

Experimental Study and Modeling of the Corrosion Inhibition of Mild Steel in 1M HCl with Novel Friendly Butanolic Extract of *Ephedra Major*

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Abstract. A novel Butanolic extract of *Ephedra major* (denoted EBEM) was investigated as corrosion inhibitor for mild steel in 1 M hydrochloric acid solution. The investigation was carried out using weight loss, electrochemical impedance spectroscopy (EIS), Tafel polarization measurements, Fourier transform infrared spectroscopy (FT-IR), and scanning electron microscopy (SEM) methods. The effect of temperature on the corrosion behavior of steel in HCl with the addition of the inhibitor was investigated in the temperature range 20-60°C. The inhibition efficiency was observed to increase with increasing concentration of the extract EBEM and decreased with increasing the temperature. Tafel curves have revealed that the EBEM possesses the indices of a mixed inhibitor. The adsorption of the inhibitor on the steel surface, follow Langmuir isotherm and its mode was found to be physical adsorption. Thermodynamic parameter (ΔG°_{ads}) and activation parameters (E_a , ΔH_a and ΔS_a) were calculated to investigate the mechanism of inhibition. Obtained data were analyzed by suggesting two mathematical models based on linear and quadratic regressions, which takes into account the effect of concentration and temperature upon the inhibition efficiency. Experimental data were in good agreement with those predicted by both models.

Keywords: *Ephedra major*; corrosion ; mild steel ; hydrochloric acid; linear regression; quadratic regression.

Resumen. Se investigó un nuevo extracto butanólico de *Ephedra major* (denominado EBEM) como inhibidor de la corrosión del acero al carbono en una solución de ácido clorhídrico HCl 1 M. La investigación se llevó a cabo mediante métodos de pérdida de peso, espectroscopia de impedancia electroquímica (EIS), mediciones de polarización de Tafel, espectroscopia infrarroja por transformación de Fourier (FT-IR) y microscopía electrónica de barrido (SEM). Se investigó el efecto de la temperatura en el comportamiento de la corrosión del acero en HCl con la adición del inhibidor en el rango de temperaturas de 20-60°C. Se observó que la eficacia de la inhibición aumentó con el incremento de la concentración del extracto EBEM y disminuye con el aumento de la temperatura. Las curvas de Tafel han revelado que el EBEM posee los índices de un inhibidor mixto. La adsorción del inhibidor en la superficie del acero sigue la isoterma de Langmuir y su modo se encontró que era de adsorción física. Se calcularon los parámetros termodinámicos (ΔG°_{ads}) y de activación (E_a , ΔH_a y ΔS_a) para investigar el mecanismo de inhibición. Los datos obtenidos se analizaron proponiendo dos modelos matemáticos basados en regresiones lineales y cuadráticas, que tienen en cuenta el efecto de la concentración y la temperatura sobre la eficacia de la inhibición. Los datos experimentales coincidieron con los predichos por ambos modelos.

Palabras clave: *Ephedra major*; corrosión; acero dulce; ácido clorhídrico; regresión lineal; regresión cuadrática.

Introduction

Due to their good mechanical properties and low cost, steels and its alloys are materials that are widely used in industry. Their applications extend from buildings, to cans of food, including electronic compounds and hulls of certain ships. Cutting tools and commonly machined parts are also and for the most part made of steel alloys. The major disadvantage of steel alloys is that they react aggressively in acidic solutions. Acid solutions are conventionally employed for removal of unwanted scale and rust in many industrial systems. Hydrochloric acid is one of the most widely used agents in the industry. This acid causes the degradation of metals, either by chemical or electrochemical reactions. For well understanding, organic inhibitors constitute an original means of combating corrosion of metals in aggressive media. These compounds are adsorbed on the metal surface and block the active sites, reducing the corrosion rate considerably. Compounds containing unsaturated bonds and / or polar atoms like oxygen (O), nitrogen (N), sulfur (S), phosphor (P) and aromatic rings in their structures are often good inhibitors corrosion of metals and in particular of steel in an acidic solution. Most of well-known corrosion inhibitors are synthetic [1-3]. The action mode of these compounds has been the subject of several works and research [4-6]. Regardless their good inhibition efficiency their utilization is restricted because of their synthesis compounds are very expensive, non-biodegradable and harmful for human beings and the environment. To overcome these inconveniences, a recent research concentrates on the corrosion inhibition properties, and is increasingly directed towards the development of non-toxic, non-polluting and stable organic molecules.

In terms of protection, the use of products of natural origin that are biodegradable and less expensive is essential. Plant extracts are generally obtained by simple extraction methods and exhibit good inhibitory properties in acidic and alkaline environment [7-10].

