# Research & Reviews: Journal of Chemistry

# Inhibition of Aluminum in NaOH Solution using *Cleome droserifolia* Leaves Extract

Qudah MMA

Chemistry Department, Yarmouk University, Irbid – Jordan

## RESEARCH ARTICLE

**\*For Correspondence**

Qudah MMA, Chemistry Department, Yarmouk University, Irbid – Jordan, Tel: 00962 777420026

**E-mail:** mqudahmm@yahoo.com/mohammadq@yu.edu.jo

### ABSTRACT

The inhibition effect of *Cleome droserifolia* leaves extract on the corrosion of aluminum metal in 1M NaOH solution has been investigated using the weight loss technique as a function of extract concentrations and temperatures at 25, 35, 45 and 55°C. Also, the surface morphology of Al metal was analyzed using scanning electron microscope. The plant extract of 14 g/l at 35°C has the highest inhibition value for the corrosion of aluminum metal with 78.6% inhibition efficiency. The values of the inhibition efficiency increase with increasing of the extract concentration and found to be temperature dependent. Entropy and enthalpy of activation were calculated and discussed. The adsorption of *Cleome droserifolia* extract on Al-surface obeys Temkin adsorption isotherm with high regression coefficients.

## INTRODUCTION

The plant, *Cleome droserifolia* (CD), grows in stony regions in Jordan and it has been subjected to severe overexploitation to be used in folk medicine for diabetes [1-6]. According to literature, the extract of the (CD) plant composed from multi natural organic compounds such as substituted thiocyanates, carotols, flavonoids and terpenoids. These naturally occurring organic substances are rich with hetero atoms such as oxygen, nitrogen, and sulfur substituents. Some of these naturally occurring substances, such as terpenoids are large branched and diverse class of organic compounds with different molecular formulas such as $C_{15}H_{26}O_2$ (25 mg/ml), $C_{34}H_{52}O_7$ (5 mg/ml) and $C_{35}H_{58}O_6$ (7 mg/ml) [7].

According to literature, the extract of naturally occurring substances played an important role in the corrosion chemistry of metals and alloys due to their inhibition effect, low cost and renewable sources of materials. A lot of investigations were done on the effect of leaves extract or seeds of different naturally occurring substances as corrosion inhibitors of different metals and alloys [8-11].

Corrosion of aluminum and its alloys has been the subject of numerous studies concerning the inhibition of aluminum corrosion using organic substances [12-14]. Herein, the effect of (CD) leaves extract on the corrosion of Al metal in 1M NaOH solution was studied as a function of temperature and leaves extract concentration using the weight loss method. The surface morphology of Al metal was analyzed by using electron scanning microscope.

## EXPERIMENTAL

Stock solution of (CD) plant leaves extracts was obtained by drying the plant for 4 hours in an oven at 80ºC and grinded to powder 7.0 g of the dried powder leaves was refluxed in 500 ml of 1M sodium hydroxide for 2 hours. The refluxed solution was filtrated to remove any contamination and then stored. The concentrations of the test solutions were 2.8, 5.6, 8.4, 11.2 and 14 g/l in 1M NaOH. Pure aluminum metal sheets (Aldrich), of dimensions 3.0 × 1.0 × 0.03 cm with a purity of 99.96% were cleaned using etching solution composed from 85% $H_3PO_4$ and 15% $HNO_3$ at 80ºC, washed with distilled water, then placed in a solution

of 40% (wt/v) sodium hydroxide at 50ºC for 20 seconds. The aluminum specimens rinsed again with distilled water, immersed in 1:1 (v/v) HNO$_3$, washed with distilled water and then dried and stored in desiccator. For weight loss determination, the aluminum specimens were hanged and immersed in the vessel of a test solution containing 10 ml of 1M NaOH and then with adding different extract concentrations to the 1M NaOH (2.8-14 g/L) at 25-55ºC using water thermostat controlled to ± 0.5ºC. After 1 hour, the aluminum specimens of each test were taken out and washed in acetone then rinsed with distilled water, dried and reweighed by using analytical balance with precision of 0.0001 g. Duplicate measurements were performed for each test solution to insure reproducibility.

