Available online: June 15, 2020

Commun.Fac.Sci.Univ.Ank.Series B.
Volume 62, Number 1, Pages 12-22 (2020)
ISSN: 1303-6017 E-ISSN: 2687-4806
https://dergipark.org.tr/tr/pub/communb/issue/52583/749033

THE INHIBITOR EFFECTS OF *CANNABIS SATIVA* L. EXTRACTS ON THE CORROSION OF ALUMINIUM in H_2SO_4 SOLUTIONS

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ABSTRACT. The aim of study was to investigate the effect of terpenoids in cannabis (*Cannabis sativa* L.) obtained from Diyarbakır line as corrosion agent on the corrosion of aluminum. Corrosion protection of aluminum (99.9% purity) with *cannabis* plant has been investigated using electrochemical methods. The methods with electrochemical impedance spectroscopy (EIS) and current potential showed that the plant has a potential to prevent corrosion of aluminum at 298 K in 0.5 M H_2SO_4 solution around 98%. The experimental results indicated that the cannabis plant can be used as an environmentally friendly inhibitor for aluminum.

1. INTRODUCTION

The standard electrode potential of aluminum is very negative (-2.35 V) compared to the Standard Hydrogen Electrode (SHE). Aluminum is known as the most widely used anode material with high energy capacity (8.1 kW h/kg) in all atmospheric environments [1-7]. Aluminum and its alloys offer a wide range of properties in different industrial fields such as the automotive industry, the aeronautical and aerospace area, construction industry, the electrical and electronic. Aluminum can easily form a thin and compact oxide film in the atmospheric environment. This film can be soluble in acidic solution. For this reason, we need to make an extra coating for preventing corrosion of aluminum in acidic solution with an inhibitor. Generally, inhibitor also should be cheap, useful, non-hazardous to health and accessible. Accordingly, *Cannabis sativa* L. plant used as an inhibitor in this study. It can be grown economically at almost any location of Turkey, where plenty of sunlight, temperature and sufficient humid climates are available. The plants from Diyarbakır

Received by the editors: April 01, 2020; Accepted: June 07, 2020.
Key word and phrases: Anti-corrosion, aromatic plant, drying conditions, cannabinoid (terpenic) compounds

line are suitable for seed production and show numerous branches and abundant flower formation preferred for the experiment. In addition, the plants contain several cannabinoids (terpenophenolic compounds) having medical benefits [8].

The use of inhibitors is one of the most practical methods to prevent corrosion of metals. Various inhibitors of aluminum in aqueous solutions have been reported [9-14]. However, many of them are hazardous, costly and not safe for the environment and human health. Therefore, it is desired if safer corrosion inhibitors for aluminum against surrounding environments are available. Environmentally friendly plant extracts can be considered as lower cost inhibitors. Phytochemicals including alkaloids, and flavonoids, heteroatoms such as N, S, O, π-electrons on the aromatic ring and π-electrons in the plant extracts are adsorbed on the metal surface to prevent corrosion.

Cannabis sativa L. preparations are derived from the female plant of *Cannabis* (Family Cannabidaceae). The use of *Cannabis sativa* L. in medicinal treatments has become widespread in recent years. Substances such as nabilone, dronabinol and its some derivatives are used in the treatment of glaucoma, multiple sclerosis and chemotherapy [15].

Presently *Cannabis sativa* L. plant is being assessed as an industrial crop in Turkey. Therefore, its cultivation is supported and promoted at the state level. The plant extract has been used to prevent corrosion of aluminum. After the treatment with the extract obtained from this plant, industrial waste is not observed. Because of these features, this plant has been found suitable for industrial use and it is recommended to carry out the necessary procedures to spread it.

2. Materials and Methods

2.1. Experimental material

Cannabis sativa L. was obtained from Department of Field Crops, Faculty of Agriculture, Ankara University, Turkey. The cannabis seeds were collected from the wild flora of Diyarbakır province. The seeds were sown in 4 m long 3 rows manually by hand followed by covering them properly with loose soil. The seeds were placed at 1 cm depth in 3 replicated rows that were separated by 30 cm on 06.05.2019. Aluminum metal (99.9% purity, 5 mm diameter of cylindrical surface area, 0.19625 cm^2 geometric area) fixed on the Teflon tube with adhesive was taken from ETİ Aluminum A.Ş, Seydişehir, Konya.

