Jordanian Journal of Engineering and Chemical Industries

Print ISSN: 2616 - 9584 Online ISSN: 2617 - 720X

Phytoconstituents of Methanolic Extract of Fenugreek Seeds as a Green Corrosion Inhibitor of Metals (Fe, Al and Cu)

Al-Mazaideh Ghassab[*)]

Department of Chemistry and Chemical Technology, Faculty of Science, Tafila Technical University, P.O.Box 179, Tafila, 66110, Jordan.

Abstract

DFT calculations were carried out on significant *Fenugreek* seed compounds (1-Methylpyridinium-3-carboxylate MPC, Apigenin-8-C-glucose ACG, and 2-Isobutyl-3-methoxypyrazine IBMP) as a green source of ecologically friendly Fe, Al, and Cu metal corrosion inhibitors. Complete geometry optimizations were performed by DFT-B3LYP/6-31G* to determine any relationship between the chemical structure and corrosion inhibition, mostly on metals' surfaces. Global computational parameters of the inhibitors and thermodynamic Gibbs process of adsorption of metals were calculated and used to evaluate each corrosion inhibitor's performance. Our findings showed that MPC has the maximum anti-corrosion efficiency across all molecules with a physical adsorption mechanism. It exhibited significant inhibition efficiency with Cu when compared with Fe and Al, based on the highest electrophilicity index (ω) values compared to other inhibitors and its impact on metals in the following manner: Cu>Fe>Al. In regards, the range of inhibitors increased by the following order: IBMP>ACG>MPC. Remarkable corrosion inhibition of MPC is demonstrated by its unique high electrophilicity, softness (σ), and lowest ΔE_{gap} on the metal surface. These outcomes are close to the experimental work.

Paper type: Research paper

Keywords: MPC, DFT, green inhibitors, *Fenugreek* seed, metals.

Citation: Al-Mazaideh G." Phytoconstituents of Methanolic Extract of *Fenugreek* seeds as a green corrosion inhibitor of metals (Fe, Al and Cu)" *Jordanian Journal of Engineering and Chemical Industries*, Vol. **4**, No.1, pp:24-30 (2021).

Introduction

Metals are integrated into a wide range of industrial products, from steel and iron used in construction materials and car parts to aluminum used in containers to titanium used in electrical components. The choice of such metals is linked to their longevity, strength, temperature resistance, *etc*. Examples of certain metals; copper, iron, and aluminum, having their particular characteristics, such as copper, which has excellent corrosion resistance, high thermal conductivity. These metals can be prone to corrosion depending on the usage environment, including oxygen and certain violent anions like Cl^- and SO_4^{-2} (Amin and Khaled, 2010). This corrosion has a detrimental impact on the efficiency of the structures that have been designed on the basis of these metals. Density functional theory (DFT) has demonstrated an excellent method in modern physical chemistry due to its capacity to provide specific electron correlation results at substantially reduced computational costs (Hohenberg and Kohn, 1964). DFT has offered an excellent foundation for designing new standards for rationalizing the prediction, interpretation, and interpretation of many aspects of organic compounds (Wang *et al*., (1999); Udhayakala, (2014)). Sulphathiazole (STZ) has been shown to serve as a potent inhibitor of corrosion of mild steel in 0.5M HCl, and quantum chemistry calculations indicate that STZ adsorbed mostly as a molecular structure on the metal surface, using nitrogen, oxygen and also some carbon atoms as its active sites. Analysis has been conducted by Obot *et al*. (Obot *et al*., 2012). The group used gravimetric and quantum chemical approaches to test the inhibition performance of STZ onto mild steel in HCl at 303–333K. Many corrosion inhibitors such as benzil (4-phenylthIosemicarcazone), Benzoin (BN), benzil (BL), and benzoin (4-phenylthiosemicarbazone) (BN4PTSC) are used as corrosion inhibitors in the acidic medium of mild steel.

[*] Corresponding author: E-mail: gmazideh@ttu.edu.jo ORCID: https://orcid.org/0000-0003-4494-4284

Received on January 4, 2021; Accepted on March 16, 2021.

