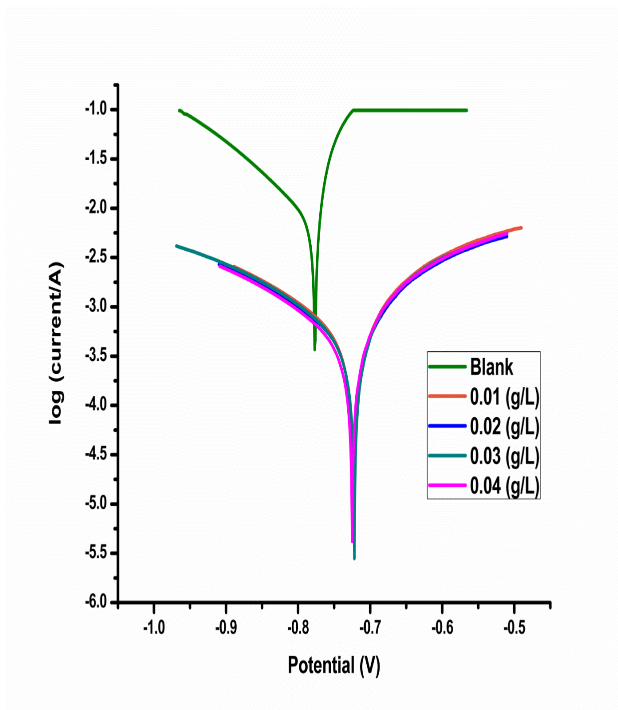


Fig. 5: Tafel results

Table IV Tafel results

C (g/L)	Corrosion potential (E_{corr}) (mV)	Anodic Tafel slope (V/dec)	Cathodic Tafel slope (V/dec)	Corrosion current (A)
Blank	-777	0.003	6.392	0.05570
0.01	-722	5.475	4.840	0.0008484
0.02	-722	5.316	4.773	0.0008218
0.03	-722	5.461	5.016	0.0007964
0.04	-725	5.498	4.981	0.0007549

3.4 Impedance studies

Impedance studies are valuable techniques to examine the inhibiting property of expired Karthika shampoo. It gives both capacitive behavior and resistive at active interface. In this part, the influence of expired Karthika shampoo on the aluminum surface in 3 M HCl solution has been thoroughly investigated. **Figure 6** shows the impedance plots without and with inhibitor of different amounts. The results obtained from the impedance plots are shown in the **Table V.** The table hints that, area of depressed semicircle in the uninhibited system is low compared to the inhibited system which clearly indicating the aluminum corrosion inhibition property of expired Karthika shampoo. An increase in the charge transfer resistance values indicates to high block of the active sites at Al-3 M HCl solution as a result of enhancing the concentration of the inhibitor **[5, 17, 18, 19].** Whereas, the values of constant phase element (Q) and double layer capacitance (C_{dl}) reduces with different amounts of expired Karthika shampoo. This may be due to increase in the electrical double layer thickness, which decreases the process of aluminum disintegration. The value of surface heterogeneity factor (n) was close to unity which shows that, Al dissolution process was controlled by charge transfer process. Chi squared value (χ^2) values confirm the good fit of proposed electrical circuit.

Table V Nyquist plot results

Concentration (g/L)	Q ($\Omega^{-1}\mu s^n$)	n	$R_{ct}\Omega$
Blank	561.00	0.8891	9.936
0.01	11.119	1.000	168.10
0.02	0.172	0.7498	284.80
0.03	0.210	0.7360	373.90
0.04	0.207	0.7350	457.50
C_{dl} (μF)	Measurement error (%)	χ^2	Protection efficiency (%)
745.40	0.6908	0.000047	94.089
29.97	11.930	0.01422	96.511
26.00	0.9728	0.00009	97.342
28.97	1.068	0.00011	97.828
34.80	1.216	0.00001	