## RESULTS AND DISCUSSION

The weight loss of the aluminum metal in the corrosive solution (1M NaOH) is given by equation 1.

$\Delta W = W_a - W_b$ .............. (1)

Where $W_b$ and $W_a$ are the weight of Al metal before and after immersion in the test corrosive solution, respectively.

The variations of the weight loss (mg) of Al in 1M NaOH solution at different immersion times containing various concentrations of (CD) extract at 25ºC are shown in **Figure 1.**
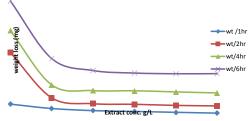


**Figure 1.** Weight loss variation of Al metal versus (CD) extract concentrations at 25ºC in 1 M NaOH at different immersion times.

According to **Figure 1**, initial addition of the (CD) extract solution (up to 5.0 g/l) in 1M NaOH has a remarkable effect on decreasing the weight loss values of Al metal in the corrosive NaOH medium, i.e., the corrosion inhibition strengthened, further increase of the (CD) extract concentration (>5.0 g/l) was followed by very small decrease in the weight loss values. The inhibition effect of the (CD) extract may be resulted from the adsorption of the available various naturally occurring organic compounds in the (CD) extract solution at the surface of Al metal through adsorption of atoms with excessive π electrons such as sulfur, nitrogen, and/or oxygen atoms at the surface of Al metal, leading to a decrease in the corrosion rate of Al metal in 1M NaOH solution, thus the Al surface is efficiently separated from the corrosive NaOH medium [13] especially at low (CD) extract solutions. Also, the weight loss values of Al increase as the immersion time increases at the same (CD) concentration, due to the corrosion of Al with NaOH solution. As a result, these naturally occurring organic compounds create a barrier between the metal surface and the corrosive media leading to an inhibition in the rate of corrosion.

The effect of temperatures on the corrosion of Al in 1M NaOH, after 1 hour immersion time over the temperature range from 25 to 55ºC in the absence and presence of different concentrations of (CD) extract solutions has been studied and presented in **Figure 2.** The weight loss values of Al metal were found to increase with increasing temperature and decrease as the concentrations of (CD) extract increase at the same temperature. The same behavior was obtained at 35, 45 and 55ºC in comparison with that obtained at 25ºC, where a remarkable drop in the weight loss values was obtained initially and almost kept constant at concentrations higher than 5.0 g/l
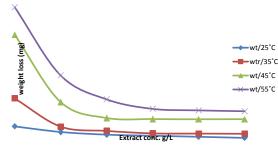


**Figure 2.** Variation of the weight loss of Al metal versus (CD) extract concentration in 1M NaOH at different temperatures after 1 h immersion time.

The percentage inhibition efficiency (%I) and the degree of surface coverage (Θ) of Al metal in 1M NaOH in the presence and absence of (CD) extract solutions were computed from equations 2 and 3. The calculated values of inhibition efficiency (%I) and the surface coverage (Θ) are collected in **Tables 1 and 2**, respectively.

$\%I = (\Delta W)/W_b \times 100$ (2)
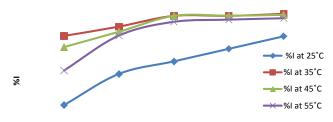
$(\Theta) = (\Delta W)/W_b$ (3)

**Table 1.** %I at different (CD) extract solutions and temperatures after 1 h immersion time.

| Extract conc. (g/l) | %I at 25 °C | %I at 35 °C | %I at 45 °C | %I at 55 °C |
|---|---|---|---|---|
| 2.4 | 32.7 | 67.5 | 61.9 | 50.1 |
| 2.8 | 48.4 | 72.2 | 67.6 | 67.4 |
| 5.6 | 54.7 | 77.6 | 77.6 | 74.6 |
| 8.4 | 61.0 | 77.8 | 77.7 | 75.7 |
| 11.2 | 67.3 | 78.6 | 78.1 | 76.4 |

