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Coffee Husk and Ziziphusspina Christi Extracts as Green Corrosion Inhibitors for Aluminum in NaOH Solutions

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ABSTRACT

The inhibition efficiency of coffee husk extract and extract of Ziziphusspina Christi on the corrosion of aluminum in 0.5 M NaOH solutions was investigated using weight loss method at 25 and 45°C. Surface was examined using energy dispersive X-ray analysis (EDX), and scanning electron microscopy (SEM). Experimental investigations showed that coffee husk extract and Ziziphusspina Christi extract reduce the corrosion of aluminum in 0.5M NaOH solutions. The inhibition mechanism was deduced from the temperature dependence of the inhibition efficiency as well as from activation parameters that govern the process. The adsorption of two extracts on the aluminum surface was found to obey Langmuir, Temkin and thermodynamic/kinetic model of adsorption isotherms. The obtained results are consistent with physisorption adsorption.

Introduction

Due to the light weight and mechanical strength, aluminum and its alloys are very attractive materials for engineering applications. The interest of these materials arises from their importance in the recent civilization. Using organic compounds as corrosion inhibitors may be the main choice to decrease the corrosion rate of metals and their alloys in different media. The presence of hetero atoms in the structure of inhibitor molecules such as O, N, S, P; enhance the adsorption process and inhibition efficiency [1-5]. Corrosion inhibition of aluminum and its alloys was the subject of numerous studies [6-10]. The natural products of plant origin are inexpensive, readily available and renewable sources of materials, eco-friendly corrosion inhibitors. The extracts from their leaves, barks, seeds, and roots compose of mixture of organic compounds and some have been reported as effective inhibitors for various metals [11-17].

The aim of the present work was used to investigate the inhibition of aluminum corrosion in 0.5 M NaOH solutions by weight loss method. Also, surface examination was tested using different techniques.

Experimental

Materials and solutions

Plant extract solutions

The Ziziphus spina Christi extract and coffee husk extract were obtained directly from the powder of dried leaves of Ziziphus spina Christi and powder of dried husk. Ziziphus spina Christi and coffee husk were soaked in methanol and left standing for 7 days. The solution was filtered and further distilled at 40°C to remove the methanol from the two plants extracts and then concentrated to dryness. The experiments were performed in 0.5 M NaOH

Chemical composition of plants extracts

The chemical composition of Ziziphus spina Christi is well known [18-21]. The main constituents of the essential oil were alpha-terpineol (16.4%) and linalool (11.5%). The main neutral hydrocarbons were n-pentacosane forms (81%). Methyl esters isolated from leaves included methyl palmitate, methyl stearate and methyl myristate. Beta-Sitosterol, oleanolic acid and maslinic acid were the main aglycones of the glycosides present in leaves.`Sugars present in leaves included lactose, glucose, galactose, arabinose, xylose and rhamnose. The plant also contains four saponin glycosides, the highest flavonoid content was found in the leaves (0.66%). No significant influence of growing site or year of harvesting on the flavonoid content was observed. As quercetin 3-O-rhamnoglucoside 7-O-rhamnoside are the main flavonoid compounds present in all plant parts investigated [22]. The composition of the plant has always proved complex in its chemistry, also contain the known alkaloids, zizyphine-F, jubanine-A and amphibine-H. Coffee husk is rich in organic matter (cellulose, hemicelluloses, pectin and lignin), and chemical nutrients such as nitrogen (N) and potassium (K). Additionally, coffee husk also contains secondary compounds such as caffeine, tannin and polyphenol [23, 24].

Weight loss measurements

The weight experiments were carried out using specimens of aluminum having dimensions (2 x 2 x 0.05 cm) and with composition more than 99.9%. The test pieces of aluminum samples were weight up to fourth decimal place using digital electronic balance. The test samples were immersed in 50 mL of 0.5 M NaOH in absence and presence of varying concentration of coffee husk extract and Ziziphusspina Christi extract taken in beaker at temperature (25and 45^{0}C) in thermostat water bath. Initial weight of samples were measured before immersion and after specified period of exposed time, each piece was taken out of the test solution, rinsed with double distilled water, dried between two filter papers and weighed again using a digital electronic balance. The difference in weight for an exposed period of 30-180 minutes was taken as the total weight loss. The experiments were carried out at various concentrations (100-500 ppm) of coffee husk extract. Triplicate samples were used to

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check reproducibility of results. From the average weight loss results (average of three replicate analysis), the corrosion rate, the percentage of inhibition efficiency (%IE) and the degree of surface coverage (θ) were calculated using equations (1and 2) [25]:

Corrosion rate = $\Delta W/AT$ mg/cm^2.min (1)

Where "ΔW" is the weight loss in mg, "A" is the area of the specimen in cm^2 and "T" is the exposure time in min.

