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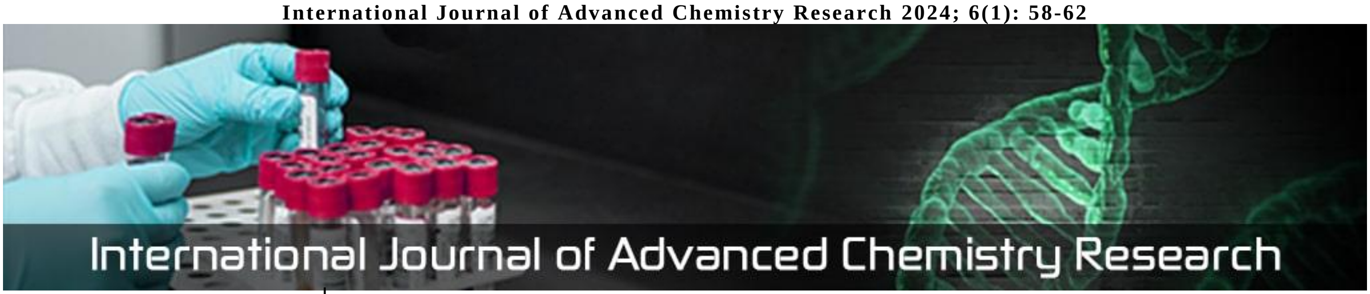

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Theoretical evaluation of corrosion inhibitor potential of phytoconstituents of male and female *Phoenix dactylifera* L. extracts

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Abstract
Phoenix dactylifera L. is a dioecious plant belonging to the Arcacaea family which means it has separate male and female saplings. In the present study, ethyl acetate extracts of male and female date palm leaves are subjected to GC-MS analysis so as to identify phytochemicals present in it. These phytochemicals were then subjected to quantum mechanical evaluation. Quantum mechanical parameters such as ionization potential, electron affinity, energy gap, global hardness, global softness, electronegativity and electron back donation were evaluated. The study concluded that the corrosion inhibition potential of male date palm extract is due to synergistic action of hexadecanoic acid, cis-7-Dodecen-1-yl acetate, 9, 12, 15-Octadecatrienoic acid and Para methaqualone while that of female date palm extract is due to n-hexadecanoic acid, octadec-9-enoic acid, Beta-sitosterol and Alpha-amyrin.

Keywords: *Phoenix dactylifera* L., corrosion, alpha amyrin, beta-sitosterol

Introduction

Corrosion can be defined as the deterioration of metal that arises upon its chemical or electrochemical dealings with its surroundings [1]. This natural and spontaneous process leads to the conversion of metal into various stable forms such as oxides, hydroxides and sulfides [2]. The approximate global annual cost of corrosion is USD 2.5 trillion which is 3-4% of the global gross domestic product [3]. The degradation of metal upon its interaction with surroundings can be classified into two classes: Dry corrosion and Wet corrosion. Dry corrosion arises upon the interaction of metals with gases at elevated temperatures. Wet corrosion takes place due to the interaction of metals with aqueous solutions or electrolytes [4]. Corrosion inhibitors are chemical substances that alleviate the corrosion process when added in minor amounts to the corrosive domain [5]. Different types of substances such as inorganic & organic compounds, polymeric materials and nanomaterials have been used as corrosion inhibitors. Their characteristics are as listed in below table 1 [6-12].

The utilization of plant extracts enriched with tannins, alkaloids, flavonoids, tannins, amino acids, anthraquinones and saponins as corrosion inhibitors is advantageous due to their cost-effective, eco-friendly, plentiful accessibility and simplified production techniques [13]. Different plant extracts such as *Asparagus racemosus*, *Areca* Palm, *Trigonella foenum-graecum* L & *Jasminum nudiflorum* Lind l have been evaluated as corrosion inhibitors for metals. Different methods such as weight loss measurements, electron impedance study, polarization techniques and density functional theory are utilized to evaluate the corrosion inhibitor potential of corrosion inhibitors [14-17].

Phoenix dactylifera L. also known as date palm is a monocotyledonous plant belonging to are caceae family [18]. Date palm is dioecious which means it has separate male and female saplings [19]. In the present study, ethyl acetate extracts of male and female *Phoenix dactylifera* L. leaves were analyzed by Gas chromatography-mass spectrometry so as to identify the phytoconstituent present in it. These phytochemicals were then subjected to quantum mechanical analysis so as to evaluate their corrosion inhibitor potential.