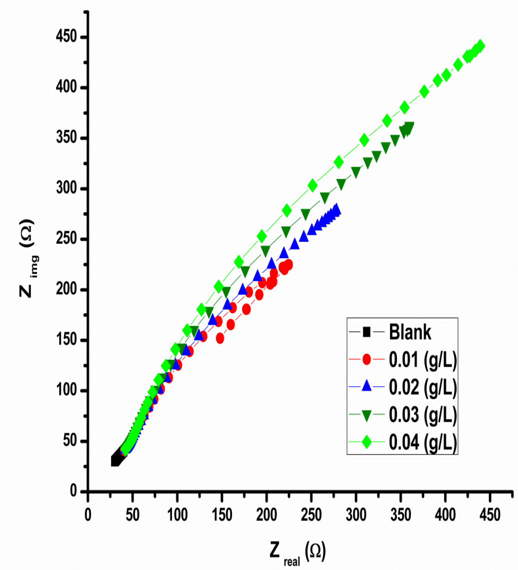
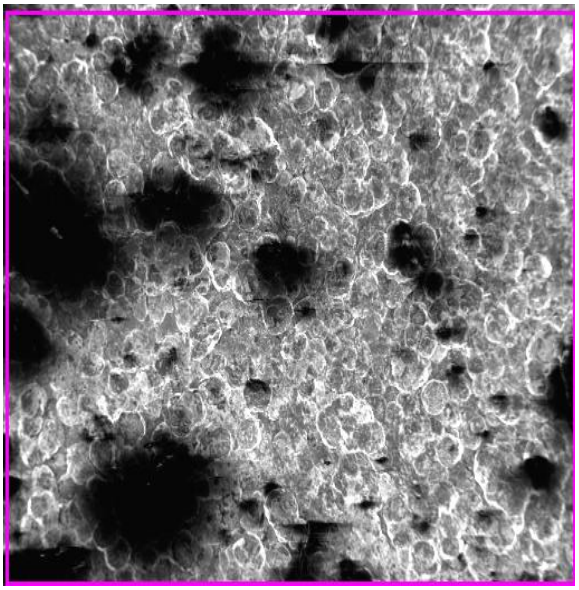


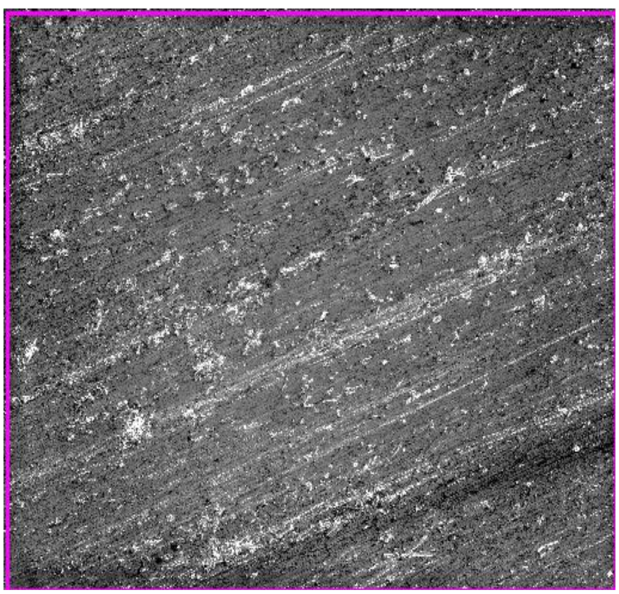
Fig. 6: Nyquist plots

Scanning electron microscopy analysis

The topography of Al treated in 3 M HCl solution without and with corrosion inhibitor are shown in the **Figure 7**. The Al submerged in the 3 M HCl solution shows rough surface with corrosion products. Whereas, the Al electrode exposed 3 M HCl solution with inhibitor exhibits smooth surface almost without any corrosion products. This is due to layer formation on the Al surface which hinders the aggressiveness of the HCl on the Al electrode.