Jordanian Journal of Engineering and Chemical Industries (JJECI), Vol.4, No.1, 2021, pp. 24-33.

Kayadibi *et al*., used the DFT equations to analyze such corrosion inhibitors' mechanism and effectiveness (Kayadibi *et al.*, 2015). The DFT model has emerged as an effective method for researching MPC, ACG, and IBMP compounds as corrosion inhibitors of Cu, Fe, and Al metals. *Fenugreek* (Trigonella *Fenugreek*-graecum) is one such medicinal plant that has rich phytoconstituents substances like alkaloids, steroids, saponins, flavonoids, terpenoids, tannins, and anthocyanin (Yadav *et al*., (2011)). These components are natural and act as a pathogenic attack, single therapeutic agents, and protective agents external effect or combined compounds in drug design (Thomas *et al*., (2006)). The seeds of *Fenugreek* were found to be effective against Gram-negative bacteria like *Escherichia coli* and *Salmonella typhi* and Gram-positive bacteria such as *Staphylococcus aureus* (Al-Mazaideh *et al*., (2020); Aldal'in *et al*., (2020)). The behavior of the aqueous solution of *Fenugreek* seeds extract has been studied experimentally as anti-corrosion activity on Aluminum (Al) metal in acidic media (1.0M HCl solution) using electrochemical techniques. The extract showed promising results in reducing the corrosion rate of Al due to the chemical composing of phytochemical constituents presence as Vitexin and Trigonelline. Three main chemical constituents of *Fenugreek* seeds extract were determined by GC-MS analysis in methanolic extract (**Figure 1**) (Ladha *et al*., (2015); Karahacane *et al*., (2017)).

This study aims to find the systematic method for analyzing the potential *Fenugreek* seed's main compounds (1-Methylpyridinium-3-carboxylate (MPC), Apigenin-8-C-glucose (ACG), and 2-Isobutyl-3-methoxypyrazine (IBMP)) to work as an inhibitor on the metals' surface interaction in the gas phase using (Density Function Theory-Becke3-parameter Lee-Yang-Parr (DFT-B3LYP)). Quantum chemical parameters obtained from this calculation and calculated Gibbs function for adsorption (ΔG_{ads}) of the potential inhibitors on Fe, Al, and Cu atoms will be used to investigate the effect of the studied compounds as green corrosion inhibitors for three metals. Achieve comparison of theoretical results with experimental data that requires developing a common strategy in constructing the inhibitor metal complex models.

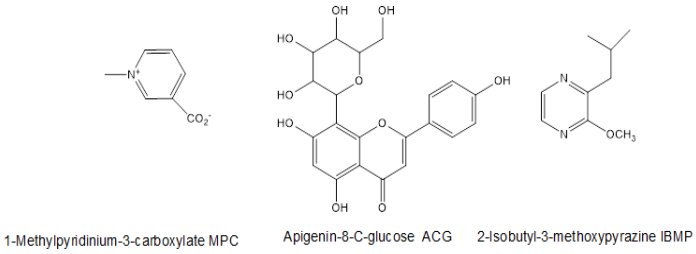

Fig.1 Main chemical constituents of *Fenugreek* seeds methanolic extract.

1 Materials and Methods

Three inhibitors (MPC, ACG, and IBMP) were used to investigate their role as potential corrosion inhibitors for Fe, Al, and Cu atoms in the gas phase at 298.15 K. DFT calculations were used in this work using B3LYP functional and 6-31G*(d,p) as basis set by Gaussian 09 (G09) software (Frisch *et al*., (2009)). All the inhibitors were optimized by DFT-B3LYP calculations. All the computational works were done under no restrictions. The results obtained after optimizing the geometrical structures include quantum parameters of inhibitors and the thermodynamic role of adsorption of the metal ΔG_{ads}. The quantum parameters of the final configuration (**Figure 2**) of the possible inhibitors after a complete optimization and estimation the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of inhibitors in the gas phase are E_{HOMO}, E_{LUMO}, ΔE_{gap}, η, σ, X, ΔN and ω (Itawi *et al*., (2019)). The author has done the effects of such calculated parameters on *Fenugreek* seeds' main compounds to associate the experimental data very well with the results (Ladha *et al*., (2015); Karahacane *et al*., (2017)).