During the last decade, there have been several scientific works and researches regarding the use of plant extracts as ecological inhibitors. Kaur et al. [11] studied the applications of new natural and eco-friendly corrosion inhibitors on steel in acidic medium. In Ref [12], the authors proposed *Syzygium cumini* leaf extract as an eco-friendly corrosion inhibitor for carbon steel in acidic medium. In another intriguing research study, the authors explored the effect of *Ceratonia Siliqua* L seeds extract as eco-friendly corrosion inhibitor for carbon steel in 1 M HCl [13].

In this study, we have proposed as a possible contribution in this area of science, the *Ephedra major* as a green inhibitor. This plant is extracted from natural resources with the aim of being used to prevent the harmful aggressions of the corrosion of metals and alloys without affecting the ecosystem of the environment.

Although *Ephedra major* has been implicated in other areas, there is no study investigating the corrosion inhibition of a Butanolic extract of *Ephedra major* on the corrosion inhibition of steel in acidic media. Therefore, this investigation describes for the first time the performance of a Butanolic extract of *Ephedra major* on mild steel corrosion in 1M HCl using weight loss measurements, potentiodynamic polarization, electrochemical impedance spectroscopy (EIS), Fourier transform infrared spectroscopy (FT-IR) and scanning electron microscopy (SEM) methods.

Mathematical modeling has proven to be an effective and useful tool to reduce the time and costs of experiments. Recently, some scientists have been providing research contributions to the development and application of new mathematical and statistical models to support the experimental work. As in Ref. [14], where the authors provided a mathematical linear model describing the inhibitory effectiveness of phenolic compounds derived from *Echium italicum* L. Khadom et al. [15] developed a suitable linear statistical model to approximate the corrosion inhibitory efficiency of *Citrus Aurantium* leaf extract, at quantum level.

In this prospect, the second part of this study was devoted to the development of two mathematical models based on linear and quadratic regression. The models were suggested to investigate effect concentration and temperature upon inhibition efficiency. Rather good results were obtained using these models; however, the polynomial model gives a better approximation of the evolution of the inhibition efficiency as a function of the temperature and the concentration of the inhibitor.

Experimental

Electrolyte Medium

The aggressive solutions were 1 M HCl prepared by dilution of 37 % w/w HCl (Merck) using double distilled water. All tests were performed in aerated medium at different temperatures 20 °C, 30 °C, 40 °C, 50 °C and 60 °C.

Plant extracts

Ephedra major is a plant whose species are widespread in countries and regions of the world characterized by temperate climates. Passing through North Africa, southwest and central Asia, China and southern Europe to North America, most ephedra species grow in coastal regions and in sandy soils exposed to direct sunlight. In this study, the plant was collected in the region of Bejaia located on the Algerian coast. *Ephedra major* leaves and stems extracts were collected, shade dried, this dry matter was cut into small parts and immersed in a hydroalcoholic solution (methanol/water, 7/3, V/V) for 24 h. Once the mixture has been filtered, the filtrate is immediately evaporated to dryness. Then boiled water is added to the acquired residue, everything is stored at room temperature. After overnight, the mixture is filtered by the use of ordinary filter paper and subjected to liquid-liquid extraction using several solvents separated in sequence of increasing polarity starting with methylene dichloride, ethyl acetate and n-butanol. At the end, the organic phase was collected for each solvent and the solutions obtained were evaporated to dryness by a rotary evaporator (Model RE52A, China, max capacity 2 L, speed range 0-150 rpm) in order to obtain the extracts of the plant.

Methods

Weight loss measurements

Gravimetric experiments were conducted in a glass vessel. 32CrMoV5 mild steel of with a composition (wt %): C 0.33 %, Cr 1.25 %, Mo 1.2%, Mn 0.9 %, Ni 0.75 %, V 0.3 %, Al 0,2 % and Fe balance, was used in this investigation. Specimens of dimension 1×1×1 cm were prepared and abraded successively with different grades of emery papers, washed with distilled water, cleaned with acetone, and dried at room temperature. After being weighed accurately with high sensitivity balance, the specimens were immersed in 100 mL 1 M HCl with and without various concentrations of the extract (200,400, 600 and 800 ppm) at different temperatures (20–60 °C) in aerated condition. After 5 h, three test pieces were taken out of the test solution, washed, dried, and weighed again. To confirm the reproducibility of the results, all tests were repeated three times.