Without inhibitor

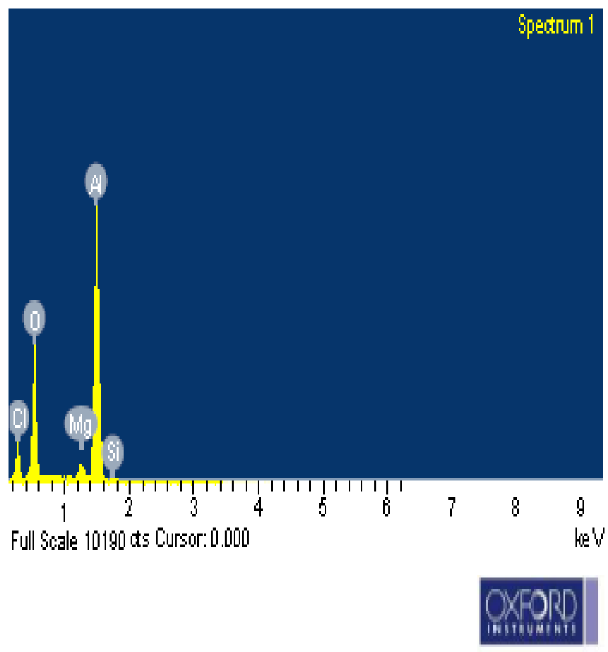


With inhibitor

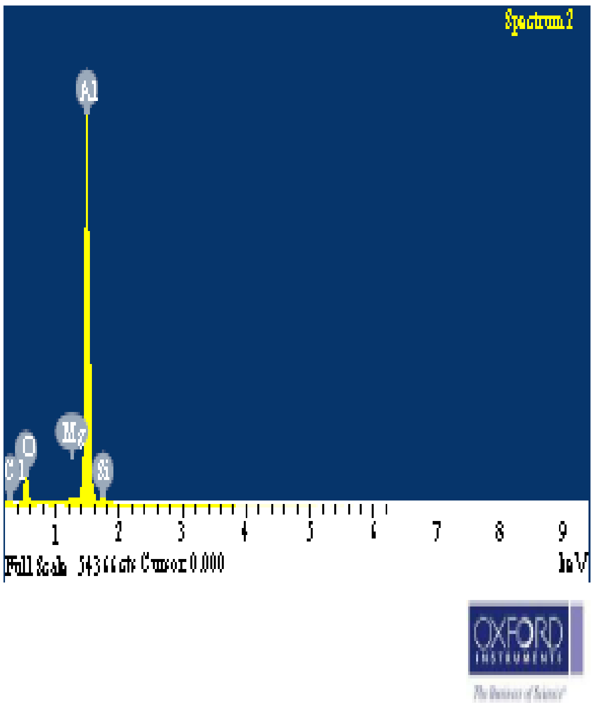
Fig. 7: SEM images without and with corrosion inhibitor

Energy Dispersive Spectroscopy (EDX) study

EDX test used to examine the Al electrode composition in unprotected and protected system in 3 M HCl solution. The results of EDX are shown in the **Figure 8** and **Table VI**. From the Table 6 and Figure 8, it is clear that, the Cl peak is suppressed in the protected system when compared to the unprotected system. This is due to the formation of protective layer on the Al in 3 M HCl solution, which suppress the attack of free Cl^- ions on the Al surface.



A)



B)

Fig. 8: EDX A) without inhibitor B) with inhibitor

Table VI Atomic contents of elements in percentage by EDX technique

System	O	Mg	Al	Si	Cl
Without inhibitor	32.69	2.08	47.81	1.07	16.35
With inhibitor	16.93	0.37	71.93	2.31	8.46

4. CONCLUSION

In this research, successfully developed an economical, practical, eco-friendly and operationally simple corrosion inhibitor. The gasometric studies show that, presence of inhibitor reduces the evolution of hydrogen gas from the Al metal surface. Atomic absorption spectroscopy shows that, the amount of dissolved aluminum in corrosive 3 M HCl solution is reduced in the presence of inhibitor. Electrochemical Tafel plot shows that, expired Karthika shampoo inhibits the Al corrosion process by mixed mode. Nyquist plots also hint the corrosion inhibition property of expired Karthika shampoo on aluminum surface in 3 M HCl medium. The SEM and EDX studies show that, the Al corrosion inhibition property of expired Karthika shampoo is mainly being due to adsorption phenomena.

Conflict of interest

Authors declare no conflict of interest.

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