Table 1: Characteristics of different types of corrosion inhibitors

Type of Corrosion Inhibitor	Characteristics
Inorganic substances (Derivatives of phosphates, chromates, dichromates and arsenates)	They are efficient inhibitors of metals in the corrosive medium at high temperatures for a prolonged time span. They have been replaced by newer entities due to their toxicity issues and reduced effectiveness in stronger acidic conditions
Organic substances	Organic compounds with hetero atoms (N, O, S) are efficiently adsorbed on the metal surface and hence prevent dissolution of the metal in the corrosive atmosphere. The limited usage of organic compounds is due to their restricted solubility, particularly in polar electrolytes and hydrophobic trait.
Polymeric substances	These substances possess adjustable viscosity, multi-functionality and an increased number of binding sites. Their restricted usage is due to their deprived adhering capacity to the metal and low mechanical strength
Nanomaterials	They impart hardness, durability, thermal stability and optical eminence to metals. Due their intrinsic porosity which promotes the diffusion of water through metal surfaces and hence reduces its action.

Materials and Methods

Preparation of male and female *Phoenix dactylifera* L. extracts: Male and female *Phoenix dactylifera* L. leaves were collected in the month of December from Anjar city of Kachchh region. They were washed with distilled water, dried under shade, powdered and further adapted in the experiment. For the preparation of extracts, 10 gm of male and female *Phoenix dactylifera* L. leaves were macerated with 100 ml ethyl acetate for 24 hours with occasional stirring. The resultant extract was filtered and utilized for the experiment.

GC-MS analysis of male and female *Phoenix dactylifera* L. extracts: GC-MS analysis was carried out using Shimadzu GC-MS QP 2010 using helium as carrier gas with a constant flow rate of 1.50 ml/min. A sample volume of 2 μL was injected into the column at the pressure 88 kPa. The mass spectrum of each component was set down between the mass range m/z 50 to m/z 750. The name, molecular weight and molecular structure of each detected compound were accomplished by comparing the mass spectra of unknown compounds with mass spectra of standard compounds found in the database of NIST 11, NIST 11s and Wiley library.

Quantum mechanical analysis of phytoconstituents of Male & Female *Phoenix dactylifera* L. extracts

E_{HOMO}, E_{LUMO} values of identified constituents by GC-MS were obtained using pit quantum repository portal [20].

Results and Discussion

Table 2: Retention time, relative percentage and name of phytoconstituents identified using NIST and WILEY library from Gas Chromatogram in male date palm ethyl acetate leaves extract

Sr. No.	Retention time (min)	Relative percentage	Compound name
A1	17.80	6.67	Neophytadiene
A2	18.96	34.42	n-hexadecanoic acid
A3	20.38	8.26	Phytol
A4	20.50	7.71	cis-7-Dodecen-1-yl acetate
A5	20.55	18.57	9,12,15-Octadecatrienoic acid
A6	20.80	2.45	Octadecanoic acid
A7	21.59	1.62	Paramethaqualone
A8	29.51	5.10	Hexacosane

Table 3: Retention time, relative percentage and name of phytoconstituents identified using NIST and WILEY library from Gas Chromatogram in female date palm ethyl acetate leaves extract

Sr. No.	Retention time (min)	Relative percentage	Compound name
B1	17.80	5.50	Neophytadiene
B2	18.97	40.05	n-hexadecanoic acid
B3	20.38	4.74	phytol
B4	20.51	8.83	8-Dodecen-1-ol, acetate
B5	20.58	5.16	octadec-9-enoic acid
B6	20.80	2.61	Octadecanoic acid
B7	24.82	2.11	Beta – sitosterol
B8	25.28	5.17	Alpha-amyrin
B9	26.23	9.18	Lupeol
B10	29.500	7.17	Hexacosane

Quantum mechanical parameters of phytoconstituents of ethyl acetate extracts of male and female *Phoenix dactylifera* L. leaves were calculated using the following equation [22]:

$$E = E_{HOMO} - E_{LUMO} \text{----}1$$

$$A = -E_{LUMO} \text{ ----}2$$

$$I = -E_{HOMO} \text{ -----}3$$

$X = \frac{I+A}{2}$ ----4

$\eta = \frac{I-A}{2}$ ----5

$\sigma = \frac{1}{\eta}$ ----6

$\omega = \frac{X^2}{2\eta}$ -----7

$E_{(back\ donation} = \frac{-\eta}{4}$ ----8

Here E= band gap (eV), E_{HOMO} and E_{LUMO} are the energies of HOMO and LUMO (eV) respectively, A = electron affinity, I = ionization potential, X= electronegativity, η = global hardness, σ = global softness, ω = electrophilicity and $E_{(back\ donation)}$ = back donation potential [22].