Electrochemical measurements

The electrochemical measurements were conducted on a Voltalab-PGZ 301 potentiostat controlled by a computer using Voltmaster 4 software. All the electrochemical setups were carried out in a three-electrode cell, open to the atmosphere. The mild steel as the working electrode (WE), saturated calomel electrode: Hg/Hg₂Cl₂/KCl_{sat} (SCE) as reference electrode (RE) and platinum electrode as counter electrode (CE). The working electrode was protected by the epoxy resin leaving a working surface equal to 0.5 cm².

Potentiodynamic polarization

The extrapolation of cathodic and anodic Tafel lines was carried out in a potential range starting from a cathodic potential of – 250 mV to an anodic potential of + 250 mV relative to the OCP at scan rate of 0.5 mV s⁻¹. To obtain the corrosion current densities (I_{corr}), the linear segments of Tafel anodic and cathodic curves were extrapolated to the corrosion potential. Before starting the experiments, the working electrode was immersed in

In all cases, there is an increase in the corrosion rate as a function of temperature. The evolution of the corrosion rate in the corrosive solution alone (1M HCl) shows a regular and rapid growth, confirming an increasing metallic dissolution with increasing temperature.

From SEM, the formation of a protective layer on the mild steel surface by the inhibitor was observed hence confirmed the high performance of inhibitive effect of EBEM.

Two mathematical models were suggested to correlate the effect of temperature and inhibitor concentration on inhibition efficiency. From the results obtained using this model it can be concluded that:

Mathematical analyses are in good agreement with experimental results confirming that inhibition efficiency is influenced by temperature, inhibitor concentration and their combined effect.

Both polynomial and linear models are suitable to represent the data with a high correlation coefficient.

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References

1. Gu, T.; Chen, Z.; Jiang, X.; Zhou, L.; Liao, Y.; Duan, M.; Wang, H.; Pu, Q. *Corros. Sci.* **2015**, *90*, 118-132. DOI: <https://doi.org/10.1016/j.corsci.2014.10.004>
2. Yıldız, R. *Corros. Sci.* **2015**, *90*, 544-553. DOI: <https://doi.org/10.1016/j.corsci.2014.10.047>
3. Zarrouk, A.; Hammouti, B.; Lakhlifi, T.; Traisnel, M.; Vezin, H.; Bentiss, F. *Corros. Sci.* **2015**, *90*, 572-584. DOI: <https://doi.org/10.1016/j.corsci.2014.10.052>
4. Lebrini, M.; Bentiss, F.; Vezin, H.; Lagrèe, M. *Corros. Sci.* **2006**, *48*, 1279-1291. DOI: <https://doi.org/10.1016/j.corsci.2005.05.001>
5. Emregül, K.C.; Aksüt, A.; Abbas. *Corros. Sci.* **2000**, *42*, 2051-2067. DOI: <https://doi.org/10.1016/j.corsci.2005.05.001>
6. Xu, F.; Duan, J.; Zhang, S.; Hou, B. *Mater. Lett.* **2008**, *62*, 4072-4074. DOI: <https://doi.org/10.1016/j.matlet.2008.05.037>
7. Hazwan Hussin, M.; Rahim, A.A.; Ibrahim, M.N.M.; Brosse, N. *Measurement.* **2016**, *78*, 90-103. DOI: <https://doi.org/10.1016/j.measurement.2015.10.007>
8. Torres, V.V.; Amado, R.S.; Faiade Sáa, C.; Fernandez, T.L.; Riehl, C.A.; Torres, A.G.; D'Elia, E. *Corros. Sci.* **2011**, *53*, 2385-2392. DOI: <https://doi.org/10.1016/j.corsci.2011.03.021>
9. Alibakhshi, E.; Ramezanzadeh, M.; Bahlakeh, G.; Ramezanzadeh, B.; Mahdavian, M.; Motamedi, M. *J. Mol. Liq.* **2018**, *255*, 185-198. DOI: <https://doi.org/10.1016/j.molliq.2018.01.144>
10. El Ouadi, Y.; Lahhit, N.; Bouyanzer, A.; Elmsellem, H.; Majidi, L.; Znini, M.; Adbel-Rahman, I.; Hammouti, B.; Costa, J. *Int. J. Dev. Res.* **2016**, *6*, 6867-6874.
11. Kaur, J.; Daksh, N.; Saxena, A. *Arab. J. Sci. Eng.* **2022**, *47*, 57-74. DOI: <https://doi.org/10.1007/s13369-021-05699-0>
12. da Silva, M.V.L.; de Britto Policarpi, E.; Spinelli, A. *J. Taiwan Inst. Chem. Eng.* **2021**, *129*, 342-349. DOI: <https://doi.org/10.1016/j.jtice.2021.09.026>
13. Abbout, S.; Chebabe, D.; Zouahri, M.; Rehioui, M.; Lakbaibi, Z.; Hajjaji, N. *J. Mol. Struct.* **2021**, *1240*, 130611. DOI: <https://doi.org/10.1016/j.molstruc.2021.130611>