Inhibition efficiency (%IE) $= \theta \times 100 = [(W_1 - W_2)/W_1] \times 100$ (2)

where W_2 and W_1 are the weight losses for aluminum sample in the presence and absence of the inhibitor and θ is the degree of surface coverage of the inhibitor.

Scanning electron microscopy (SEM)

A scanning electron microscope (SEM) model HITACHI S-3000H coupled to an analyzer EDAX –RONTEC, were used to analyze the morphology of the aluminum surface without and with inhibitor added. Images of the samples were recorded after 24h exposure time in 0.5 M NaOH without and with different concentration of two plant extracts.

Results

Weight loss studies

Tables 1and 2 show the experimental data of weight loss (ΔW), percentage of inhibition efficiency (%IE), corrosion rate (C.R.) and degree of surface coverage (θ) for aluminum in 0.5 M NaOH in absence and presence of various concentrations of different plant extracts at different temperatures. The corrosion rate values were plotted against the concentration of the two extracts in 0.5 M NaOH and are shown in Figures 1 and 2. Corrosion rate values of aluminum decrease when the concentration of extracts increases and the magnitude of adsorption and surface coverage by extracts on aluminum surface increases with concentration of the extracts. From Figures 3 and 4 the inhibition efficiency increases with increasing concentration of extracts.

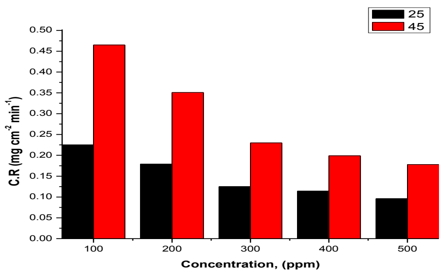

Figure 1. Corrosion rates of various concentrations of Ziziphus spina Christi extract on aluminum in 0.5 M NaOH at 25 and 45^{0}C

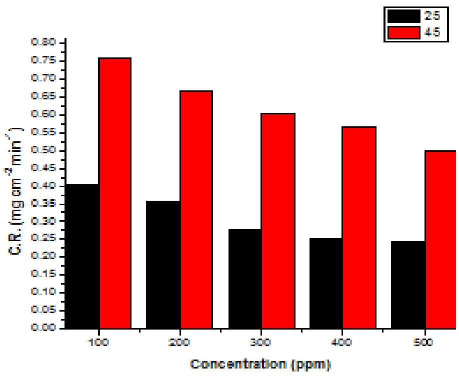

Figure 2. Corrosion rates of various concentrations of coffee husk extract on aluminum in 0.5 M NaOH at 25 and 45^{0}C

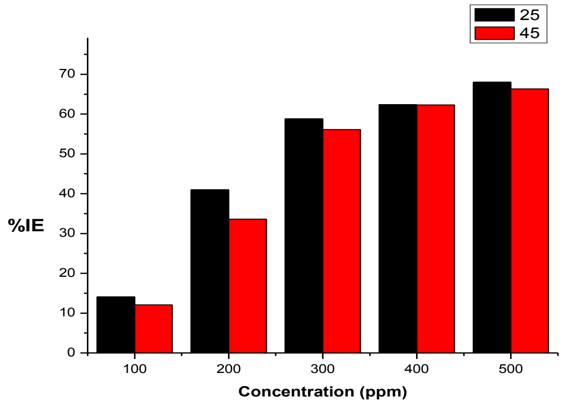

Figure 3. The variation of inhibition efficiency with Ziziphus spina Christi extracts concentration of aluminum in 0.5 M NaOH solutions

