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Study the Effect of Peganum Harmala Seeds Extracts to Protect Iron Alloy from Corrosion in Salt Media

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Abstract

This work describes the inhibition effect of different concentration of an aqueous extract of Peganum harmala seed on the corrosion of carbon steel in 3.5 % sodium chloride solution using potentiostatic polarization techniques at the temperature range of 25°C to 55°C. The result show that inhibition efficiency increased with increasing concentration of the inhibitor extracts and temperature. The adsorption of inhibitor on carbon steel surface was fit into Langmuir adsorption isotherm. Kinetic and thermodynamic parameters governing the corrosion and adsorption process were calculated and discussed.

Keywords: carbon steel, seed, Peganum harmala, salt and inhibition efficiency.

دراسة تأثير المستخلص المائي لبذور الحرمل في حماية سبائك الحديد من التآكل في الاوساط الملحية

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الخلاصة

يصف هذا العمل تأثير تثبيط التآكل لتراكيز مختلفة من المستخلص المائي لبذور الحرمل على حديد الكاربون في محلول 3.5% من كلوريد الصوديوم باستعمال تقنية المجهد الساكن وفي مدى من درجات الحرارة 25-55°م. اظهرت النتائج ان كفاءة التثبيط تزداد بزيادة تراكيز المثبط المستخلص ودرجة الحرارة. عملية الامتزاز للمثبط على سطح المعدن تخضع لمتساوي حرارة لنكماير، المعاملات الحركية والثرموديناميكية المصاحبة لعملية التآكل والامتزاز تم حسابها ومناقشتها.

Introduction

Several researches have been carried out to protect the metal against corrosion; these researches revealed that one of the best methods is uses inhibitor. Inhibitor is a chemical substance that, when added in small concentration to an environment, effectively decreases the corrosion rate [1]. There has been a growing trend in the use of natural products as corrosion inhibitors for metals in various corrosive media, known as non-toxic compounds, called also green inhibitors, [2]. The term "green inhibitor refers to the substance that is biocompatibility in nature, environmentally acceptable readily available and renewable source [3]. Most of the well-known inhibitors are natural product of plant origin containing different organic compound [4]. Organic compounds having hetero atoms are found to higher basicity and electron density and thus assist in corrosion inhibition [5]. Seed extract was one of these plants. The seeds of Peganum harmala (Syrian rue) are a wild-growing flowering plant belonging to the Zygophyllaceae family and are found abundantly in Middle East and North Africa [6] Peganum harmala, commonly known as Harmel. The pharmacological and the reported therapeutic effects of Peganum harmala may be attributed to a number of phytochemicals that have been isolated

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from *Peganum harmala* seeds, such as the β -carboline alkaloids (harmine, harmaline, harmalacidine, harmol, harmalol, and tetrahydroharmine) [7]. The chemical structure of this compound is as shown in Figure-1 [8]. The most significant harmala alkaloid is harmaline [9]. Systematic (IUPAC) name of harmaline is 4,9-Dihydro-7-methoxy-1-methyl-3H-pyrido[3,4-b] indole, from the structure it can be seen that harmaline has hetero atoms in their heterocyclic structure and it is therefore expect to be a good corrosion inhibitor.

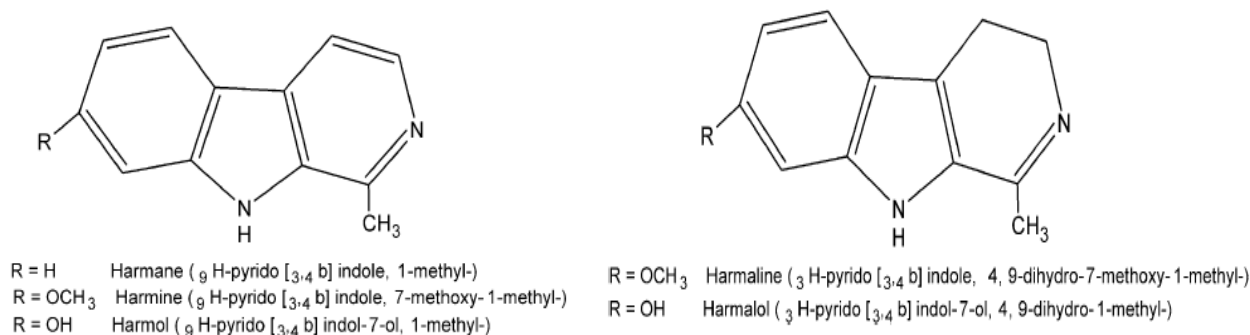


Figure 1-The chemical structure of β -carboline alkaloids (harmine, harmaline, harmalacidine, harmol and harmalol, isolated from *Peganum harmala* seeds.