**Table 2.** Θ values at different extract (CD) concentrations and temperatures after 1 h immersion time.

| Extract conc. (g/l) | Θ at 25 °C | Θ at 35 °C | θ at 45 °C | Θ at 55 °C |
|---|---|---|---|---|
| 2.4 | 0.327 | 0.675 | 0.619 | 0.501 |
| 2.8 | 0.484 | 0.722 | 0.676 | 0.674 |
| 5.6 | 0.547 | 0.776 | 0.776 | 0.746 |
| 8.4 | 0.610 | 0.777 | 0.777 | 0.757 |
| 11.2 | 0.673 | 0.786 | 0.781 | 0.764 |



**Figure 3.** Inhibition efficiency versus (CD) extracts concentrations for aluminum in 1M NaOH at different temperatures after 1 h immersion time.

**Table 1** shows the percentage inhibition efficiency of the (CD) extract inhibitors at various concentrations in 1M NaOH after 1 h immersion time at different temperatures (25-55ºC). The results showed that the values of the inhibition efficiency increased as the concentration of the (CD) extract increased from 2.8 to 14 g/l **(Figure 3)**. The maximum inhibition efficiency was 78.8% at 35ºC for 14 g/l of extract concentration. According to **Table 1** and **Figure 3**, the followings were observed:

a) At the same temperature, the %I values increase as the concentrations of (CD) extract concentration increases.

b) At the same (CD) extract concentration, the %I values were increased as temperature increases from 25 to 35ºC reaching a maximum at 35ºC followed by a decrease at 45 and 55ºC, respectively.

c) Above 5.0 g/l extract concetration, the %I increase slightly with increasing extract concentration at all temperatures.

The above mentioned observations could be explained as

1- Adsorption of the naturally organic compounds in the (CD) extract solutions via the rich π electron of N, S and/or O atoms was occurred over the temperature range from 25 to 55ºC and at the different (CD) extract concentrations through an increase in the %I values, thus the Al- surface is efficiently separated from the corrosive media [15].

2- The presence of large and branched naturally occurring molecules such as terpenoids in the (CD) extract solution will be adsorbed partially at the Al-surface (steric effect), causing weak adsorption. Dilute extract solutions (below 5.0 g/l) containing low concentrations of terpenoids will be adsorbed freely at the surface of Al metal, producing much higher inhibition effect than at high concentration

3- The above mentioned steric effect also explains the trend of inhibitions observed at 45 and 55ºC (negative $Q_{ad}$ values, ), where adsorption became more weaker than that obtained at 35ºC and 25ºC (positive $Q_{ad}$ vlues), due to an increase in kinetic energy of molecules with increasing temperature, which overcome the interaction between adsorbent-adsorbate. The same explanations can be obtained from the variations of (Θ) with temperature and (CD) extract concentrations.

The corrosion rate (CR) of Al is calculated according to equation 4:

$$CR = \Delta W / A.t \tag{4}$$

Where A and t are the surface area of Al metal and t the immersion time, respectively. Logarithmic plot of the corrosion rate versus the reciprocal of temperature (T) in Kelvin gives straight lines **(Figure 4)** according to the following Arrhenius equation [16]:

$$CR = A_{exp}(-Ea/RT) \tag{5}$$

Where A, R and Ea are the pre-exponential factor, universal gas constant (8.314 J/K mol) and the apparent activation energy,

respectively. The values of Ea were calculated and listed in **Table 3**. The Ea for the reaction of Al metal in 1M NaOH solution was found to be 57.3 kJ/mol. Upon addition of the (CD) extract solution, the values of Ea were dropped and reaching 43.7 kJ/mol at 14.0 g/l extract concentration. The value of $E_a$ is higher in the uninhibited solution (in NaOH) compared to that obtained with (CD) extract solutions, this implies that the (CD) extracts functioned through adsorption at the surface of Al metal via mixed inhibition mechanisms under the studied conditions [18].
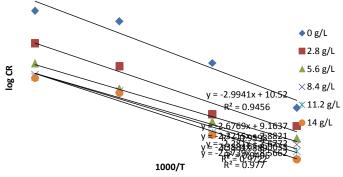