2.2. Harvesting and drying

Upper leaves and flowers of the female *Cannabis sativa* L. were harvested on 04.09.2019 in the morning at 06:00 and dried under cool and shady conditions [16].

2.3. Processing

The dried sample was ground to powder. This dry sample of 10 g was dissolved in 200 mL of 0.5 M sulfuric acid and stirred for 1 day with a heating without boiling. The homogenized mixture was heat filtered to give 30 mL solution for each of 2, 6 and 24 h.

2.4. Extraction

Cannabis sativa L. extract was used to prevent corrosion of pure aluminum. The extraction was carried out following modified method of Turner and Mahlberg [17].

2.5. Electrochemical Impedance Spectroscopy (EIS)

The electrochemical impedance method provides information about the mechanisms occurring on the surface with applying sinusoidal potential perturbation to the electrode surface, and measuring both the current flow and the shift in the phase of the resulting current [18]. Electrochemical impedance was carried out using 5 mV amplitude sinusoidal signal at the low frequency 0.1 Hz. Electrochemical impedance measurement results of the aluminum in extract solution are shown in Fig.1.

2.6. Electrochemical analysis and measurement of corrosion inhibition

Corrosion of aluminum in *Cannabis sativa* L. extract were carried out by electrochemical system. This system consist of CHI 660 B instrument potentiostat, polyscience thermostat, glass cell and a computer for obtaining corrosion parameters. Glass cell consists three electrodes; aluminum metal, reference electrode (3 M solution with chloride (Cl^-) concentration, Ag/AgCl) and platinum (platin wire) electrode. Potentials were obtained by this reference electrode. Aluminum metal surface polished with alumina and washed with double distilled water before experiments. After washing aluminum were immersed in *Cannabis sativa* L. extract solution, the impedance measurements were carried out at the open circuit potential

(-0.688 V) and samples in a steady state during 20 min, when impedance was measured. The current potential measurements were performed (scan rate 1mV/s).

$$\text{E (C} - \text{P)(\%)} = \frac{i_{corr}(\text{blank}) - i_{corr}(\text{C. sativa L.})}{i_{corr}(\text{blank})} \times 100 \qquad \text{Eq. 1}$$

$$\text{E}\left(\text{R}_\text{p}\right)(\%) = \frac{[\text{R}(C.\,sativa\;L.) - \text{R(blank)}]}{\text{R}(C.\,sativa\;L.)} \times 100 \qquad \text{Eq. 2}$$

$$i_{corr}\ (\text{Stern} - \text{Geary}) = \left[\frac{\beta_a \cdot \beta_c}{2{,}303(\beta_a + \beta_c)}\right] \times \frac{1}{\text{Rct}} \qquad \text{Eq. 3}$$

Corrosion rates (i_{corr}) were obtained from current potential curves with extrapolation anodic and cathodic Tafel slope to the corrosion potential (Fig.2) from CHI660B instrument. Corrosion inhibition efficiencies E (C-P, %) and E (S-G, %) were calculated using i_{corr} and from polarization and charge transfer resistances (Rct), using Eq.1 and Eq.2 [18], respectively. i_{corr} calculated from M. Stern and A. L. Geary equation (Eq.3) [19-21] using R_p resistance from current potential curves. In this equation, the β_a is the anodic slope, the β_c is the cathodic slope, the R_p resistance from the current potential curves (Table 2).

3. Results and Discussion

3.1. Meteorological observations

Comparing the meteorological data for long term with the data of year 2019, it was obvious that the temperature and relative humidity values for 2019 and long term were very close to each other (Table 1). However, precipitation showed a significant increase during May and remarkable reduction during June to August 2019 period when compared to the long term averages. Furthermore, the average of climatic data for 2019 showed average temperature, precipitation and relative humidity of 20.65°C, 28.28 mm and 49.35% during 2019 in the same order. Total precipitation remained 113.10 mm.

TABLE 1. Averages of meteorological data for long term and 2019*.