Carbon steel is alloyed, singly or in combination [10] the combination are two elements, iron and carbon, where other elements are present in quantities too small to affect the properties [11]. The inhibition efficiency of plant extracts in controlling corrosion of metals in various environments has been investigated [12].

Materials and Methods

The materials used for this study was carbon steel (C.S.), its composition is given in Table-1.

Table 1: The composition of carbon steel.

Metal	C	Si	Mn	S	Ni	Cr	P
wt%	0.42	< 0.40	0.50-0.80	< 0.045	0.40	< 0.40	< 0.045

Sheet of C.S. was mechanically pressed cut into circular with 2.5 cm diameter, used as a flat working electrode and the exposed measuring surface was 1 cm². Each sheet were polished to mirror finish with grade emery polishing papers, degreased by washing with ethanol dipped in acetone and allowed to dry in air and stored in desiccator until used. All reagent used for the study were annular, grade and double distilled water was used for their preparation. The seeds of *Peganum Harmala* (P. h.) were collected from local markets in Baghdad city, clean and dried. The seeds were ground to a fine powder using a coffee grinder and placed in a clean, dry beaker. An aqueous extract was prepared by taking different weight (2,4,6,8) g of finely powdered seeds and extract three time with 1000 ml of boil distilled water, the solid material was removed using a filter system with a Bucher funnel, the filtered then used freshly. Electrochemical measurement carried out by using the potentiostatic technique how is a constant potential maintained? This is done by means of a device called a potentiostat, (model 200 (2007) Germany). Its working depends on a continuing measurement of the potential difference between the working electrode and the reference electrode in glass cell with a capacity of 1000mL, a platinum electrode and a saturated silver –silver chloride electrode were used as a counter electrode and reference electrode respectively, the carbon steel electrode (working electrode) was then placed in the test solution (uninhibited and inhibited solution) for 15 minutes before electrochemical measurement. The Tafel polarization measurement was made for a potential range of -200 mV to +200mV with respect to open circuit potential.

Results and discussion

Potentiostatic polarization

The potentiostatic parameters such as corrosion potential (E_{corr}), cathodic and anodic Tafel slopes (bc and ba), corrosion current density (I_{corr}) were tabulated in Table 1., it appear that the addition of

Peganum harmala extracts (P.h.e.) at all the studied concentration resulted in decrease in the corrosion current density (I_{corr}). The decrease in the corrosion density was followed by substantial decrease in the corrosion rate (k). There was a shifted in the corrosion potential (E_{corr}) value to more negative potential. According to the reported literature , if the corrosion potential is more than ± 85 mV with respect to the corrosion potential of the blank, the inhibitor can be considered distinctive cathodic or anodic type, in this study it's less than ± 85 mV; so a mixed-type inhibitor be there [13]. The inhibition efficiency %IE was calculated using the following equation [14].

$$\%IE = (I_{corr}^0 - I_{corr}) / I_{corr}^0 \times 100\% \quad \dots\dots\dots 1$$

Where I_{corr}^0 and I_{corr} are the corrosion current densities in absence and presence of P.h.e. respectively. From Table-2, it can be show that the Inhibition efficiency increased with increasing the extract concentration of inhibitor and temperature.

Table 2-Electrochemical corrosion parameters for carbon steel in 3.5% NaCl solution containing different concentrations of P.h.e. at temperature range (25-55) °C.