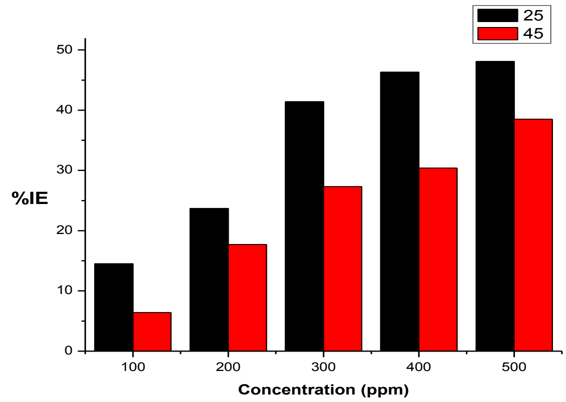

Figure 4. The variation of inhibition efficiency with coffee husk extracts concentration of aluminum in 0.5 M NaOH solutions

Adsorption isotherms

The action of an inhibitor in aggressive alkaline media is assumed to be due to its adsorption at the metal /solution interface. The adsorption mode will be dependent on factors such as the extract composition, chemical changes to the extract and the nature of the surface charge on metal. An anion adsorption is favored by a positive surface charge and negative surface charge will favor the adsorption of cations. In order to obtain the adsorption isotherm, the degree of surface coverage (θ) of the extract must be calculated. There are a number of mathematical expressions having thus developed to take into consideration of non-ideal effects. The most used isotherms are, Frumkin, De Boer, Parsons, Temkin, Flory-Huggins and Bockris-Swinkels [26-30]. The values of surface coverage, θ, corresponding to different concentrations of extracts at 25, 45º C have been used to determine the best adsorption isotherm. Figures 5 and 6 confirm that the inhibition process is due to adsorption of the extract components on Al surface. This is because a straight line is obtained when Log (C/θ) is plotted against log C and the linear correlation coefficient of the fitted data is close to 1. This indicates that the adsorption of the extract molecules obeys the Langmuir adsorption model [31] which is expressed as:

$$\frac{C}{\theta} = \frac{1}{K} + C \qquad (3)$$

Where C is the inhibitor concentration and K is the equilibrium constant for the adsorption /desorption process of the inhibitor molecules on the metal surface

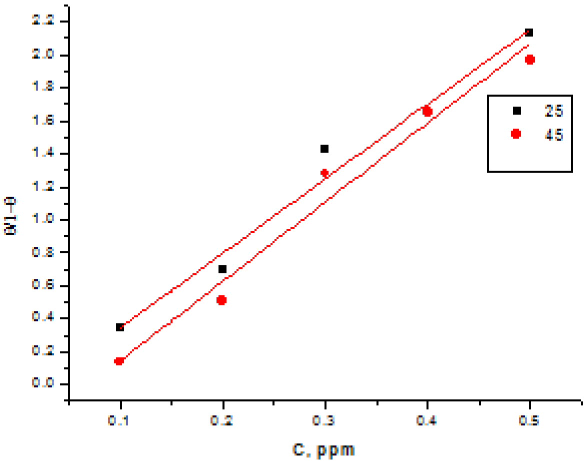

Figure 5. Langmuir isotherm for Ziziphus spina Christi adsorption on aluminum in 0.5 M NaOH at two different temperatures after 120 min immersion

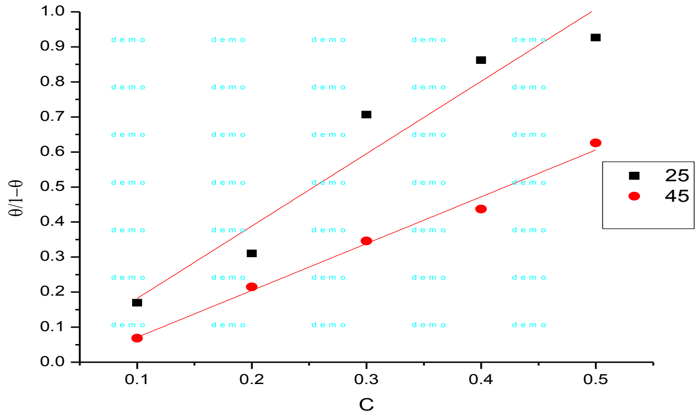

Figure 6. Langmuir isotherm for coffee husk adsorption on aluminum in 0.5 M NaOH at two different temperatures after 120 min immersion

The extracts also obey Temkin adsorption isotherm which is present in Figures 7 and 8. Values of adsorption parameters deduced from the plots are recorded in Tables 3 and 4. Temkin isotherm is defined as in eq. 4:

$$a\,\theta = \ln K C \qquad (4)$$

a is a molecular interaction parameter depending upon molecular interactions in the adsorption layer and the degree of heterogeneity of the surface.

