International Research Journal of Pure & Applied Chemistry

23(4): 16-22, 2022; Article no.IRJPAC.83870
ISSN: 2231-3443, NLM ID: 101647669

Computational Study of Some Heterocyclic Compounds as Anti-corrosion Agents for Aluminum using DFT Method

Manal Ahmed Erteeb [a*], Farah Mahmoud [a] and Abdulsatar S. kareem [a]

[a] Department of Chemistry, Higher Institute of Sciences and Technology, Azizia, Libya.

Authors' contributions

This work was carried out in collaboration among all authors. All authors read and approved the final manuscript.

Article Information

DOI: 10.9734/IRJPAC/2022/v23i430469

Open Peer Review History:
This journal follows the Advanced Open Peer Review policy. Identity of the Reviewers, Editor(s) and additional Reviewers, peer review comments, different versions of the manuscript, comments of the editors, etc are available here: https://www.sdiarticle5.com/review-history/83870

Original Research Article

Received 01 January 2022
Accepted 03 March 2022
Published 03 August 2022

ABSTRACT

DFT Calculations were performed on Oxazole, Pyrazole, Imidazole, Isoxazole, Thiazole and Isothiazole as corrosion inhibitors for Al with full optimization of geometries in DFT-B3LYP/6-31 G*Level (d, P) to find a relation between the molecular structure and corrosion inhibition. The electronic properties such as the energy of the highest molecular orbital that is occupied (HOMO), the energy of lowest unoccupied orbital (LUMO), the energy gap (LUMO–HOMO), quantum chemical parameters such as hardness, softness, the fraction of the electron transferred, and the electrophilicity index. In order to know the relationship of molecular structure and corrosion inhibition on surface of the quantum chemical parameters, boundary orbital's isothiazole has been found the highest anti-corrosion efficiency as compared to other.

Keywords: Al; DFT; corrosion; heterocyclic compounds; inhibitor.

1. INTRODUCTION

Automobiles, aviation, domestic appliances, packaging, and electrical devices all employ aluminum as a material [1,2]. The quick development of oxide coatings on the surface of aluminum accounts for its resistance to corrosion in aqueous conditions. In the presence of corrosive acids, however, aluminum is easily corroded [1,2]. Because of its wide range of

**Corresponding author: E-mail: Manal.rateeb8503@gmail.com;*

applications, research into the corrosion behavior of aluminum in many harsh settings has remained popular. Hydrochloric acid is one of the most often used industrial chemicals, and it corrodes metals like aluminum. As a result, inhibitors are required to slow down the metal dissolving process [3] mong several techniques used in mitigating corrosion problems, the use of chemical inhibitors remains the most cost-effective and practical method [4].In the realm of corrosion chemistry, the development of aluminum corrosion inhibitors based on organic molecules is gaining popularity [5].The reason for this is that, despite the fact that inorganic substances such as phosphates, chromates, and dichromates are inorganic, inorganic substances such as phosphates, chromates, and dichromates are organic and arsenates have been proven to be effective as metal corrosion inhibitors, but their main disadvantage is their toxicity, which has led to harsh condemnation of their use [6]. Organic inhibitors have been demonstrated to be practical and helpful since they are effective, environmentally friendly, and relatively inexpensive [7,8] and are more effective than inorganic chemicals [9].

2. METHODOLOGY

Theoretical calculations of the quantum chemical parameters were carried out employing comprehensive geometry optimizations the standard Gaussian-09 software package39. Optimizations to the geometry were made using B3LYP functional at the 6-31G* (d,p) basis set and at the density functional theory (DFT) level.

3. RESULTS AND DISCUSSION

The inhibitor's efficacy could some heterocyclic compounds be determined from the quantum chemical parameters calculated from the optimized structure. These global parameters include the frontier Molecular Orbital's : E_{HOMO} (the molecular orbital with the most occupied molecular orbital)and E_{LUMO} (the lowest molecular orbital that isn't occupied ; the energy gap (ΔEgap) between E_{HOMO} and E_{LUMO}; the global hardness (η) of the inhibitor; the softness (σ); the fraction of the electron transferred (ΔN); the electrophililcity index (ω) is a measure of how electrophilic a substance is.