concentration g/l	T /K	I_{corr} $\mu A/Cm^2$	E_{corr} V	b_a V/decade	b_c V/decade	IE%
blank	289	92.47	0.43	0.22	0.25	
	308	153.49	0.45	0.35	0.41	
	318	298.84	0.61	0.49	0.11	
	328	551.30	0.63	0.52	0.13	
2	289	71.76	0.44	0.09	0.05	16.29
	308	105.41	0.55	0.11	0.06	27.64
	318	159.46	0.58	0.14	0.09	46.46
	328	216.12	0.62	0.22	0.05	60.32
4	289	60.46	0.49	0.08	0.05	22.67
	308	90.22	0.49	0.09	0.07	30.46
	318	128.51	0.53	0.07	0.06	50.72
	328	168.17	0.58	0.08	0.07	67.23
6	289	52.31	0.48	0.05	0.08	31.76
	308	74.06	0.52	0.06	0.05	37.43
	318	97.85,	0.53	0.07	0.07	53.34
	328	122.32	0.55	0.08	0.07	70.35
8	289	43.77	0.49	0.05	0.04	52.66
	308	55.35	0.55	0.09	0.04	63.93
	318	65.41	0.63	0.07	0.06	77.07
	328	73.73	0.66	0.07	0.04	86.62

The dependence of the rate constant (k) of chemical reaction on the temperature T is expressed by the Arrhenius equation [15].

$$k = A e^{-E_a/RT} \quad \dots\dots\dots 2$$

The effect of temperature on the corrosion process in presence of inhibitor leads to get more information on the electrochemical behavior of metals in aggressive media. The calculation of kinetic and thermodynamic parameters for the corrosion processes were reported in Table 3. .The linear regression plots between log k and 1/T are presented in Figure-2. Where A is the pre-exponential factor in the rate equation which depends on the metal type, k is the rate constant, which is directly proportion to the corrosion current (I_{corr}). R is the gas constant, and T is the absolute temperature.

From the results it is apparent that the activation energies for the corrosion of C.S. in the presence of P.h.e. decreased with increase in the concentration of inhibitor ranged from 21.06 to 6.07 kJ mol⁻¹. The lower activated energy in an of inhibitor than in absence of inhibitor means the possibility of increase in the corrosion current in the presence of P.h.e., but it has been observed that in presence of inhibitor the corrosion current density is decreased, which indicates the change in the mechanism of

the corrosion process when inhibitor is used, where it was attributed to be due to the nature of interaction between inhibitor molecules and the C.S. surface [16].

Table 3-Arrhenius plot relating log I_{corr} with $1/T$ for the corrosion of carbon steel in 3.5 % NaCl solution containing various concentration of P. h. e.

C (g/l)	R ²	E _a (kJ/ mol ⁻¹)	A ×10 ³⁰	ΔH* (k J/mol ⁻¹)	ΔS* (J / mol ⁻¹)	R ²
0	0.994	21.06	16200	45.92	-53.89	0.99
2	0.997	13.03	7.72	27.47	-117.33	0.99
4	0.995	12.00	2.50	24.98	-123.17	0.99
6	0.994	9.92	0.31	20.26	143.95	0.99
8	0.98	6.07	0.0075	11.56	174.59	0.99

The other Thermodynamic parameters like enthalpy of activation (ΔH*) and entropy of activation (ΔS*) were calculated using the transition state equation (3) [17]

$$k = [RT/Nh] \exp [\Delta S^*/R] \exp [-\Delta H^*/RT] \dots\dots\dots 3$$

Where h is Plank’s constant and N is Avogadro's number. A plot of ln (k /T) vs. 1/T gave a straight line with slope = -ΔH*/R and intercept = ln(R/Nh) +ΔS*/R, as shown in Figure-3. Negative values of entropies show that the activated complex in the rate determining step is an association rather than dissociation step, meaning that a decrease in disordering takes place on going from reactants to the activated complex [18]. Positive values of ΔH* ranged from 45.92 to 11.56kJ.mol⁻¹ indicated that corrosion process was endothermic in nature.

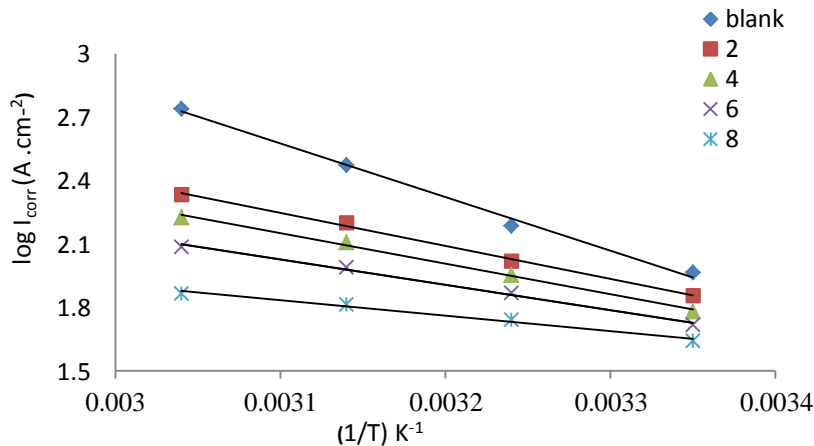


Figure 2- plot of log I_{corr} versus $1/T$ for the corrosion of carbon steel in 3.5% NaCl solution containing Various concentration of P.h.e.