Fig. 2 The final configuration of the potential inhibitors after optimization (dark blue (N), gray (C), red (O), white (H)).

2 Results and Discussion

After a geometric optimization of all potential structure inhibitors using the Kohn-Sham method at the DFT level, all quantum chemical parameters have been achieved. **Table 1** displays *Fenugreek* extract compounds under investigation as MPC, ACG, and IBMP after optimization with their orbitals HOMO and LUMO.

The FMO (Frontier Molecular Orbital theory) of the inhibitors showed the molecule's adsorbing capacity over the metal surface (Gece *et al*., (2009)). The E_{HOMO} indicates a molecule's ability to donate electrons to the appropriate inhibitor acceptor with unoccupied metal d-orbitals (**Table 1**). Conversely, the E_{LUMO} indicates its ability to accept electrons. Therefore, the lower E_{LUMO} value indicates that the molecules have a more remarkable ability to accept electrons, leading to a better inhibitor efficiency (Li *et al*., (2009)). Also, by increasing HOMO and decreasing LUMO energy level, the inhibitor's binding capacity to the metal surface increases. To determine the type of interaction, the values for E_{HOMO} and E_{LUMO} for Fe, Al and Cu were compared to those calculated for MPC, ACG, and IBMP. Energy gaps (ΔE_{gap}) is equal to the differences between E_{HUMO} and E_{LOMO} (E_{LUMO}-E_{HOMO}) for the interplay of metals with inhibitors in given in **Table 2**.

Table 1 Calculated E_{HOMO} and E_{LUMO} of the investigated compounds.

Inhibitor	E_{HOMO} (eV)	E_{LUMO} (eV)	ΔE (eV)	Dipole moment
MPC	-5.387	-4.071	1.316	15.00
ACG	-3.396	1.050	4.446	4.90
IBMP	-8.934	-1.460	7.474	1.99

Table 2 The calculated E_{LUMO}-E_{HOMO} gap interaction of metals with the inhibitors.

Inhibitor	Fe*		Al*		Cu*	
	$E_{LUMO:inhib}$-$E_{HOMO:Fe}$	$E_{LUMO:Fe}$–$E_{HOMO:inhib}$	$E_{LUMO,\ inhib}$ - $E_{HOMO:Al}$	$E_{LUMO:Al}$–$E_{HOMO:inhib}$	$E_{LUMO:inhib}$-$E_{HOMO:Cu}$	$E_{LUMO:Cu}$ –$E_{HOMO:\ inhib}$
MPC	3.831	5.236	1.914	5.820	3.655	4.152
ACG	8.952	3.396	7.035	3.829	8.776	2.161
IBMP	6.442	8.934	4.525	9.367	6.266	7.699

**Fe/E_{HOMO}=-7.902eV, Fe/E_{LUMO}= -0.151 eV; Al/E_{HOMO}=-5.985eV, Al/E_{LUMO}=0.433eV; Cu/E_{HOMO}=-7.726 eV, Cu/E_{LUMO}=-1.235eV (Lide, (2007))*