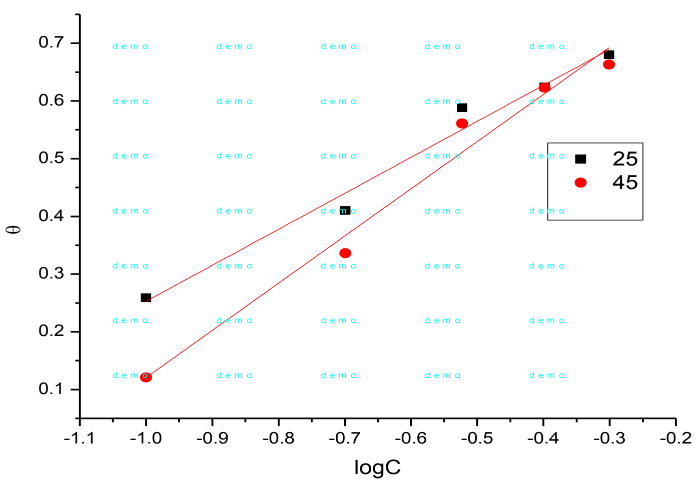

Figure 7. Temkin adsorption isotherm plot as θ against Log C for Ziziphus spina Christi extract at two different temperatures

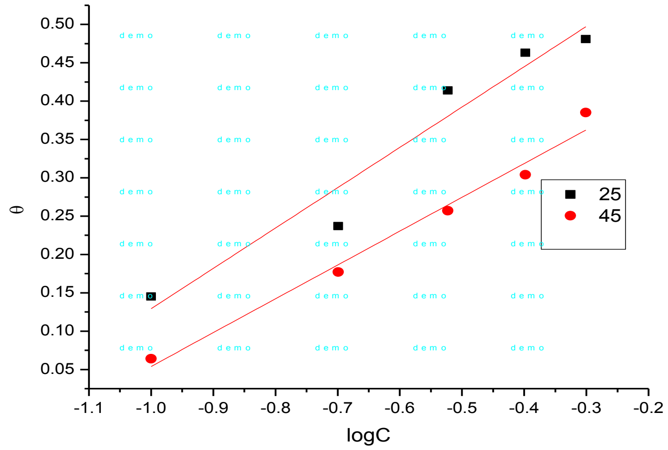

Figure 8. Temkin adsorption isotherm plot as θ against Log C for coffee husk extract at two different temperatures

A Plot of log θ/ 1-θ against log C Figures 9 and 10 at different concentrations of extracts, straight lines were obtained indicating that adsorption follows kinetic thermodynamic model according eq. 5 [32]:

$$\text{Log } \theta/1\text{-}\theta = \log (K') + y \log C \qquad (5)$$

The equilibrium constant of adsorption is $K_{ads} = K'^{(1/y)}$, where 1/y is the number of surface active sites occupied by one inhibitor molecules and C is the bulk concentration of the inhibitor. It is important to note that values of 1/y less than unity imply the formation of multilayers of the inhibitors on the surface of the metal and values of 1/y greater than unity mean that a given inhibitor molecule will occupy more than one active site. According to the data in this Tables 3, 4 it is seen that the values of 1/y are nearly 1 indicating that each inhibitor molecule occupies one active site.

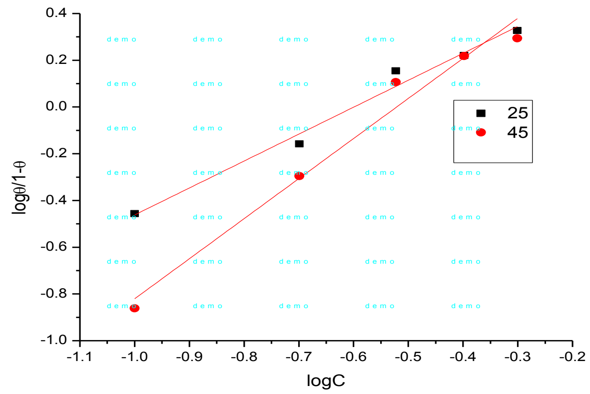

Figure 9. The kinetic thermodynamic for Ziziphus spina Christi extract determined on aluminum at two different temperatures