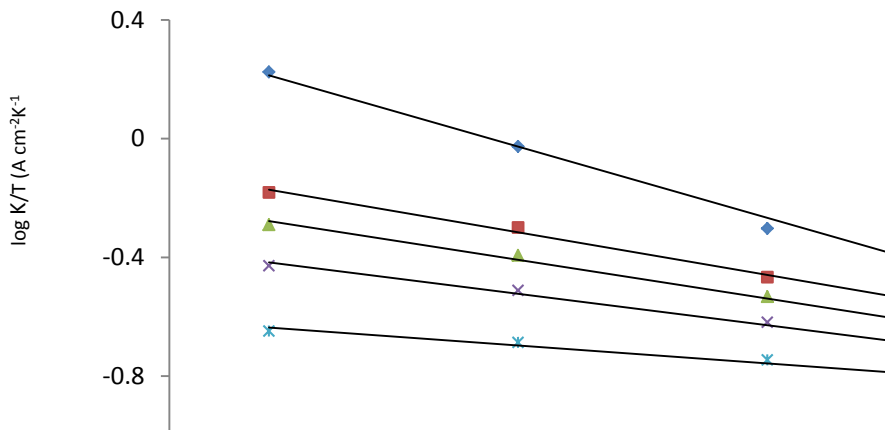


Figure 3-Plot of log (k/T) versus 1/T for the corrosion of C.S. in 3, 5% NaCl solution containing various concentration of P.h.e.

Adsorption process

In order to understand the mechanism of corrosion inhibition, the adsorption behavior of the adsorbate (P.h.e.) on the C.S. surface must be known. Isotherms as equations of state relate the physical quantities that define the adsorbed molecules in the electrochemical system, these physical quantities are the number of adsorbed molecules or the degree of surface coverage (θ) for different concentrations of inhibitor which are evaluated from potentiostatic polarization measurements by using equation 4 [19].

$$\theta = \frac{IE\%}{100} \dots\dots\dots 4$$

Where IE (%) is the percentage inhibition efficiency as calculated by using equation (1). Langmuir isotherm is one of the first isotherms, derived back in 1918 [20]. Its isotherm focuses on the basic process of transferring a molecule from the bulk to the electrode and the degree of surface coverage (θ) is related to equilibrium adsorption desorption - constant K_{ads} and concentration (C) by equation 4a [21].

$$\frac{\theta}{C} = \frac{1}{K_{ads}} + C \dots\dots\dots 4a$$

The plot of C / θ vs. C gave a straight line as shown in Figure-4.

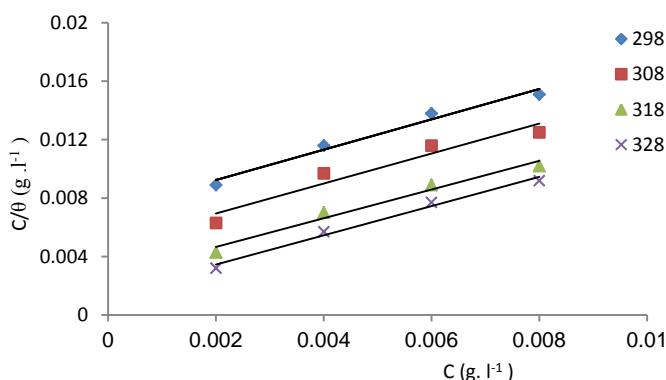


Figure 4-Langmuir's isotherm plot for the adsorption of P.h.e. at different temperature

The values of Langmuir isotherm parameters are presented in table-4 .The result show that all the linear correlation coefficients (R^2) values are very close to unity, indicating that the adsorption of the P.h. extract on C.S. surface good obeyed Langmuir adsorption isotherm and the values of equilibrium constant K_{ads} decreased with increasing temperature, which indicated that the P.h. extract is easily and strongly adsorbed onto the C.S. surface at lower temperature, weak and difficult at higher temperature[22].