These global parameters include the frontier Molecular Orbital's on Al According to Koopman's theorem [10], the absolute electronegativity (χ), the absolute hardness (η), the softness (σ) and the electrophililcity index (ω) are given as follow [11]:

$$\omega = \frac{\mu^2}{2\eta}, \qquad (\ \mu = -\chi)$$

$$\chi = \frac{I+A}{2}\ , \qquad \chi = -\frac{E_{HOMO}+E_{LUMO}}{2}$$

$$\eta = \frac{I-A}{2}\ , \quad \eta = -\frac{E_{HOMO}-E_{LUMO}}{2}$$

$$\sigma = 1/\eta$$

Where the electron affinity (E) and the ionization potential (I) are calculated using the following relations according to the Molecular Orbital theory.

$$I = -E_{HOMO}\ , \quad A = -E_{LUMO}$$

$$\Delta E_{(gap)} = E_{LUMO} - E_{HOMO}$$

The absolute electronegativity (μ) is considered to be equal to the negative of the chemical potential (χ). Parr proposed the concept of an inhibitor's electrophilic power (ω) [12]. Herein, electrons flow from the less electronegative inhibitor (χ_{inh}) to higher electronegative Aluminum (χ_{Al}) until the chemical potentials become equal.The number of electrons transported from the inhibitor to the metallic surface (ΔN) was estimated using the values of χ and η as well. Follow [13]:

$$\Delta N = \frac{\chi_{Al} - \chi_{inh}}{2(\eta_{Al} + \eta_{inh})}$$

where χ_{Al} and χ_{inh} signify the absolute electronegativity of Al and the inhibitor, respectively, and Al and inh denote the absolute hardness of Al and the inhibitor. The electron transport is driven by the difference in electronegativity(χ_{Al} - χ_{inh}), whereas (η_{Al} + η_{inh}) acts as resistance [14] In this study, the theoretical values of χ_{Al} = 3.2093eV and η_{Al} =2.7764 eV were used to calculate the number of electrons transferred [15]. All calculations have been performed for the molecules in the gas phase.

The inhibitors' frontier Molecular Orbitals (FMO) demonstrate the molecule's potential to adsorb on metal surfaces [16]. E_{HOMO} refers to a molecule's ability to donate electrons to an acceptable acceptor level of inhibitor with vacant metal d-orbitals. Its ability to receive electrons is indicated by the letter E_{LUMO}. As a result, a lower E_{LUMO} value indicates that the molecule has a greater potential to receive electrons, resulting in improved inhibitor efficiency [17]. As a result, boosting the HOMO energy while decreasing the

LUMO energy increases the inhibitor's capacity to bind to the metal surface.

Chemical reactivity is a consequence of the in traction between the HOMO and LUMO levels of the reacting species, according to the frontier molecular orbital (FMO) theory [19,20]. E_{HOMO} is a quantum chemical parameter that refers to a molecule's ability to donate electrons. A high E_{LUMO} value is likely to suggest that the molecule has a low empty molecular orbital energy tendency [21]. E_{LUMO}, or the energy of the lowest unoccupied molecular orbital, reflects the molecule's ability to receive electrons [22]. As a result, the lower the value of E_{LUMO}, the more electrons the molecule accepts. As a result, as the HOMO and LUMO energy values grow, the inhibitor's ability to attach to the metal surface increases.

Aluminum acts as a Lewis base, whereas the inhibitors Isoxazole, Thiazole, and Isothizole act as Lewis acids, as shown in Table 2. As a result, Aluminum will use the HOMO orbital of the Isoxazole, Thiazole, and Isothizole to commence the reaction with the LUMO orbital of the Isoxazole, Thiazole, and Isothizole. Because the LUMOinh–HOMOAl gap values are between 4 and 5 eV, the interaction will have an ionic character. Only if the LUMOinh–HOMOAl gap is close to zero can a strong covalent bond be expected [23,24]. Oxazole, Pyrazole, and Imidazole inhibitors operate as a Lewis base, while aluminum acts as a Lewis acid.

Thus Isoxazole, Thazole, Isothizole act as a cathodic inhibitor while Oxazole, Pyrazole, Imidazole act as an anodic inhibitor Table 3 show the calculated global reactivity parameters which were used to study the effectiveness of the inhibitors. The electronegativity (X), global hardness (η), global softness (σ), proportion of electron transmitted (ΔN), and electrophilicity index (ω) of the molecules are among these metrics