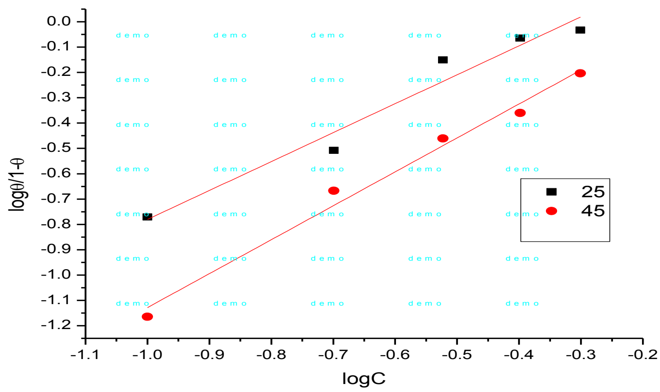

Figure 10. The kinetic thermodynamic for coffee husk extract determined on aluminum at two different temperatures

The corrosion data fit the first- order reaction rate law according to equation 6 [33]

$$\text{Log } [W_i\text{-}\Delta W] = - Kt/2.303+\text{Log}W_i \quad (6)$$

Where W_i is the initial weight of aluminum specimen, ΔW is the weight loss of aluminum specimen at time t,$[W_i\text{-}\Delta W]$ is the residual weight of aluminum specimen at time t and K is the first –order rate constant. The linear plots obtained with correlation coefficients close to 1 confirm first -order kinetics for the corrosion of aluminum in 0.5 M NaOH solution in the presence and absence of Ziziphus spina Christi and coffee husk extract.

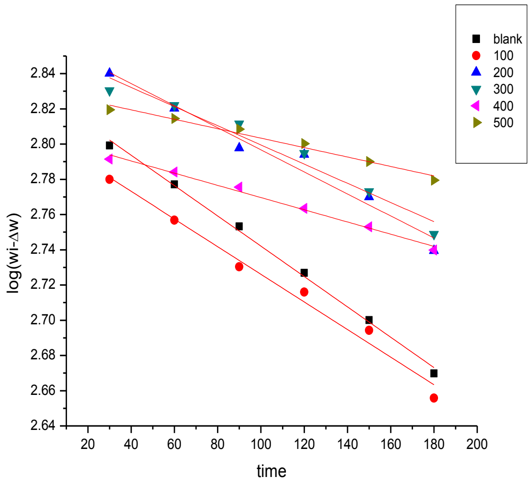

Figure 11. Plot of log (W_i-ΔW) versus time for Al in 0.5 M NaOH solution without and with Ziziphus spina extract

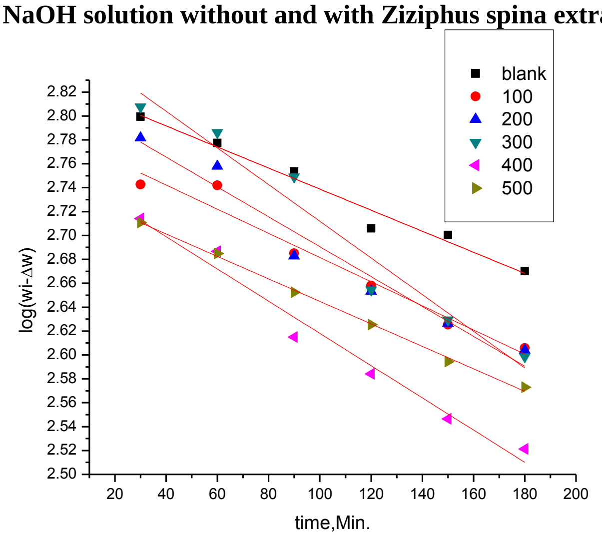

Figure 12. Plot of log (W_i-ΔW) versus time for Al in 0.5 M NaOH solution without and with coffee husk extract

It is well known that the equilibrium constant of adsorption (K) is related to the standard adsorption free energy (ΔG^o_{ads}) and can be calculated from eq. 7 [34]:

$$K = 1/55.5 \exp [-\Delta G^o_{ads}/RT] \quad (7)$$

Values of free energy of adsorption calculated from equation 7 using K values obtained from Langmuir adsorption and Temkin adsorption isotherm are presented in Tables 3 and 4. The values are negative and less than - 40 kJ mol^{-1}. This implies that the adsorption of the extract on aluminum surface is spontaneous and confirms the physical adsorption isotherm mechanism [33].