Such computational quantum simulations with an inhibitor design may be a successful approach to estimate the inhibitor's effectiveness, regardless of the experimental work results (Karahacane *et al*., (2017)). Metals will then act as a Lewis acid, whereas the inhibitor MPC and IBMP might serve as a Lewis base. Therefore, MPC and IBMP use HOMO to activate the reaction of metals with LUMO. The $E_{LUMO,Fe,Al,Cu}$ minus $E_{HOMO,ACG}$ gap quantities, and the interaction have a certain amount of ionic character, roughly falling between 1.9 to 9eV. It is only possible to predict a powerful covalent bond if the $E_{LUMO,ACG}$-$E_{HOMO,Fe,Al,Cu}$ difference is approximately zero (Lide, (2007); Khalil *et al*., (2008)). ACG functions as a cathodic inhibitor for this case. ACG will serve as Lewis acid, while Lewis will be based on metals. Metals use HOMO to initiate the response to HOMO of ACG. Due to the $E_{LUMO,\ MPC,IBMP}$-$E_{HOMO,Fe,Al,Cu}$ gap values, the association has a certain degree of ionic character, roughly falling between 2 to 9eV. MPC and IBMP serve as anodic inhibitors in this situation. The primary responsibility for the chemical reactivity is the interaction between the HOMO and the LUMO levels based on the FMO. The energy gap at ΔE_{gap} is an important parameter and shows the inhibitor's responsiveness to adsorption on the metallic surface. Furthermore, the reduction of ΔE_{gap} is increased. This means that the inhibitors' excitability increases and the potency of the inhibitor are improved (Al-Mazaideh *et al*., (2018)). The study indicates that ACG sees **Figure 3**, which shows the best potential to coordinate metal vacancy d-orbital links by providing and accepting electrons. In the meantime, other universal reactivity parameters have been used to research the efficacy of inhibitors (Arslan *et al*., (2009)). **Table 3** shows the global hardness (η), electronegativity (X), global softness (σ), a fraction of electron transferred (ΔN), and electrophilicity index (ω) of the inhibitors.

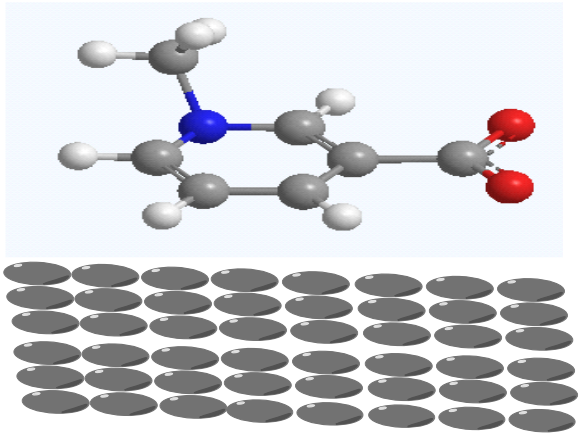

Fig. 3 Adsorption of ACG on the metal's surface (ACG–Metal complex).

In Hard-Soft-Acid-Base (HSAB) term, the inhibitors' bonding tendencies towards the metal atom can be used. This term tells that hard acid favors the coordination of bases with hard characteristics, and soft acids favor coordinating bases with soft characteristics. Therefore, metal atoms are classified as weak acids, even though soft molecules have a small E_{gap}, while complex molecules have a high E_{gap} (Al-Mazaideh *et al*., (2016)). The Δthree inhibitors' E_{gap} values (**Figure 4**) increase in the order: IBMP>ACG>MPC. Consequently, for metals, inhibitors that are classified as soft bases are the most effective (Li *et al*., (2009)). Accordingly, compared to many other inhibitors, MPC (Fig. 4), which has the least E_{gap} and the largest softness (σ), is expected to have good inhibitor effectiveness. This result is verified by calculating the inhibitor's softness (σ) and thus its reactivity. Compared with other inhibitors, Table 3 shows that MPC has the highest value. Furthermore, the lowest hardness (η) of MPC among other inhibitors is observed (Table 3). This tendency is the reversal of what has been achieved for softness (σ). As a result, the MPC also with highest softness values (σ) and the lowest hardness value (η) is the best inhibitor. Soft molecules are more reactive than complex molecules (Al-Mazaideh *et al*., (2016)). The fraction of transferred electrons (ΔN) is also calculated and shows that most of the electronic transition to the metals' surface arises from MPC molecules compared to other inhibitors. The electrophilicity index (ω) measures the ability of the inhibitor to accept electrons from metals. The MPC has the highest electrophilicity index (ω), especially on Cu metal compared to the other inhibitor due to low E_{LUMO}. Its metal effect in the order: Cu>Fe>Al. This is a good understanding of the published experiment (Ladha *et al*., (2015); Karahacane *et al*., (2017)). The computational results have shown that MPC adsorbs quickly and forms a thick protective cover to support the metals' surface. A reaction between nitrogen atoms and metal sites helps prevent oxide formation, and the MPC-Metal complex is produced. This observation, therefore, confirms that it is highly able to accept metal electrons. Metals, therefore, function as the base of Lewis and Lewis acids as all inhibitors (cathodic inhibitors). Inhibitor electrons are accepted by metal as a coordinated bond. Depending on the orientation of the inhibitor's optimized structure on the space, an inhibitor can also accept electrons from the metal into back-donating links. As donations and re-donation processes strengthen the adsorption of inhibitors to metal's surface, the inhibition efficiency will increase.