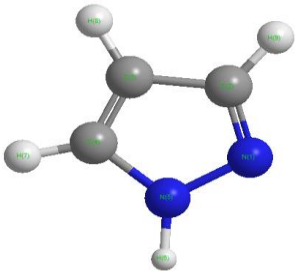
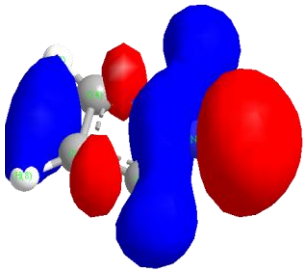
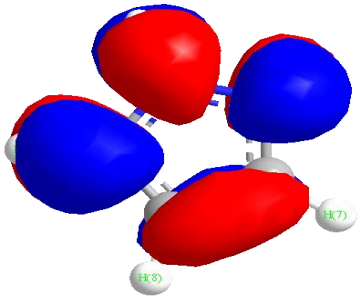
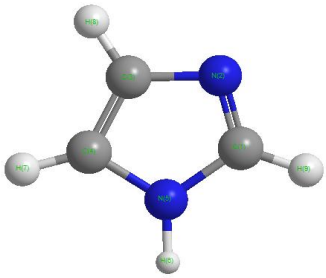
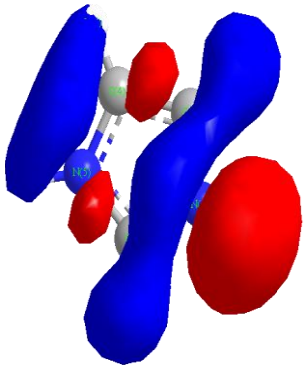
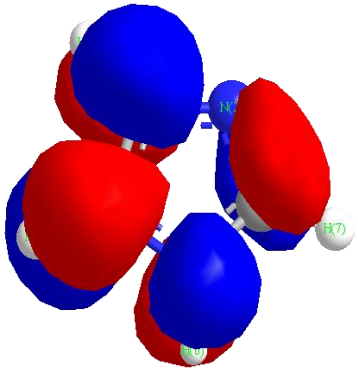
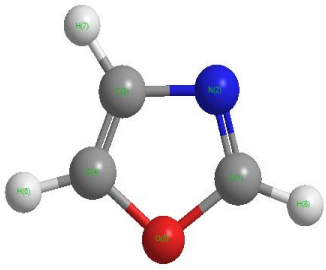
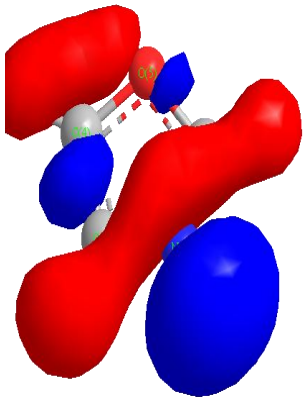
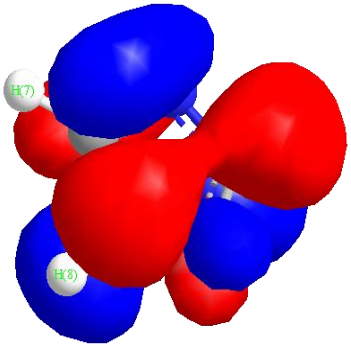
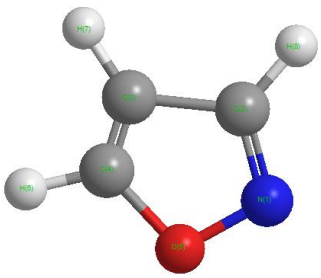
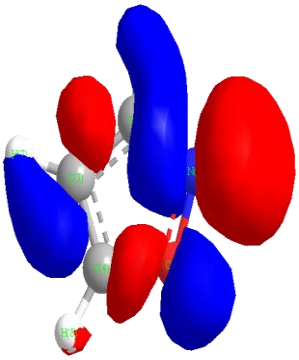
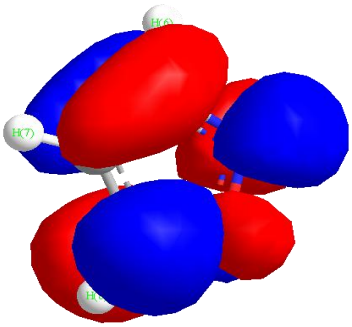
The values of ΔN represent the inhibition efficiency caused by the aluminum inhibitor's electron donating [25]. The capacity of these inhibitors to give electrons to the metal enhances their inhibition efficiency, and the bulk of the transferred electrons are connected with the best inhibitor, and (ω) indicates the inhibitor's ability to take aluminum electrons.