Effect of temperature

Thus in examining the effect of temperature on the corrosion process, the apparent activation energies(E_a) was calculated using evaluated from Arrhenius equation equation(8):

$$\text{Log}(C.R.)_2/ (C.R.)_1= E_a/2.303R \left(\frac{1}{T1} - \frac{1}{T2}\right) \quad (8)$$

Whereas estimates of the heats of adsorption (Q_{ads}) can be obtained from the trend of surface coverage with temperature as follows [34]:

$$Q_{ads} = 2.303R \left[\log \left(\frac{\theta 2}{1-\theta 2}\right) - \log \left(\frac{\theta 1}{1-\theta 1}\right)\right] \times \frac{T1T2}{T2-T1} \quad (9)$$

Where θ_1 and θ_2 are the degrees of surface coverage at temperatures T_1 and T_2, respectively. The calculated values for E_a^* and Q_{ads} are given in Tables 5 and 6.

Increased activation energy, E_a^* in inhibited solutions compared to the blank suggests that the extract is physically adsorbed on the corroding metal surface while either unchanged or lower E_a^* in the presence of extract suggest that chemisorption [35]. The negative values of Q_{ads} are indicative of less surface coverage with rise in temperature, supporting the proposed mechanism of physisorption [36].

Surface studies

Figure 13 represents the micrograph obtained for aluminum samples in presence and in absence of Ziziphusspina Christi extract and coffee husk extract after exposure for 24 h immersion. It can be seen from Fig. 13(a) that the aluminum samples before immersion seems smooth and appears some abrading scratches on the surface shows the smooth surface of the metal. This shows the absence of any corrosion products or inhibitor complex formed on the metal surface. It is clear that aluminum surfaces suffer from severe corrosion attack in the blank sample as shown in Fig. 13(b). Furthermore, the corrosion products appear very uneven and cube-shaped morphology. It is important to stress out that when the Ziziphusspina Christi extract and coffee husk extract are present in the solution Figure 13 (c, d) the morphology of aluminum surfaces is quite different from the previous one, and the specimen surfaces were smoother. We noted the formation of a film which is distributed in a random way on the whole surface of the aluminum. This may be interpreted as due to the adsorption of the Ziziphusspina Christi extract and coffee husk extract on the aluminum surface incorporating into the passive film in order to block the active site present on the aluminum surface. On the other hand, due to the involvement of inhibitor molecules in the interaction with the reaction sites of aluminum surface, resulting in a decrease in the contact between aluminum and the aggressive medium and sequentially exhibited excellent inhibition effect [37, 38].

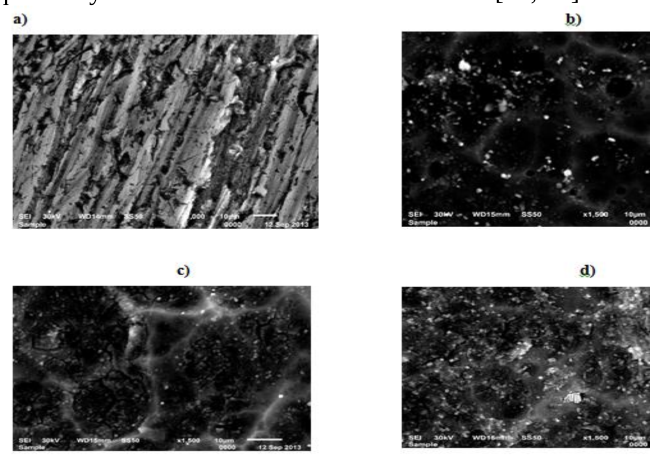

Figure 13. Scanning electron microgram of polished aluminum (1500x) (a)alone(b) after exposure to 0.5M NaOH (c)after exposure to 0.5M NaOH containing 500ppm of Ziziphusspina Christi extract (d) after exposure to 0.5 M NaOH containing 500ppm of coffee husk extract

Table 1. Data from weight loss of Al in 0.5 M NaOH for various concentrations of Ziziphus spina Christi after 120 min immersion at 25 ^{0}C and 45 ^{0}C