Table 3 Calculated global quantum chemical parameters of MPC, ACG and IBMP**.**

Parameter	MPC	ACG	IBMP
$I=-E_{HOMO}$	5.387	3.396	8.934
$A=-E_{LUMO}$	4.071	1.050	1.460
$\chi=(I+A)/2$	4.729	2.223	5.197
$\eta=(I-A)/2$	0.658	1.173	3.737
$\sigma=1/\eta$	1.519	0.852	0.267
$\Delta N=(\chi_{Fe}-\chi_{inh})/2(\eta_{Fe}+\eta_{inh})$	0.077	0.178	0.076
$\Delta N=(\chi_{Al}-\chi_{inh})/2(\eta_{Al}+\eta_{inh})$	0.221	0.124	0.152
$\Delta N=(\chi_{Cu}-\chi_{inh})/2(\eta_{Cu}+\eta_{inh})$	0.031	0.255	0.051
$\omega_{Fe}=\mu 2/2\eta$	12.316	6.909	2.168
$\omega_{Al}=\mu 2/2\eta$	7.824	4.389	1.377
$\omega_{Cu}=\mu 2/2\eta$	15.251	8.555	2.685

(X_{Fe}=4.026, η_{Fe}=3.875, X_{Al}=3.209, η_{Al}=2.776, X_{Cu}=4.480, η_{Cu}=3.250) ((Awad *et al*., (2010))

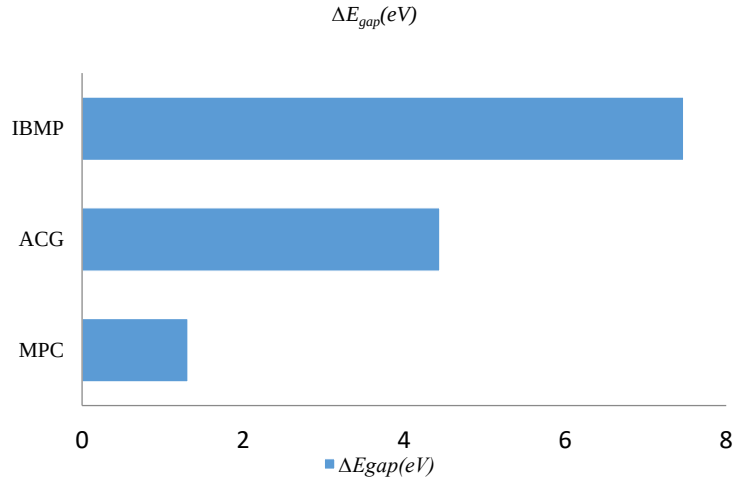

Fig. 4 ΔE_{gap} of all inhibitors.

Gibbs free adsorption energy (ΔG_{ads}) values of the inhibitors on the metal surface are calculated by using the following equations:

Cathodic inhibitor:

$$\Delta G_{ads}=\mu\ (\text{inhibitor})-\mu\ (\text{M}) \quad (1)$$

Anodic inhibitor:

$$\Delta G_{ads}=\mu\ (\text{M})-\mu\ (\text{inhibitor}) \quad (2)$$

As (μ) references to the chemical potential and it equals to the negative value of electronegativity (X) (Li *et al*., (2009); Al-Mazaideh *et al*., (2017)), the calculated results of ΔG_{ads} for all inhibitors are given in **Table 4**.