14. Boudiba, S.; Hanini, K.; Boudiba, L.; Saouane, I.; Benahmed, M. in : F. A. Badria (Ed.) Phenolic Compounds - Chemistry, Synthesis, Diversity, Non-Conventional Industrial, Pharmaceutical and Therapeutic Applications. London, United Kingdom. **2021**. doi: 10.5772/intechopen.94825
15. Khadom, A. A.; Kadhim, M. M.; Anaee, A. R.; Mahood, H. B.; Mahdi, M. S.; Salman, A. W. *J. Mol. Liq.* **2021**, 343,116978. DOI: <https://doi.org/10.1016/j.molliq.2021.116978>
16. Daoud, D.; Douadi, T.; Hamani, H.; Chafaa, S.; Al-Noaimi, M. *Corros. Sci.* **2015**, 94, 21-37. DOI: <https://doi.org/10.1016/j.corsci.2015.01.025>
17. Aytaç, A. *J. Mater. Sci.* **2010**, 45,6812-6818. DOI: <https://doi.org/10.1007/s10853-010-4779-7>
18. Emregül, K. C.; Atakol, O. *Mater. Chem. Phys.* **2004**, 83, 373-379. DOI: <https://doi.org/10.1016/j.matchemphys.2003.11.008>
19. Hasanov, R. M.; Sadikoğlu, M.; Bilgiç, S. *Appl. Surf. Sci.* **2007**, 253, 3913-3921. DOI: <https://doi.org/10.1016/j.apsusc.2006.08.025>
20. JO'M, B.; Drazic, D. *Electrochim. Acta.* **1962**, 7, 293-313. DOI: [https://doi.org/10.1016/0013-4686\(62\)87007-8](https://doi.org/10.1016/0013-4686(62)87007-8)
21. Fiala, A.; Boukhedena, W.; Lemallem, S.E.; Brahim Ladouani, H.; Allal.H. *J. Bio- Tribo-Corros.* **2019**, 5,1-17. DOI: <https://doi.org/10.1007/s40735-019-0237-5>
22. Satapathy, A. K.; Gunasekaran, G.; Sahoo, S. C.; Amit, K.; Rodrigues, P.V. *Corrosi. Sci.* **2009**, 51, 2848-2856. DOI: <https://doi.org/10.1016/j.corsci.2009.08.016>
23. Hussin, M. H.; Kassim, M. J. *Mater. Chem. Phys.* **2011**, 125, 461-468. DOI: <https://doi.org/10.1016/j.matchemphys.2010.10.032>
24. Gunasekaran, G.; Chauhan, L. *Electrochim. Acta.* **2004**, 49, 4387-4395. DOI: <https://doi.org/10.1016/j.electacta.2004.04.030>
25. El-Etre, A. *Mater. Chem. Phys.* **2008**, 108, 278-282. DOI: <https://doi.org/10.1016/j.matchemphys.2007.09.037>
26. Uwah, I. E.; Okafor, P.; Ebiekpe, V. *Arab. J. Chem.* **2013**, 6, 285-293. DOI: <https://doi.org/10.1016/j.arabjc.2010.10.008>
27. Bentiss, F.; Lebrini, M.; Lagrenée, M. *Corros. Sci.* **2005**, 47, 2915-2931. DOI: <https://doi.org/10.1016/j.corsci.2005.05.034>
28. Aljourani, J.; Raeissi, K.; Golozar, M. *Corro. Sci.* **2009**, 51, 1836-1843. DOI: <https://doi.org/10.1016/j.corsci.2009.05.011>
29. Ammar, I.; El Khorafi, F. *Corros. Mater.* **1973**, 24, 702-707. DOI: <https://doi.org/10.1002/maco.19730240806>
30. Krishnegowda, P. M.; Venkatesha, V. T.; Krishnegowda, P. K. M.; Shivayogiraju, S. B. *Ind. Eng. Chem. Res.* **2013**, 52, 722-728. DOI: <https://doi.org/10.1021/ie3018862>
31. Benabid, S.; Douadi, T.; Issaadi, S.; Penverne, C.; Chafaa, S. *MEAS.* **2017**, 99, 53-63. DOI: <https://doi.org/10.1016/j.measurement.2016.12.022>
32. Bei, Q.; Jing, W.; Meng, Z.; Baorong, H. *Corros. Sci.* **2013**, 75, 184-192. DOI: <https://doi.org/10.1016/j.corsci.2013.06.001>
33. El-Askalany, A. H.; Mostafa, S. I.; Shalabi, K.; Eid, A. M.; Shaaban, S. *J. Mol. Liq.* **2016**, 223, 497-508. DOI: <https://doi.org/10.1016/j.molliq.2016.08.088>
34. Labjar, N.; Lebrini, M.; Bentiss, N. E. C.; El Hajjaji, S.; Jama, C. *Mater. Chem. Phys.* **2010**, 119, 330-336. DOI: <https://doi.org/10.1016/j.matchemphys.2009.09.006>
35. Bentiss, F.; Traisnel, M.; Vezin, H.; Hildebrand, H. F.; Lagrenée, M. *Corros. Sci.* **2004**, 46, 2781-2792. DOI: <https://doi.org/10.1016/j.corsci.2004.04.001>