Table 4-The standard thermodynamic parameters of adsorption of different concentration of P.h.e. on C.S. surface in 3.5% NaCl solution

Temp. K	R^2	$K_{ads} \times 10^{-3}$	ΔG°_{ads} (kJ/mol)	ΔS°_{ads} (J/mol)	ΔH°_{ads} (kJ/mol)
298	0.98	7.2	-7.34	191.47	-45.72
308	0.93	4.9	-10.8		
318	0.97	2.7	-15.79		
328	0.98	1.4	-21.30		

The standard electrochemical free energy of adsorption (ΔG°_{ads}) can be written in a general form as [23].

$$K_{ads} = 1/55.5 \exp (- \Delta G^{\circ}_{ads} /RT) \dots\dots\dots 5$$

The negative values for calculated ΔG°_{ads} indicate that the adsorption process is spontaneity and the stability of the adsorbed layer on C.S. surface. Generally, value of ΔG°_{ads} up to -20 kJ mol^{-1} is consistent with the electrostatic interaction between the charged molecules and the charged metal (physical adsorption) while the value more negative than -20 kJ mol^{-1} involves sharing or transfer of electrons from the inhibitor molecules to the metal surface to form a coordinate type of bond (chemisorption)[24]. In the present study the mean values of ΔG°_{ads} was negative and $= -13.80 \text{ kJ mol}^{-1}$ less than -20 kJ mol^{-1} so the adsorption of P.h.e. on the C.S. surface was physisorption process.

The adsorption heat ΔH_{ads} can be regarded as the standard adsorption heat ΔH°_{ads} by using Van't Hoff equation (eq. 6). Because all experimental was carried out at the standard pressure and low concentration [22].

$$\text{Ln } K_{ads} = - (\Delta H^{\circ}_{ads} /RT) + C \dots\dots\dots 6$$

The slope of variation of $\text{Ln } (K_{ads}/T)$ vs. $1/T = -\Delta H^{\circ}_{ads} = -45.72 \text{ kJ mol}^{-1}$ (Fig 5) which is approximately equal to that estimated by the slope of straight line for variation of $\Delta G^{\circ}_{ads}/T$ with $1/T$ (using the thermodynamic basic equation eq.7) $\Delta H^{\circ}_{ads} = -45.64 \text{ kJ/mol}$ as shown in Figure-6.

$$\Delta G^{\circ}_{ads} = \Delta H^{\circ}_{ads} - T\Delta S^{\circ}_{ads} \dots\dots\dots 7$$

Negative value of the standard adsorption heat indicated that the adsorption process of inhibitor is exothermic process, in an exothermic process physisorption is distinguished from chemisorption by considering in an exothermic value of a physisorption process is lower than -40 kJ mol^{-1} while the adsorption heat of chemisorption process approaches -100 kJ mol^{-1} [25]. In this study the standard adsorption heat is $\Delta H^{\circ}_{ads} = -45.64 \text{ kJ mol}^{-1}$ postulates that physical adsorption is more favored. The heat of adsorption is usually a negative quantity and indicates the strength of the bonds that have to be broken and formed during the adsorption process, including those related to the different electrode sites and the standard adsorption entropy indicates how mobile the molecules are in their adsorbed site [26]. The positive value of standard adsorption entropy suggested that the adsorption is coupled with an increase of system disorder due to the adsorption of P.h.e. on the carbon steel surface.

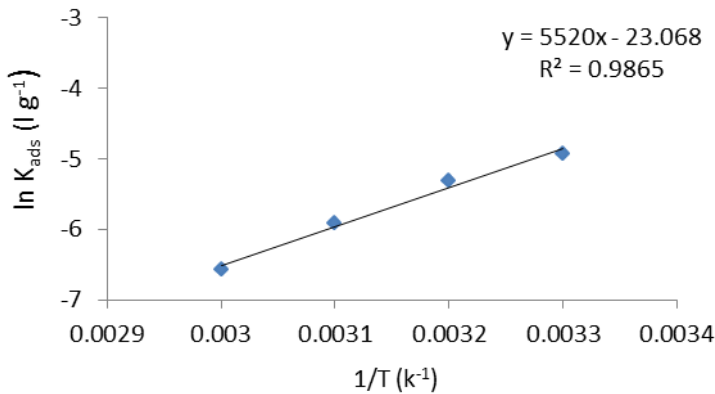


Figure 5-Langmuir isotherm plot for the adsorption of P.h.e. on the surface of C.S.