Conc., Ppm	298 K				318K			
	ΔW mg cm^{-2}	θ	% IE	C.R. mg cm^{-2} min^{-1}	ΔW mg cm^{-2}	θ	%IE	C.R. mg cm^{-2} min^{-1}
Blank	36.45	-----	-----	0.303	63.50	------	-----	0.529
100	27.00	0.259	14.1	0.225	55.83	0.121	12.1	0.465
200	21.50	0.410	41.0	0.179	42.15	0.336	33.6	0.351
300	15.00	0.588	58.8	0.125	27.59	0.561	56.1	0.230
400	13.68	0.624	62.4	0.114	23.91	0.623	62.3	0.199
500	11.65	0.680	68.0	0.096	21.36	0.663	66.3	0.178

Table 2. Data from weight loss of Al in 0.5 M NaOH for various concentrations of Coffee husk after 120 min immersion at 25 ^{0}Cand 45 ^{0}C

Conc., ppm	298 K				318K			
	ΔW mg cm^{-2}	θ	%IE	C.R. mg cm^{-2}min^{-1}	ΔW	θ	%IE	C.R. mg cm^{-2}.min^{-1}
Blank	56.33			0.470	97.25	----	----	0.810
100	48.14	0.145	14.5	0.401	91.00	0.064	6.4	0.758
200	43.00	0.237	23.7	0.358	80.00	0.177	17.7	0.666
300	33.00	0.414	41.4	0.275	72.28	0.257	25.7	0.602
400	30.25	0.463	46.3	0.252	67.70	0.304	30.4	0.564
500	29.25	0.481	48.1	0.243	59.77	0.385	38.5	0.498

Table 3. Langmuir, Temkin and Kinetic model adsorption parameters for adsorption of Ziziphus spina extract on aluminum in 0.5 M NaOH for 120 min immersion period at two different temperatures

Temp.	Langmuir isotherm			Temkin isotherm				Kinetic model			
	K	R^2	-ΔG°	a	Log K	R^2	-ΔG°	1/y	Log K	R^2	-ΔG°
25 ^{0}C	4.81	0.97	13.84	3.71	1.51	0.97	18.57	0.58	0.52	0.97	12.92
45 ^{0}C	4.51	0.97	14.60	2.81	1.07	0.97	17.14	0.87	0.60	0.98	14.27

Table 4. Langmuir, Temkin and Kinetic model adsorption parameters of adsorption of coffee husk extract on aluminum in 0.5 M NaOH for 120 min immersion at two different temperatures

Temp.	Langmuir isotherm			Temkin isotherm				Kinetic model			
	K	R^2	-ΔG		K	R^2	-ΔG		K	R^2	-ΔG
25 ^{0}C	1.34	0.99	10.68	25 ^{0}C	1.34	0.99	10.68	25 ^{0}C	1.34	0.99	10.68
45 ^{0}C	2.07	0.92	12.54	45 ^{0}C	2.07	0.92	12.54	45 ^{0}C	2.07	0.92	12.54

Table 5. Calculated values of apparent activation energy (E_a^*) and heat of adsorption (Q) of Ziziphus spina extract on aluminum in 0.5 M NaOH two different temperatures

Extract concentration ppm	E_a^* kJ mol^{-1}	$-Q_{ads}$ kJ mol^{-1}
0.5M NaOH	21.96	--------
100	25.60	36.71
200	26.53	12.49
300	27.02	4.35
400	28.95	3.17
500	29.33	3.03

Table 6. Calculated values of apparent activation energy (E_a^*) and heat of adsorption (Q_{ads}) of coffee husk extract on aluminum in 0.5 M NaOH two different temperatures

Extract concentration ppm	E^* kJ mol^{-1}	$-Q_{ads}$ kJ mol^{-1}
0.5 M NaOH	21.45	--------
100	25.09	35.79
200	26.46	34.48
300	30.87	28.14
400	31.74	26.79
500	32.27	15.46

Table 7. Surface composition (weight %) of aluminum before and after immersion in 0.5 M NaOH without and with 500 ppm of coffee husk and Ziziphusspina Christi extract at 25 ^{0}C

(Mass %)	Al	C	O	Si	Na
Pure	73.24	26.49	---	0.27	---
Blank	48.56	25.94	25.49	----	---
Ziziphusspina Christi extract	51.05	27.24	21.1	0.26	0.36
Coffee husk extract	54.352	16.68	28.49	0.48	----