Table 4 Calculated ΔG_{ads} values in kJ/mol for the investigated inhibitors**.**

Inhibitors	Fe		Al		Cu	
	Anodic Inhibitors	Cathodic Inhibitors	Anodic Inhibitors	Cathodic Inhibitors	Anodic Inhibitors	Cathodic Inhibitors
MPC	67.829		146.66		24.024	
ACG		173.963		95.134		217.767
IBMP	112.984		191.813		69.180	

Adsorption of all of the Fe, Al, and Cu inhibitors demonstrates that all of them have positive values for ΔG_{ads} as shown in **Figure 5**. Most inhibitors act as anodic inhibitors of all metals except ACG. The amount of the value of ΔG_{ads} depends on whether adsorption is chemical or physical adsorption. In physical adsorption, the value of ΔG_{ads} is between 0 and -40kJ/mol, while the value of ΔG_{ads} in chemical adsorption is between -80 and -400kJ/mol (Toliwal *et al*., (2010)). The suggested mechanism with all inhibitors is spontaneous chemical adsorption because its value of ΔG_{ads} is between -80 and –40kJ/mol except for MPC with Cu, whereas ΔG_{ads} is within the range of 0 to -40 kJ/mol, and therefore it is physical adsorption. This is in line with the experimental work recently published (Ladha *et al*., (2015); Karahacane *et al*., (2017)).

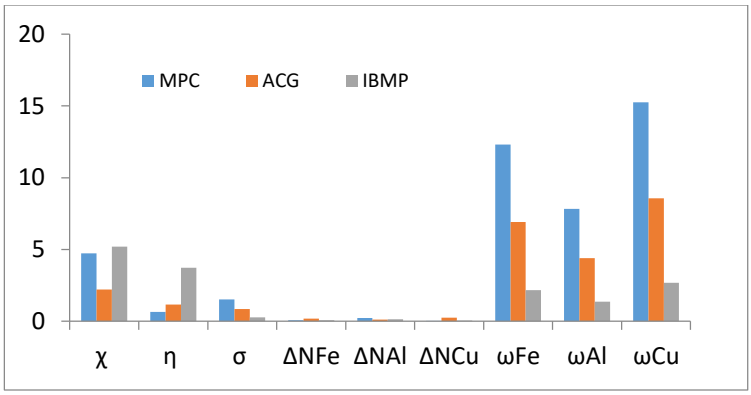

Fig. 5 Quantum chemical parameter values of all inhibitors**.**

Conclusions

Theoretical calculations provided a good view of the impact of *Fenugreek* seeds' main compounds (MPC, ACG, and IBMP) as green inhibitors, mainly on the corrosion rate of Fe, Al, and Cu metals. Our theoretical calculations exhibited the most excellent adsorption of the MPC inhibitor mostly on metal surfaces researched, mainly Cu metal, to make this one of the promising corrosion attacks. MPC has shown inhibition efficiency since it has the least E_{LUMO}, enabling a better linkage with Cu (more than Fe, Al), behaving as an anodic inhibitor. More than the maximum electrophilicity of the MPC compared to the other compounds, the electrophilicity of the molecule is measured. All inhibitors show non-spontaneous energy, and MPC has the maximum value of (ω), especially compared to other compounds, which recommend that inhibition of corrosive environment is mainly due to MPC. It can be concluded that the MPC is the best inhibitor due to its maximum value of softness (σ), the highest value of ΔN, and the highest value of (ω). This comes to fulfilling the experimental electrochemical findings of MPC nitrogen atoms' contact to surfaces forming MPC–Metal complex that prevented oxide formation.

Acknowledgments

The author would like to acknowledge the Tafila Technical University (TTU) for supporting my application for sabbatical leave at the University of Sains Malaysia (USM) during 2019-2020.

Nomenclature

ACG	=Apigenin-8-C-glucose	[-]
BL	=Benzil	[-]
BN	=Benzoin	[-]
BN4PTSC	=Benzoin (4-phenylthiosemicarbazone)	[-]
B3LYP	=Becke, 3-parameter, Lee-Yang-Parr	[-]
ΔE_{gap}	=Energy gap	[eV]
DFT	=Density Functional Theory	[-]
ΔN	=Fraction of electron transferred	[-]
E_{HOMO}	=Energy of highest occupied molecule orbital	[eV]