Months	Temperature (Cº)		Precipitation (mm)		Relative Humidity (%)	
	Long Term	2019	Long Term	2019	Long Term	2019
May	18.1	16.0	35.9	51.8	48.9	57.3
June	22.4	19.9	42.6	34.7	52.2	52.0
July	23.0	23.4	33.9	14.1	42.1	44.5
August	24.3	23.3	28.7	12.5	40.5	43.6
Average	21.95	20.65	35.28	28.28	45.93	49.35
Total			141.10	113.10		

* The Directorate general of Meteorology Ankara.

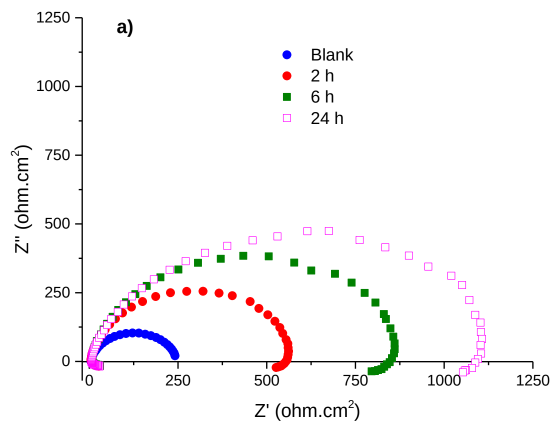
3.2. Inhibition efficiency

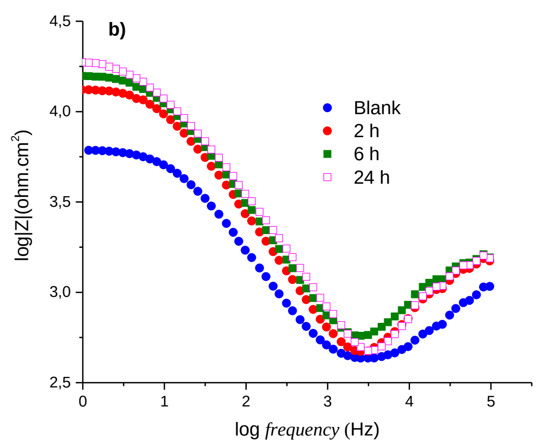
The inhibition efficiency of the extract was evaluated using polarization resistance obtained from electrochemical impedance curves (Fig.1). In the impedance method, the resistance increases at the metal/solution interface that occurs on the metal surface without the current passing through the same mechanism in real (Z′) and imaginary (Z″) axes. The Nyquist plots obtained during the immmersion time for 2 h, 6 h and 24 h exhibit a depressed semicircle from high frequency(100 kHz) region to low frequency region (0.1 Hz). Semicircular curves showed that this mechanism has charge transfer controlled [18,22-24]. Moreover, the radius of the semicircles observed for the aluminum resistance increases with increasing immersion time (Fig.1(a)), demonstrating an increase in the corrosion resistance. The corresponding Bode and Bode-phase plots were shown in Fig.1(b) and (c), respectively. Both the resistance value and the phase angle (θ) increase with increasing duration of the immersion.

$$C_{dl} = \left[\frac{1}{2\pi f\,(Z''_{max})}\right] \times \frac{1}{R_{ct}} \qquad \text{Eq. 4}$$

Double layer capacitance (C_{dl}) was also calculated in this study. Charge transfer resistance (R_{ct}) was found benefit from Fig.1(a). In this equation, R_{ct} shows the charge transfer resistance and f is the frequency corresponding to the maximum value of Z″. This is given in Eq.4. The C_{dl} value in the table decreases gradually for

2 h, 6 h and 24 h respectively. The reason for this is that aluminum is well coated with *Cannabis sativa* L. and the ability of capacitance decreases on aluminum surface. In other words, the reduction of the surface slows down as the surface coated. Consequently, the corrosion rate slows down as C_{dl} decreases. As the coating time increases, the passage of electrons on the aluminum surface slows down (Table 2).