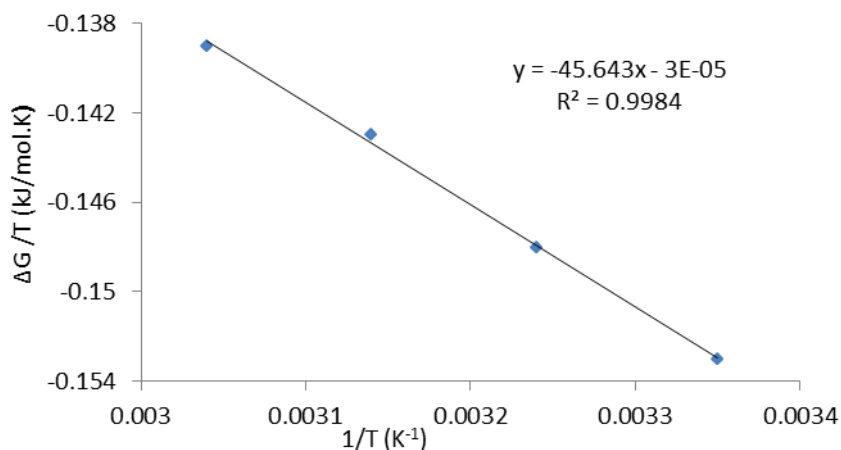


Figure 6-The variation of $\Delta G_{\text{ads}}^{\circ}/T$ vs. $1/T$ for the adsorptions of the P.h.e. On the C.S. surface.

Conclusion

- The aqueous extract of Peganum harmala seeds acts as a good inhibitor for the corrosion of carbon steel in 3.5% NaCl solutions.
- The inhibition efficiency increases with the increasing the concentration of the Peganum harmala extract and the temperature.
- Aqueous extract of Peganum harmala seeds act as a mixed type inhibitor.
- The adsorption process of the Peganum harmala inhibitor follows Langmuir adsorption isotherm and physisorption process.

References

1. Pierre, R. **1999**. *Handbook of Corrosion Engineering*. McGraw-Hill P: 833.
2. Leelavathi, S. and Rajalakshmi, R. **2013**. Dodonaea viscosa (L.) Leaves Extract as Acid Corrosion Inhibitor for Mild Steel – A Green Approach. *Journal of Material and Environment Science*, 4(5), PP: 625-638.
3. Manoj, A. **2013**. Green inhibitors for prevention of metal and alloys Corrosion: *An Overview .chemistry and materials research*, 3 (6), pp: 16-24.
4. Adindu, C. Oduagwa, F. Stan, C. Ekenyem, O. and Geoffrey, O. **2013**. Corrosion inhibition of stainless steel (3161) using cola nitida, cola a cuminata and cola garcinia .*The International journal of engineering and science*, 2 (3), PP: 141-48.
5. Matheswarn, P. and Ramasamy A.K. **2010**. A Study of Mild Steel Corrosion Using Adhatoda Vasica (AV) Extract as Inhibitor in Different Acid Medium. *E-Journal of Chemistry*, 7(4), PP: 1284-1289.
6. Hamid, R. Ali, G. and Mehrdad, I. **2004**. Antinociceptive Effects of Peganum Harmala L. Alkaloid Extract On Mouse Formalin Test. *Canadian Society For Pharmaceutical Sciences*, 7(1), PP: 65-69.
7. Fatima, L. Mustapha, Z. Akino, J. Abdellatif, S. Zafar, H. and Badiaa, L. **2013**. Cytotoxicity Of Alkaloids Isolated From Peganum Harmala Seeds. *Pakistan Journal Of Pharmaceutical Science*, 26 (4), pp: 699-706.
8. Dinara, J. Moural, Marc, F. R. Jane M. B. Joaõ, A. Peêgas, H. and Jenifer S. **2007**. Antioxidant Properties of β -Carboline Alkaloids are related to Their Antimutagenic and Antigenotoxic Activities. *Mutagenesis*, 22(4), pp: 293-302.
9. Alyssa, B. jeremy L. Brian, K. Cathy, H. and James, S. **2009**. The Free Base Extraction of Hermaline from Pergamum Harmala, *American Journal of Undergraduate Research*, 8 (60), PP: 2 - 3.
10. Fontana, M. **1986**. *Corrosion engineering*. Third addition. McGraw – Hill book Company, P: 225.
11. Smith, W.F. and Hashemi, J. **2006**. *Foundations of Materials Science and Engineering*. Forth Addition. Mcgraw-Hill.
12. Ambrish, S. Eno, E. and Quraishi1, A. **2012**. Corrosion Inhibition Of Carbon Steel In HCl Solution By Some Plant Extracts. *International Journal of Corrosion*, Article ID 897430, PP: 1-20.