**Figure 4.** Arrhenius plot for Al dissolution in 1.0M NaOH with and without of (CD) extracts after 1 h immersion time.

**Table 3.** Activation parameters for the dissolution of Al in 1M NaOH in with and without of (CD) extract after 1 h immersion time.
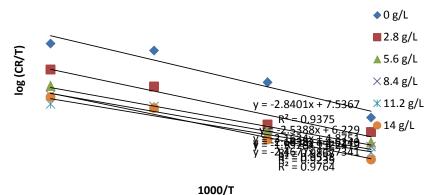
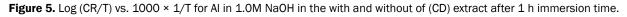| Extract conc. (g/l) | $r^2$ | Ea (kJ/mol) | $r^2$ | ΔH* (kJ/mol) | ΔS*(J/mol.K) | $Q_{ads}$ (kJ/mol) ΔT$_1$ ΔT$_2$ |
|---|---|---|---|---|---|---|
| 0 | 0.95 | 57.3 | 0.93 | 54.4 | -53.7 | |
| 2.8 | 0.96 | 51.2 | 0.95 | 48.6 | -78.3 | 55.2 -18.3 |
| 5.6 | 0.96 | 44.4 | 0.98 | 42.4 | -104.2 | 30.5 -4.3 |
| 8.4 | 0.97 | 43.7 | 0.95 | 40.3 | -109.0 | 26.6 -3.4 |
| 11.2 | 0.98 | 43.6 | 0.92 | 38.2 | -116.4 | 18.1 -2.3 |
| 14.0 | 0.98 | 43.7 | 0.97 | 47.2 | -95.6 | 11.8 -1.9 |

An alternative formulation of the Arrhenius equation is Eyring formula [15] for the transition state (equation 6)

$$CR=(K_bT/h)\ exp^{(ΔS*/R)}\ exp^{(-ΔH*/RT)} \tag{6}$$

Where h, $K_b$, ΔS*, ΔH* are Planck's constant, Boltzmann constant, the entropy- and the enthalpy of activation, respectivly.

**Figure 5** shows a plot of log (CR/T) against (1/T, K$^{-1}$). Straight lines were obtained and from their slopes and intercepts, the values of ΔH* and ΔS* were calculated and listed in **Table 3.** The values of ΔH* were endothermic nature due to Al metal dissolution. It has been mentioned elsewhere [8-11] that physisorbtion prevailed with ΔH* values less than 48kJ/mol, whereas, ΔH* values approaching 100 kJ/mol indicating chemisorptions [14]. In this study, the values of ΔH* were less than 48kJ/mol confirming physical adsorption. The values of ΔS* in the absence of the (CD) extract inhibitors are negative and became more negative in the presence of the (CD) extract solutions. This could be attributed to the libration of large fraction of more disordered water molecules that were adsorbed on the surface of the metal and replaced with less disordered organic compounds in the (CD) extract solution. This implies that the activation complex is the rate determining step, representing association rather than dissociation mechanism (adsorption at the surface of Al metal by the various naturally organic compounds), indicating that an increase in order takes place on going from reactant to the activated complex [16].



**Figure 5.** Log (CR/T) vs. 1000 × 1/T for Al in 1.0M NaOH in the with and without of (CD) extract after 1 h immersion time.