Table 4: Quantum mechanical parameters of phytochemicals of male *Phoenix dactylifera* L. extract

	E HOMO (eV)	E LUMO(eV)	Electron affinity (A)	Ionization potential (I)	Electronegativity χ	Energy gap (E)	Global Hardness (n)	Global softness (σ	Electrophilicity (w)	E (back donation)
A1	-9.85	3.82	-3.82	9.85	3.015	13.670	6.835	0.146	0.665	1.709
A2	-8.95	-0.68	0.68	8.95	4.815	8.270	4.135	0.242	2.803	1.034
A3	-9.32	1.22	-1.22	9.32	4.050	10.540	5.270	0.190	1.556	1.318
A4	-9.55	0.88	-0.88	9.55	4.335	10.430	5.215	0.192	1.802	1.304
A5	-9.5	0.94	-0.94	9.5	4.280	10.440	5.220	0.192	1.755	1.305
A6	-10.81	3.98	-3.98	10.81	3.415	14.790	7.395	0.135	0.789	1.849
A7	-9.02	-0.61	0.61	9.02	4.815	8.410	4.205	0.238	2.757	1.051
A8	-10.56	3.78	-3.78	10.56	3.390	14.340	7.170	0.139	0.801	1.793

Table 5: Quantum mechanical parameters of phytochemicals of female *Phoenix dactylifera* L. extract

	E HOMO (eV)	E LUMO(eV)	Electron affinity (A)	Ionization potential (I)	Electronegativity χ	Energy gap (E)	Global Hardness (n)	Global softness (σ	Electrophilicity (w)	E(back donation)
B1	-9.85	3.82	-3.82	9.85	3.015	13.670	6.835	0.146	0.665	1.709
B2	-8.95	-0.68	0.68	8.95	4.815	8.270	4.135	0.242	2.803	1.034
B3	-9.32	1.22	-1.22	9.32	4.050	10.540	5.270	0.190	1.556	1.318
B4	-9.64	4.14	-4.14	9.64	2.750	13.780	6.890	0.145	0.549	1.723
B5	-9.62	0.9	-0.9	9.62	4.360	10.520	5.260	0.190	1.807	1.315
B6	-10.81	3.98	-3.98	10.81	3.415	14.790	7.395	0.135	0.789	1.849
B7	-9.24	1.26	-1.26	9.24	3.990	10.500	5.250	0.190	1.516	1.313
B8	-8.95	1.45	-1.45	8.95	3.750	10.400	5.200	0.192	1.352	1.300
B9	-9.53	1.28	-1.28	9.53	4.125	10.810	5.405	0.185	1.574	1.351
B10	-10.56	3.78	-3.78	10.56	3.390	14.340	7.170	0.139	0.801	1.793

From above Table 2, we see that male *Phoenix dactylifera* L hexane extract contains different phytochemicals like neophytadiene, n-hexadecanoic acid, cis-7-Dodecen-1-yl acetate, 9, 12, 15-Octadecatrienoic acid, Octadecanoic acid, phytol, Paramethaqualone and Hexacosane. Similarly, female *Phoenix dactylifera* L. hexane extract is enriched with neophytadiene, n-hexadecanoic acid, phytol, 8-Dodecen-1-ol, acetate, octadec-9-enoic acid, Octadecanoic acid, lupeol, alpha amyrin, beta-sitosterol and Hexacosane. In this quantum mechanical parameters such as band gap E (eV), E_{HOMO} and E_{LUMO} are the energies of HOMO and LUMO (eV) respectively, electron affinity A, ionization potential I, electronegativity X, global hardness η, global softness σ, electrophilicity ω and back donation potential $E_{(back\ donation)}$ are evaluated. The energy level of the HOMO orbital signifies the tendency of donating an electron to a low-lying metal orbital. So, the higher energy of the HOMO orbital enhances the tendency of an inhibitor molecule to donate electrons and higher the inhibitor potential of the molecule. For male date palm leaves extract, the order for HOMO energy could be shown as A2>A7>A3>A5>A4>A1>A8>A6. Similarly, for the female date leaves extract the order of HOMO orbital could be shown as B2>B8>B7>B3>B9>B5>B4>B1>B10>B6. The energy level of LUMO accounts for the tendency of a molecule to accept the electrons. Hence lower the energy value of LUMO, the higher is the inhibitor efficiency of a molecule to prevent the corrosion of metal. For female date palm extract, the increasing order of LUMO energy levels can be shown as B2<B5<B3<B7<B9<B8<B10<B1<B6<B4. Similarly for the male date palm extract, the increasing energy level of LUMO energy levels could be shown as A2<A7<A4<A5<A3<A8<A1<A6.