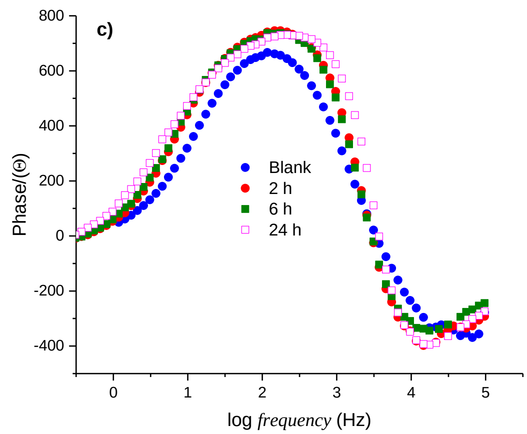


FIGURE 1. Electrochemical impedance curves of aluminum **a)** Nyquist **b)** Bode-|Z| **c)** Bode-phase plots in the presence of *Cannabis sativa* L. extract in 0.5 M H_2SO_4 with during 2 h, 6 h and 24 h.

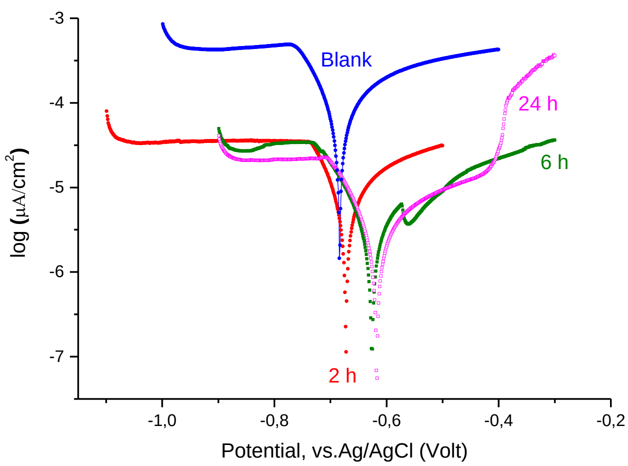


FIGURE 2. Potentiodynamic current potential curves of aluminum in 0.5 M H_2SO_4 in the presence of *Cannabis sativa* L. extract with during 2 h, 6 h and 24 h.

There are many organic compounds in *Cannabis sativa* L. These compounds are most commonly phenolic mono or poly terpene compounds [16,17]. These compounds interact with aluminum deposited on the metal surface without passing into the study solution. The resistance at the metal/solution interface increase from nearly 225 $\Omega.cm^2$ to 1200 $\Omega.cm^2$. As the resistance increased, aluminum showed the ability to cover the metal surface in acidic solution by means of activated carbon centered carbanions of these compounds. Thus, the average corrosion inhibition increased to 98% and the corrosion of aluminum was significantly reduced. A reduction potential was observed at -0.55 V (Fig.2). It is shown that more than one compound in the *Cannabis sativa* L. extract can give together less soluble compounds on the aluminum metal surface. Corrosion rate and other parameters were obtained from electrochemical current potential curves in the presence of *Cannabis sativa* L. at 298 K shown in Table 2.

TABLE 2. Corrosion parameters obtained from current potential curves for pure aluminum in 0.5 M H_2SO_4 solution in the presence of *Cannabis sativa* L. extract during 2 h, 6 h and 24 h at 298 K.

Media	E_{corr} (Volt)	β_a (mV/dec)	β_c (mV/dec)	R_p ($\Omega.cm^2$)	C_{dl} ($\mu F/cm^2$)	R_{ct} ($\Omega.cm^2$)	Corrosion Rate (i_{corr}, $\mu A/cm^2$) C-P	Corrosion Rate (S-G)$_{Rp}$	E (%) (S-G)$_{Rct}$	E (%) C-P	E (%) (S-G)$_{Rp}$	E (%) Avrg
Blank	-0.686	196	359	295	2131	225	470	187	-	-	-	-
+*C. sativa* L.												
2 h	-0.668	325	239	3721	473	690	16	16	67	96	91	85
6 h	-0.610	318	38	4592	448	880	3.25	3.2	74	99	98	90
24 h	-0.607	293	31	4926	70	1200	2.50	2.4	81	99	99	93

Avrg: Average, C-P: Current Potential, S-G: Stern-Geary.