The heat of adsorbed materials ($Q_{ads}$) at the surface of Al metal in the presence of the (CD) extract inhibitor values of the adsorbed materials at the surface of Al metal is calculated by the following equation [17].

$$Q_{ads}=2.303R \left[\log (\Theta_2/1-\Theta_2)-\log (\Theta_1/1-\Theta_1)\right] \times (T_2T_1/T-_2T_1) \tag{7}$$

To explain the previous behavior, where maximum adsorption took place at 35ºC, two different temperature ranges were used upon applying equation 7. The first temperature range ($\Delta T_1$), in which %I increases with increasing temperature from 25 to 35ºC, while the second temperature range ($\Delta T_2$), where %I decreases with increasing temperature from 45 to 55ºC. $Q_{ads}$ values **(Table 2)** in the first temperature range were positive and decreases with increasing (CD) extract concentration. In the second temperature range, the values of $Q_{ads}$ were small negative values and increases with increasing (CD) extract concentration.

The positive values of $Q_{ads}$ suggests an increase in adsorption efficiency in the first temperature rang ($\Delta T_1$) and a decrease in adsorption efficiency in the second temperature region range ($\Delta T_2$) [18]. Generally, the adsorption efficiency is greater in the first temperature than in the second one.
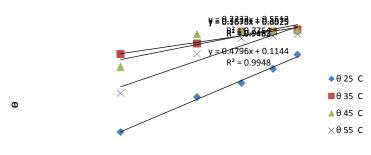
The inhibition effect of (CD) extract solutions for the reaction of Al metal in 1.0M NaOH solution obeys Temkin adsorption isotherm relationship [19] as represented by equation 8.

$$\Theta=A+B \log C \tag{8}$$

Where A and B are constants, respectively.

This isotherm takes the account of adsorbate–adsorbent interaction and it assumes that the activation adsorption heat (function of temperature) of all molecules in the layer would decreased linearly rather than logarithmic with increasing coverage [20].

The variation of Θ vs log C is shown in **Figure 6**, where straight lines with high $R^2$ values (>0.96), which confirms the applicability of Temkin adsorption isotherm.



**Figure 6.** Temkin adsorption isotherm plot (Θ against log C) for Al in 1M NaOH with (CD) extract after 1 h immersion time at different temperatures.

## SURFACE TOPOLOGY

A scanning electron microscope was used to investigate the topologic changes of Al surface in presence and absence of (CD) plant extract in 1.0 M NaOH after 1 h immersion time. The surface of Al metal infected remarkably in the presence of corrosive NaOH solution only as shown in **Figure 7A** through the formation of an irregular voids along the surface of the metal sheet, indicating clear attack of Al metal by NaOH solution. On the other hand, **Figure 7B** showed the image for the surface of Al metal in 11.2 g/l (CD) extract solution, the surface of Al metal is smoother than that obtained in the corrosive NaOH medium, due to the formation of a protective layer at the surface of Al metal.
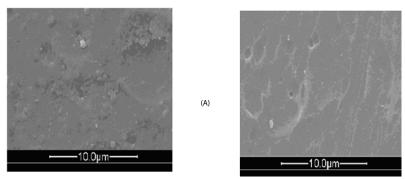


**Figure 7.** Scanning electron micrographs of (A) aluminum surface in 1.0M NaOH solution, (B) aluminum surface in 11.2 g/l of (CD) extract concentration.

## CONCLUSIONS

The following main conclusions can be deduced from the present study:

➢ The (CD) extract was found to be a good inhibitor for Al metal in 1M NaOH solution.

➢ The %I values were increased with increasing the (CD) extract concentration at the same temperature to attain a maximum value of 78.8% (14.0 g/l) at 35ºC.

➢ The %I values of %I and $Q_{ad}$ were found to be temperature dependent, where maximum adsorption obtained at 35ºC

➢ The $E_a$ values for Al metal in NaOH solution in the presence of the (CD) inhibitor were less than $E_a$ values obtained for Al metal in NaOH solution without the (CD) inhibitor.

➢ Temkin adsorption isotherm was found to fit the data obtained for the adsorption of (CD) extract at the Al-surface

# REFERENCES

1.  Seifeld  AA, Darwish FA,  Abou dania A, Egypt J Pharm Sci 1987; 28:313.

2.  Fushiya S, Kishi Y, Hattori K, batkhuu F. Flavonoids from Cleome droserifolia suppress NO production in activated macrophages in vitro. Planta med 1999; 65: 404-407.