Compounds with the lowest value of band gap are improved corrosion inhibitors. For the male date palm leaves extract, the order of components with increasing order of band gap can be shown as A2<A7<A4<A5<A3<A1<A8<A6. For the female date palm leaf extract, the order of components with increasing order of band gap can be shown as B2<B8<B7<B5<B3<B9<B1<B4<B10<B6. The compounds with low global hardness (n) and high global softness (σ) exhibit a higher tendency to donate electrons to the metal surface and hence form the protective layer on the metal surface thereby reducing corrosion. For male date palm leaf extract, increasing order of global hardness can be shown as A2<A7<A4<A5<A3<A1<A8<A6. For female date palm extract, increasing order of global hardness can be shown as B2<B8<B7<B5<B3<B9<B1<B4<B10<B6. The values of global softness follow the reverse trend. Compounds with lower values of electronegativity are known to exhibit enhanced anti-corrosive traits. The increasing order of compounds of male date palm extracts in terms of electronegativity can be shown as A1<A8<A6<A3<A5<A4<A2<A7. The increasing order of compounds of female date palm extracts in terms of electronegativity can be shown as B4<B1<B10<B6<B8<B7<B3<B9<B5<B2. The ionization potential I and electron affinity A signify the electron donating and electron accepting tendency of the molecules. The higher the value of ionization potential lower is electron electron-donating tendency of an inhibitor molecule. Compound A2 and A6 among male date palm leaf extract

possess the lowest and highest values of ionization potential respectively. Considering compounds A2, A7, A4 and A5 of male date palm leaves extract the trend of ionization potential can be shown as A2<A7<A5<A4. For female date palm extract, compounds B2 and B6 are the compounds with the lowest and highest values of ionization potential respectively. Considering the compounds B2, B7, B8 and B5, the trend of ionization potential can be shown as B2<B8<B7<B5. Higher the value of electron affinity, higher is the tendency of a molecule to accept electrons. Amongst male and female date palm leaves extracts compounds A2 and B2 possess the highest electron affinity. Electrophilicity ω accounts for the stabilization of inhibitor molecules on the surface of the metal. Lower the values of electrophilicity enhanced are the electron donating potential and stabilization of the inhibitor molecules on the surface of metals. Considering compounds A2, A7, A4 and A5 of male date palm leaf extract, the trend of electrophilicity can be shown as A5<A4<A7<A2. For the female date palm extract, considering the compounds B2, B5, B7 and B8 the trend of electrophilicity can be shown as B8<B7<B5<B2. Corrosion inhibition properties of molecules are enhanced with back donation which is the tendency of a molecule to accept electrons from the d-orbital of metal. The trend of back donation among compounds A2, A7, A4 and A5 of male date palm extract can be shown as A5>A4>A7>A2. The trend of back donation among compounds B2, B5, B7 and B8 of female date palm extract B5>B7>B8>B2. The electronegativity of all the above-mentioned compounds of both male and female extracts is lower than that for metals signifying their ability to transfer electrons to the metal surface [20-23].

Conclusion

In the present study, a theoretical evaluation of phytoconstituents of male and female date palm extracts for the potential to prevent corrosion was carried. Different quantum mechanical parameters such as E_{HOMO}, E_{LUMO}, ionization potential, electron affinity, band gap, electrophilicity, electron back donation and electronegativity were evaluated. Based on the findings it can be concluded that a compound with enhanced corrosion inhibition properties is that which exhibits a higher value of HOMO, global softness, back donation and lower values of LUMO, electrophilicity, global hardness and ionization potential. The corrosion inhibition property of male date palm leaf extract could be attributed to the synergistic action of n-hexadecanoic acid, cis-7-Dodecen-1-yl acetate, 9, 12, 15-Octadecatrienoic acid and Paramethaqualone. The potential of female date palm extract to prevent corrosion could be attributed to the synergistic action of n-hexadecanoic acid, octadec-9-enoic acid, Beta-sitosterol and Alpha-amyrin. However practical evaluation is further required to evaluate their mechanism of action.

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