13. Deepa, P. and Rao, P. **2013**. Corrosion Inhibition Of 6063 Aluminum Alloy By Coriandrum Sativum L Seed Extract in Phosphoric Acid Medium. *Journal of Material and Environmental Science*, 4 (5), PP: 732-743.
14. Sribharathy, V. and Sathiyabama, J. **2013**. Inhibition Action of Phyllanthus Amarus Extracts on the Corrosion of Mild Steel in Seawater. *Chemical Science Transactions*, 2910, PP: 315-321.
15. Milan, P. **2006**. *Fundamentals of electrochemical Deposition*. Second Edition. John Wiley & Sons, Inc., New Jersey, Canada, P: 78.
16. Al-Khaldi, M. A. and Al-qahtani, K. Y. **2013**. Corrosion Inhibition of Steel By Coriander Extracts In Hydrochloric Acid Solution. *Journal of Material and Environmental Science*, 4(5), PP: 593-600.
17. Deepa, P. and Padmalatha, R. **2013**. Garcinia Indica as an Environmentally Safe Corrosion Inhibitor for Aluminum in 0.5M Phosphoric Acid. *International Journal of Corrosion. Article ID 945143*, PP: 1-30.
18. Nnabuk, O. Eddy Eno E.Ebenso. **2010**. Adsorption, Synergistic inhibitive Effect and Quantum Studies of Ampicillin and Halides for the Corrosion of Mild Steel in H₂SO₄. *Journal Appl. Electrochem*, 40, PP: 445-456.
19. Magda, A. Azza, G. and Amany, F. **2012**. Electrochemical corrosion Inhibition of Al-Alloy in Phosphoric Acid. *Chemistry and Material Research*, 2(1), PP: 41-56.
20. Dahman, M. Et-Touhami, M. A. Al-Deyab, S.S. Hammouti, B. Bouyanzer, A. 2010. Corrosion Inhibition of C38 Steel in 1 M HCl: A Comparative Study of Black Pepper Extract and Its Isolated Piperine. *International Journal of Electrochemical Science*, 5, PP: 1060 – 1069.
21. Zarrouk1, A. Dafali1, A. Hammouti, B. Zarrok H. Boukhris, S. Zertoubi, M. **2010** Synthesis, Characterization and Comparative Study of Functionalized Quinoxaline Derivatives Towards Corrosion Of Copper in Nitric Acid Medium. *International Journal of Electrochemical Science*, 5, PP: 46 – 55.
22. Hui Cang, Zhenghao Fei, Jinling Shao, Wenyan Shi, Qi-Xu. **2013**. Corrosion inhibitor of mild steel by aloes extract in HCl solution. *International Journal of Electrochemical Science*, 8, PP: 720,734.
23. Khamis, A .Mahmoud M. Saleh, Mohamed I. Awad, El-Anadouli B.E. **2014**. Inhibitory action of quaternary ammonium bromide on mild steel and synergistic effect with other halide ions in 0.5 M H₂SO₄. *Cairo University, Journal of Advanced Research*, 5, PP: 637–646.
24. Hui, C., Zhenghao, F. Wenyan, S. **2012**. Experimental and Theoretical Study for Corrosion Inhibition of Mild Steel by L-Cysteine. *International Journal of Electrochemical Science*, 7, PP: 10121 – 10131.
25. Zarrouki, A. Warad, I. B.Hammouti, B. **2010**. The Effect of Temperature on the Corrosion of Cu /HNO₃ In The Presence Of Organic Inhibitor: Part-2, *International Journal of Electrochemical Science*, 5, PP: 1516-1526.
26. John O.M. Bockris, Amulya K. N. Reddy and Maria G.Aldeco. **2002**. *Modern Electrochemistry 2A Fundamentals of Electrodicts*. Kluwer Academic Publishers. Second Edition, 2A, P: 964.