3.  Netzar Y, Palevitch D, Perl M, Schilcher H, Phillipson JD, et al. The effect of some plant extracts on body weight and on some biochemical activities on rats. Acta Hort 1993; 332: 207-217

4.  Nicola WG, Ibrahim KM, Mikhail TH, Girgis RB, Khadr ME. Role of the hypoglycemic plant extract cleome droserifolia in improving glucose and lipid metabolism and its relation to insulin resistance in fatty liver. Boll chim farm 1996; 135: 507-517.

5.  El-Shenawy NS, Abdel-Nabi IM. Hypoglycaemic effect of Cleome droserifolia ethanolic leaves extract in experimental diabetes and their effect on non-enzymatic antioxidant glycogen content thyroid hormones and insulin levels. Diabetologia Croatica 2006; 35: 15-22.

6.  Vats V, Yadav SP, Grover JK. Ethanolic extract of Ocimum sanctum leaves partially attenuates streptozotocin-induced alterations in glycogen content and carbohydrate metabolism in rats. J Ethnopharmacol 2004; 90: 155-160.

7.  El-Askary H. Terpenoid constituents from Cleome droserifolia (FORSSK.)DEL. molecules 2005; 10: 971-977.

8.  Abiola  OK, Otaigbe JOE. Effect of common water contaminants on the corrosion of aluminium alloys in ethylene glycol–water solution corrosion science 2008; 50: 242-247.

9.  Saleh RM, Shams Eldin. Efficiency of organic acids and their anions in retarding the dissolution of aluminium Corros. Sci 1972; 12: 689 -697.

10.  Gunsekaran G, Chauhan LR. Eco friendly inhibitor for corrosion inhibition of mild steel in phosphoric acid medium. Electrochem Acta 2004; 49:4387-4395.

11.  Okafor PC, Ekpe UJ, Ebenso EE, Umoren, Leizou KE. Inhibition of mild steel corrosion in acidic medium by allium sativum extracts Bull. Electrochem 2005; 21: 347-352.

12.  Fares MM, Maayta AK, Al-Qudah MM. Pectin as promising green corrosion inhibitor of aluminum in hydrochloric acid solution. Corr Sci 2012; 60: 112-117.

13.  13. Oguzi EE. Corrosion Inhibitive Effect and Adsorption Behaviour of Hibiscus Sabdariffa Extract on Mild Steel in Acidic Media Port. Electrochim acta 2006; 26: 303-314.

14.  Oguzi EE.  Studies on the inhibitive effect of Occimum viridis extract on the acid corrosion of mild steel. Mater Chem phys 2006; 99: 441-446.

15.  Umoren SA, Obet IB, Ebenso PC, oguzie EE. Gum Arabic as a potential corrosion inhibitor for aluminium in alkaline medium and its adsorption characteristics. Anti corros methods and Mater 2006; 53: 277-282.

16.  Trabanelli G, Mansfeld F (eds) Corrosion Mechanisms, Marcel dekkar,NY 1987; 119.

17.  Awad MA. Eco friendly corrosion inhibitors: Inhibitive action of quinine for corrosion of low carbon steel in 1 m HCl.  J Appl Electrochem 2006; 36: 1163-1168.

18.  Valek L, Marteniz S. Copper corrosion inhibition by Azadirachta indica leaves extract in 0.5 M sulphuric acid. Matterlett 2007; 61: 148-151.

19.  Megahed HE. Ethoxylated Fatty Esters as Corrosion Inhibitors for Copper in Nitric Acid Solutions. Port Electrochim Acta 2011; 29:287-294.

20.  Piccin JS, Dotto GL, and Pinto LA. Adsorption isotherms and thermochemical data of FD&C Red n° 40 binding by Chitosan. Braz J Chem Eng 2011; 28: 8-15.