36. Hamani, H.; Douadi, T.; Al-Noaimi, M.; Issaadi, S.; Daoud, D.; Chafaa, S. *Corros. Sci.* **2014**, 88, 234-245. DOI: <https://doi.org/10.1016/j.corsci.2014.07.044>
37. Bommersbach, P.; Alemany-Dumont, C.; Millet, J. P.; Normand, B. *Electrochim. Acta.* **2005**, 51, 1076-1084. DOI: <https://doi.org/10.1016/j.electacta.2005.06.001>
38. Lebrini, M.; Robert, F.; Lecante, A.; Roos, C. *Corros. Sci.* **2011**, 53, 687-695. DOI: <https://doi.org/10.1016/j.corsci.2010.10.006>
39. Hegazy, M.; Abdallah, M.; Awad, M. K.; Rezk, M. *Corros. Sci.* **2014**, 81, 54-64. DOI: <https://doi.org/10.1016/j.corsci.2013.12.010>
40. Benahmed, M.; Selatnia, I.; Djeddi, N.; Laouer, H. *Afr. J. Chem.* **2020**, 3, 251-261. DOI: <https://doi.org/10.1007/s42250-019-00093-8>
41. Bobina, M.; Kellenberger, A.; Millet, J.P.; Muntean, C.; Vaszilcsin, N. *Corro. Sci.* **2013**, 69, 389-395. DOI: <https://doi.org/10.1016/j.corsci.2012.12.020>
42. Li, X.; Li, Q.; Xu, X.; Su, Y.; Yue, Q.; Gao, B. *J. Taiwan Inst. Chem. Eng.* **2016**, 60, 564-572. DOI: <https://doi.org/10.1016/j.jtice.2015.10.027>
43. Döner, A.; Solmaz, R.; Özcan, M.; Kardas, G. *Corros. Sci.* **2011**, 53, 2902-2913. DOI: <https://doi.org/10.1016/j.corsci.2011.05.027>
44. Tebbji, K.; Faska, N.; Tounsi, A.; Oudda, H.; Benkaddour, M.; Hammouti, B. *Mater. Chem. Phys.* **2007**, 106, 260-267. DOI: <https://doi.org/10.1016/j.matchemphys.2007.05.046>
45. Hamdy, A.; El-Gendy, N. S. *Egypt. J. Pet.* **2013**, 22, 17-25. DOI: <https://doi.org/10.1016/j.ejpe.2012.06.002>
46. Ostovari, A.; Hoseinich, S. M.; Peikari, M.; Shadizadeh, S. R.; Hashemi, S. J. *Corros. Sci.* **2009**, 51, 1935-1949. DOI: <https://doi.org/10.1016/j.corsci.2009.05.024>
47. Ramya, K.; Revathi Mohan, K. K.; Anupama, A. J. *Mater. Chem. Phys.* **2015**, 149, 632-647. DOI: <https://doi.org/10.1016/j.matchemphys.2014.11.020>
48. Fan, B.; Hao, H.; Yang, B.; Li, Y. *Res. Chem. Intermed.* **2018**, 44, 5711-5736. DOI: <https://doi.org/10.1007/s11164-018-3451-8>
49. Khadom, A. A.; Abd, A. N.; Ahmed, N. A. S. *Afr. J. Chem. Eng.* **2018**, 25, 13-21. DOI: <https://doi.org/10.1016/j.sajce.2017.11.002>
50. El bribri, A.; Tabyaoui, M.; El Attari, H.; Boumhara, K.; Siniti, M.; Tabyaoui, B. *J. Mater. Environ. Sci.* **2011**, 2, 156-165.