4. CONCLUSIONS

Electrochemical methods showed that the compounds in *Cannabis sativa* L. exhibit better inhibitive effect on the corrosion of pure (purity 99.9%) aluminium. It was noticed that the *Cannabis sativa* L. extract significantly reduced the corrosion rate and increased the resistance of surface aluminum (98%). The extract shifts the potential of aluminum in a positive direction from -0.686 to -0.607 V. It acted as a anodic inhibitor. Corrosion resistances were measured by the current potential and impedance methods for 2 h, 6 h and 24 h, respectively. According to the impedance curves, the reaction between *Cannabis sativa* and aluminum occur by the same mechanism. This mechanism is charge transfer controlled. The impedance measurements showed that a protective layer is formed on the aluminum during the period. Moreover, double layer capacitance (C_{dl}) decreases as resistance increases, which shows that molecular coating ability decreases on aluminum surface. Impedance and current potential methods are compatible with each other in this study. The experimental results showed that the *Cannabis sativa* L. plant can be used as an environmentally friendly inhibitor for aluminum.

Acknowledgement. The authors acknowledge and thank Department of Field crops, Faculty of Agriculture and Department of Chemistry, Faculty of Science Ankara University for supporting the study.

Özet

Bu çalışmanın amacı, Diyarbakır hattına ait kenevir (*Cannabis sativa* L.) içindeki terpenik bileşiklerin alüminyumun korozyonuna etkisini araştırmaktır. Alüminyumun (%99.9 saflıkta) kenevir bitkisi ile korozyona karşı korunması elektrokimyasal yöntemler kullanılarak araştırıldı. Elektrokimyasal empedans spektroskopisi (EIS) ve akım potansiyel yöntemler, bitkinin 298 K de 0.5 M H_2SO_4 ortamında %98 civarında alüminyumun korozyonunu önleme potansiyeline sahip olduğunu gösterdi. Deneysel sonuçlar, kenevir bitkisinin alüminyum için çevre dostu bir inhibitör olarak kullanılabileceğini belirtti.

Anahtar Kelimeler: Korozyon önleyici, Aromatik bitki, Kurutma koşulları, Kannabinoid (terpenik) bileşikler.

References

[1] Wang, L., Wang, W., Yang, G., Liu, D., Xuan, J., Wang, H., Leung, M. K.H., Liu, F., A hybrid aluminum/hydrogen/air cell system, *International Journal of Hydrogen Energy*, 38(34) (2013), 14801-14809.

[2] Topaktaş, M., Yanardağ, T., Aksut, A. A., Inhibition effects of Co^{+2}, Ni^{+2}, La^{+3} and Ce^{+2} ions on the corrosion of aluminum and aluminum alloys in the NaCl solution, *Communications Faculty of Science University of Ankara Series B: Chemisty and Chemistry Engineering*, 54(1) (2008) 1-13.

[3] Pourbaix, M. (Ed.), Atlas of Electrochemical Equilibria in Aqueous Solutions, 1st Edition, Pergamon Press, New York, 1966.

[4] Solé, A., Miró, L., Barreneche, C., Martorell, I., Cabeza, L. F., Corrosion of metals and salt hydrates used for thermochemical energy storage, *Renewable Energy*, 75 (2015), 519-523.

[5] Martínez-Salazar, A. L., Melo-Banda, J. A., Coronel-García, M. A., Gonzalez-Barbosa, J. J., Domínguez-Esquivel, J. M., Hydrogen generation by aluminum alloy corrosion in aqueous acid solutions promoted by nanometal: Kinetics study, Renewable Energy, 146 (2020), 2517-2523.

[6] Chen, Y. J., Liu, C. C., Zhou, J., Wang, F. S., Effect of alternate corrosion factors on multiaxial low-cycle fatigue life of 2024-T4 aluminum alloy, *Journal of Alloys and Compounds*, 772 (2019), 1-14.

[7] Temelli, G., Mori, A., Haghayeghi, R., Reliability of a high-pressure die cast Al alloy radiator, *Engineering Failure Analysis*, 105 (2019), 87-97.

[8] Koob, G., Arends, M., Moal, M. L., Drugs, Addiction, and the Brain, 1st Edition, Elsevier, 2014.