E_{LUMO}	=Energy of lowest un-occupied molecular orbital	[eV]
FMO	=Frontier Molecular Orbital theory	[-]
ΔG_{ads}	=Gibbs function for adsorption	[kJ/mol]
G09	=Gaussian 2009	[-]
HOMO	= The highest occupied molecular orbital	[-]
HSAB	=Hard-Soft-Acid-Base	[-]
IBMP	=2-Isobutyl-3-methoxypyrazine	[-]
LUMO	=The lowest unoccupied molecular orbital	[-]
MPC	=1-Methylpyridinium-3-carboxylate	[-]
STZ	=Sulphathiazole	[-]
σ	=Global softness	[-]
μ	= Dipole moment	[Debye, D]
η	=Global hardness	[-]
Ω	=Electrophililcity index	[-]
X	=Electronegativity	[-]

References

Aldal'in, H., Al-Mazaideh, G., AL-Nadaf, A., Al-Rimawi, F., Afaneh, A., Marashdeh, A., Abu-Lafi, S., Alakhras, F., Ayyal-Salman, H., and Jamhour, R. "Phytochemical Constituents of Securigera securidaca Seed Extract Using", *Trop. J. Nat. Prod. Res.*, **4**, 540-544 (2020).

Aldal'in, H.,Wedian, F., Al-Mazaideh, G., Ayyal Salman, H., AL-Rimawi, F. Alakhras, F.; Abu Lafi, S., and AL-Nadaf, A." Comparative Analysis of Phytochemical Composition of Ethanolic Extract of Jordanian Silvia officinalis", *Pak. J. Biol. Sci.*, **23**, 989-994 (2020).

Al-Mazaideh, G. "Carbohydrates as Green Corrosion Inhibitors of Copper: Ab initio Study", *Jordanian J. Chem.*, **12**, 189-200 (2017).

Al-Mazaideh, G., and Al-Quran, S." Effect of Methanolic Extract of Securigera securidaca as Antioxidant and Antibacterial Activities", *J. Pharm. Res. Inter.*, **3,** 10-17 (2020).

Al-Mazaideh, G., and Al-Quran, S. "Inhibitive action of Chamomile extract on the corrosion of Iron: Density Functional Theory", *Mor. J. Chem.*, **6**, 195-202 (2018).

Al-Mazaideh, G., Al-Zereini, W., Al-Mustafa, A., and Khalil, S., "The effect of nitro maleimides from a marine vibrio species compounds as a source of environment-tally friendly corrosion inhibitors for metals: A computational Study", *Adv. Environ. Biol.*, **10**, 159-168 (2016).

Arslan, T., Kandemirli, F., Benso, E., Love, I., and Alemu. H. "Quantum chemical studies on the corrosion inhibition of some sulphonamides on mild steel in acidic medium", *Corros. Sci*., **51**, 35-47 (2009).

Amin, M., and Khaled, K. "Copper corrosion inhibition in O^{-2} saturated H_2SO_4 solutions", *Corros. Sci.*, **52**, 1194-1204 (2010).

Awad, M., Mustafa, M., and Abo Elnga, M. "Computational simulation of the molecular structure of some triazoles as inhibitors for the corrosion of metal surface", *J. Mol. Struct.* (Theorem), **959**, 66-74 (2010).

Duran, B., Bereket, G., and Duran, M. "Electrochemical synthesis and characterization of poly (m-phenylenediamine) films on copper for corrosion protection", *Prog. Org. Coat.*, **73**, 162-168 (2012).

Frisch, M., Trucks, G., and Schlegel, H., *et al*., Gaussian, Inc., Wallingford CT, (2009).

Gece, G., and Bilgic, S. "Quantum chemical study of some cyclic nitrogen compounds as corrosion inhibitors of steel in NaCl media", *Corros. Sci.*, **51**, 1876-1878 (2009).

Hohenberg, P., and Kohn, W. "Inhomogeneous Electron Gas", *Phys. Rev*., **136**, B864-B871 (1964).

Itawi, H., Al-Mazaideh, G., Al-Rawajfeh, A., Al-Ma'abreh, and Marashdeh, A. "The effect of some green inhibitors on the corrosion rate of Cu, Fe and Al metals", *Inter. J. Corr. Scal. Inhib*., **8**, 199-211 (2019).