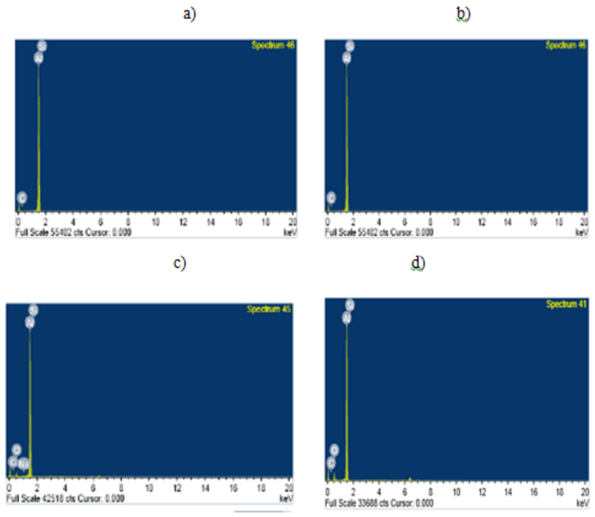

Figure 14. EDX spectra of aluminum: (a) before of immersion in 0.5 M NaOH, (b) after 24 h of immersion in 0.5 M NaOH and (c) after 24h of immersion in 0.5 M NaOH + 500 ppm Ziziphusspina Christi extract at 25°C and (d) after 24h of immersion in 0.5 M NaOH + 500 ppm coffee husk extract at 25°C

EDX survey spectra were used to determine which elements were present on the Al surface before and after exposure to the inhibitor solution. After aluminuim has been immersed in 0.5 NaOH in the absence and presence of Ziziphusspina Christi extract and coffee husk extract 24 h, its surface film composition was determined by EDX. The results are displayed in Figure 14. Figure 14b represents the surface of uninhibited aluminuim, oxygen were detected, which indicated that the passive film contained Al_2O_3. Figure 14c shows the intensities of C signal are enhanced and the signal of oxygen is decreased , which indicate that Ziziphusspina Christi extract have adsorbed on the metal surface which contain more carbon atom than oxygen but in Figure 14d shows the intensities of oxygen signal are enhanced and the signal of carbon is decreased which indicate that coffee husk extract have adsorbed on the metal surface which contain more oxygen atom than carbon. These results confirm those from electrochemical measurements which suggest that a surface film inhibits the metal dissolution, and hence retard the hydrogen evolution reaction [39, 40].

Discussion

In discussing corrosion inhibition by surface – active organic compounds, various factors including the number and types of adsorbing groups and their electron structure are taken into consideration. Inhibitor molecules may be either physically or chemically adsorbed on the surface of a corroding metal. Physisorbed molecules are attached to metal at local cathodes and retard corrosion by shifting the cathode reaction whereas chemisorbed molecules protect anodic areas and reduce the inherent reactivity of the metal at the sites where they are attached [41]. In accounting for the observed protective effect, it should be noted that the extracts comprise mixture of organic and resinous matter some of which have good corrosion inhibiting abilities. The complex chemical compositions make it rather difficult to assign the inhibiting action to a particular constituent or group constituents. The degree of protection varies for different extracts. The aluminum surface in alkaline solutions acquire negative charge. It is easier for the protonated molecules to approach the negatively charged aluminum surface due to electrostatic attraction. In case of adsorption, this involves the displacement of water molecules from the aluminum surface and sharing of electrons between the heteroatoms and aluminum. Also, the inhibitor molecules can adsorbed on aluminum surface on the basis of donor –acceptor interactions between π-electrons of aromatic rings and vacant p-orbitals of surface of aluminum atoms. Extract component molecules contain many compounds possess several heteroatoms (mainly oxygen atoms) containing active constituents, and therefore there may be a synergism between the molecules accounting for the good inhibition efficiencies.

Conclusion

Ziziphus Spina Christi and coffee husk extracts act as a good inhibitors for the corrosion of aluminum in 0.5 M NaOH. Adsorption characteristics were approximated by the Langmuir and Temkin isotherms, which authenticates the physisorbed and chemisorbed adsorption mechanism. The negative values of ΔG^o_{ads} show the spontaneity of the adsorption. The inhibitive action of both extracts is basically controlled by temperature, exposure period and concentration of the inhibitor.

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