[9] Mercier, D., Herinx, M., Barthes-Labrousse, M.G., Influence of 1,2-diaminoethane on the mechanism of aluminum corrosion in sulphuric acid solutions, *Corrosion Science*, 52 (2010) 3405-3412.

[10] Fares, M. M., Maayta, A. K., Al-Qudah, M.M., Pectin as promising green corrosion inhibitor of aluminum in hydrochloric acid solution, *Corrosion Science*, 60 (2012), 112-117.

[11] Liang, M., Melchers, R., Chaves, I., Corrosion and pitting of 6060 series aluminium after 2 years exposure inseawater splash, tidal and immersion zones, *Corrosion Science*, 140 (2018) 286-296.

[12] Feng, L., Yuan, P., Corrosion protection mechanism of aluminum triphosphate modified by organic acids as a rust converter, *Progress in Organic Coatings*, 140 (2020), 105508.

[13] Piao, N., Wang, L., Anwar, T., Feng, X., Sheng, S., Tian, G., Wang, J., Tang, Y., He, X., Corrosion resistance mechanism of chromate conversion coated aluminium current collector in lithium-ion batteries, *Corrosion Science*, 158 (2019), 108100.

[14] Rochet, C., Veron, M., Rauch, E. F., Lowe, T. C., Arfaei, B., Laurino, A., Harouard, J. P., Blanc, C., Influence of equal-channel angular pressing on the microstructure and corrosion behaviour of a 6xxx aluminum alloy for automotive conductors, *Corrosion Science*, 166 (2020), 108453.

[15] Gerra, G., Zaimovic, A., Gerra, M. L., Ciccocioppo, R., Cippitelli, A., Serpelloni, G. Somaini, L., Pharmacology and toxicology of Cannabis derivatives and endocannabinoid agonists, *Recent Patents on CNS Drug Discovery*, 5 (2010), 46-52.

[16] Bayraktar, N., Yanardağ, T., Özgen, Y. Yanardağ, Y. K., Chemical characterization of two local lines of *Cannabis sativa* L. under warm temperate climatic conditions of Ankara, *1. International Aromatic Plants and Cosmetics Symposium-AROPCOS*, 03-06 September (2019), Iğdır-Turkey.

[17] Turner, J. C. Mahlberg, P. G., Separation of acid and neutral cannabinoids in *Cannabis sativa* L. using HPLC. *In: S. Agurell, W. L. Dewey, R. E. Willete, editors, The cannabinoids: chemical, pharmacologic and therapeutic aspects. (Orlando, Fla: Academic Press Inc)* (1984), 79-88.

[18] Yanardağ, T., Aksut, A. A., Effect of conversion coatings and oxalate ion on corrosion of pure zinc in 1 M NaCl solution, *Asian Journal of Chemistry*, 24/1 (2012), 345-349.

[19] Yanardağ, T., Küyükoğlu, M., Aksut, A. A., The effect of organic compounds on the corrosion of zinc in aqueous soultions, *Communications Faculty of Science University of Ankara Series B: Chemisty and Chemistry Engineering*, 56(1) (2010), 1-13.

[20] Stern, M., Geary, A. L., Electrochemical polarization: I. A theoretical analysis of the shape of polarization curves, *Journal of Electrochemical Society*, 104 (1957), 56-63.
[21] Yanardağ, T., Elektrokimyasal Empedans Spektroskopisi, Gazi Kitabevi, Ankara, 2019.
[22] Wang, C. T., Wiedinmyer, C., Ashworth, K., Harley, P. C., Ortega, J., Vizuete, W., Leaf enclosure measurements for determining volatile organic compound emission capacity from *Cannabis* spp, *Atmospheric. Environment,* 199 (2019), 80-87.
[23] Gileadi, E. Kirowa-Eisner, E., Some observations concerning the Tafel equation and its relevance to charge transfer in corrosion, *Corrosion Science*, 47 (2005), 3068-3085.
[24] Levich, V.G., Delahay, P. (Eds.), Advances in Electrochemistry and Electrochemical Engineering, Interscience Publication, New York, 4 (1966) 249-371.

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