Karahacane, H, Khadraoui, A., Hachama K., Karim, S., Serdaroğlu, G., Aouniti, A., and Kaya, S. "An overview on plant extracts as potential green corrosion inhibitors for metals and alloys", *Arab. J. Chem. Env. Res.*, **4**, 46-62 (2017).

Kayadibi, F., Sagdinc, S., and Kara, Y. "Density Functional Theory Studies on the Corrosion Inhibition of Benzoin, Benzil, Benzoin-(4-Phenylthiosemicarbazone) and Benzil-(4-Phenylthiosemicarbazone) of Mild Steelin Hydrochloric Acid", *Prot. Met. Phys. Chem. Surf.*, **51**, 143-154 (2015).

Khalil, S., and Jarjis, H. "A theoretical study of fulvene radical ions", *Z. Naturforsch*, **46a**, 247-255 (1990).

Krishnaiah, D., Sarbatly, R., and Nithyanandam, R. "A review of the antioxidant potential of medicinal plant species", *Food Bioprod. Proc.*, **89**, 217-33 (2011).

Ladha, D., Wadhwani, P., Kumar, S., and Shah, N. "Evaluation of corrosion inhibitive properties of Trigonellafoenum-graecum for pure Aluminium in hydrochloric acid", *J. Mater. Environ. Sci.*, **6**, 1200-1209 (2015).

Lide, D., CRC Handboo k of Chemistry and Physics, 88th Edn., (2007-2008).

Li, X., Deng, S., Fu, H., and Li, T. "Adsorption and inhibition effect of 6-benzylaminopurine on cold rolled steel in 1.0 M HCl", *Electrochem. Acta*, **54**, 4089-4098 (2009).

Martins, S., Amorim, E., Peixoto, T., Saraiva, A., Pisciottano, M., Aguilar, C., Teixeira, J., and Mussatto, S. "Antibacterial activity of crude methanolic extract and fractionsobtained fromLarrea tridentataleaves", *Ind. Crop. Prod.*, **41**, 306-11 (2013).

Obot, I., Ebenso, E., Akpan, I., Gasem, Z., and Afolabi, A. "Thermodynamic and Density Functional Theory Investigation of Sulphathiazole as Green Corrosion Inhibitor at Mild Steel/Hydrochloric Acid Interface", *Int. J. Electrochem. Sci.*, **7**,1978-1996 (2012).

Sumayya, A., Srinivasan, S., and Amatullah, N. "Screening and Biochemical Quantification of Phytochemicals in Fenugreek (Trigonellafoenum-graecum)", *Res. J. Pharm. Biol. Chem. Sci*., **3**, 165-169 (2012).

Thomas, J., Basu, S., and Acharya, S. "Identification of Trigonella accessions which lack antimicrobial activity and are suitable for forage development", *Can. J. Plant Sci*., **86**, 727-732 (2006).

Toliwal, S., Kalpesh, J., and Pavagahh, I. "Inhibition of Corrosion of Mild Steel 1N HCl Solutions by Schiff Base Derived From Non Traditional Oils", *J. Appl. Chem. Res.*, **2**,24-36 (2010).

Udhayakala, P. "Density functional theory calculations on corrosion inhibitory action of five azlactoneson mild steel", *J. Chem. Pharm. Res.*, **6** , 117-127 (2014).

Wedian, F., Al-Qudah, M., and Al-Mazaideh, G. "Corrosion Inhibition of Copper by Capparis spinosa L. Extract in Strong Acidic Medium: Experimental and Density Functional Theory", *Int. J. Electrochem. Sci.,* **12**, 4664-4676 (2017).

Wang, D., Li, S., Ying, Y., Wang, M., Xiao H., and Chen, Z., "Theoretical and Experimental Studies of Structure and Inhibition Efficiency of Imidazoline Derivatives", *Corros. Sci.,* **41**, 1911-1919 (1999).

Yadav, R., Tiwari, R. Chowdhary, P., and Pradhan, C. "A pharmacognostical monograph of Trigonella foenum-graecum seeds", *Int. J. Pharm. Pharm. Sci*., **3**, 442-445 (2011).