Table 1. The DFT approach was used to calculate the inhibitors' (HOMO-LUMO) energies [18]

Compounds	HOMO	LUMO
Al	-5.9857*	-0.4328*
Imidazole	-6.3598	0.6522
Pyrazole	-6.7286	0.3806
Oxazole	-7.2616	-0.4745
Isoxazole	-7.5438	-0.9140
Thiazole	-7.1346	-1.0492
Isothiazole	-7.2614	-1.2841

Table 2. The calculated HOMO-LUMO gap interaction of Al with the inhibitors

Inhibitors	$(LUMO)_{Inh}$- $(HOMO)_{Al}$ (eV)	$(LUMO)_{Al}$- $(HOMO)_{Inh}$ (eV)
Imidazole	6.6379	05.927
Pyrazole	6.3663	6.2958
Oxazole	5.5112	6.8288
Isoxazole	5.0717	07.111
Thiazole	4.9365	6.7018
Isothiazole	4.7016	6.8286

Inhibitor	Structure	HOMO	LUMO
Pyrazole			
Imidazole			
Oxazole			
Isoxazole			

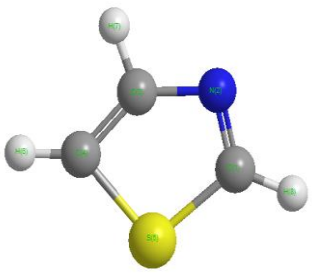
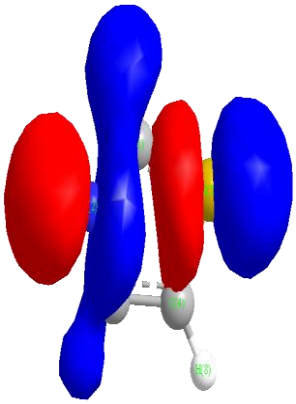
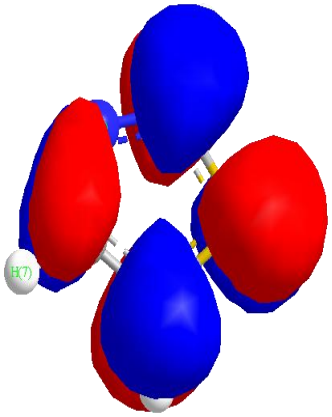
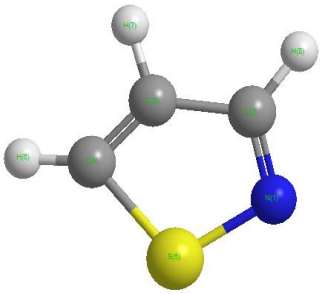
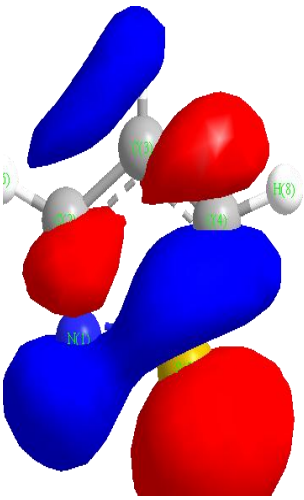
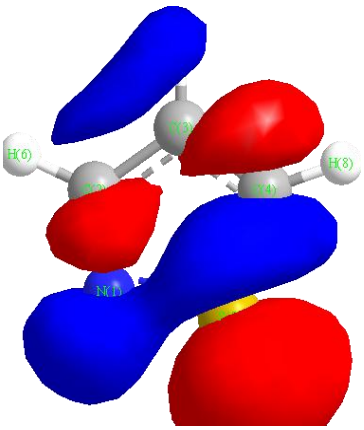
Inhibitor	Structure	HOMO	LUMO
Thiazole			
Isothiazole			

Fig. 1. HOMO & LUMO of the optimized fragments

Table 3. Quantum chemical properties of inhibitors were calculated

Quantum parameter	Imidazole	Pyrazole	Oxazole	Isoxazole	Thiazole	Isothiazole
E_{HOMO}	-6.3598	-6.7286	-7.2616	-7.5438	-7.1346	-7.2614
E_{LUMO}	0.6522	0.3806	-0.4745	-0.9140	-1.0492	-1.2841
ΔE(gap)	007.01	7.1091	6.7871	6.6298	6.05854	5.9773
I(eV)	6.3598	6.7286	7.2616	7.5438	7.1346	7.2614
A(eV)	-0.6522	-0.3806	0.4745	0.9140	1.0492	1.2841
X (eV)	2.8538	03.174	3.8680	4.2289	4.0919	4.2727
Ƞ(eV)	03.506	3.5546	3.3935	3.3149	3.0427	2.9886
σ	0.2852	0.2813	0.2946	0.3016	0.3286	0.3346
ΔN	0.0282	0.0027	0.0185	0.0837	0.0758	0.0922
ω	1.1614	1.4117	2.2044	2.6974	2.7514	3.0542

X_{Al}= 3.2093, η_{Al}= 2.7764

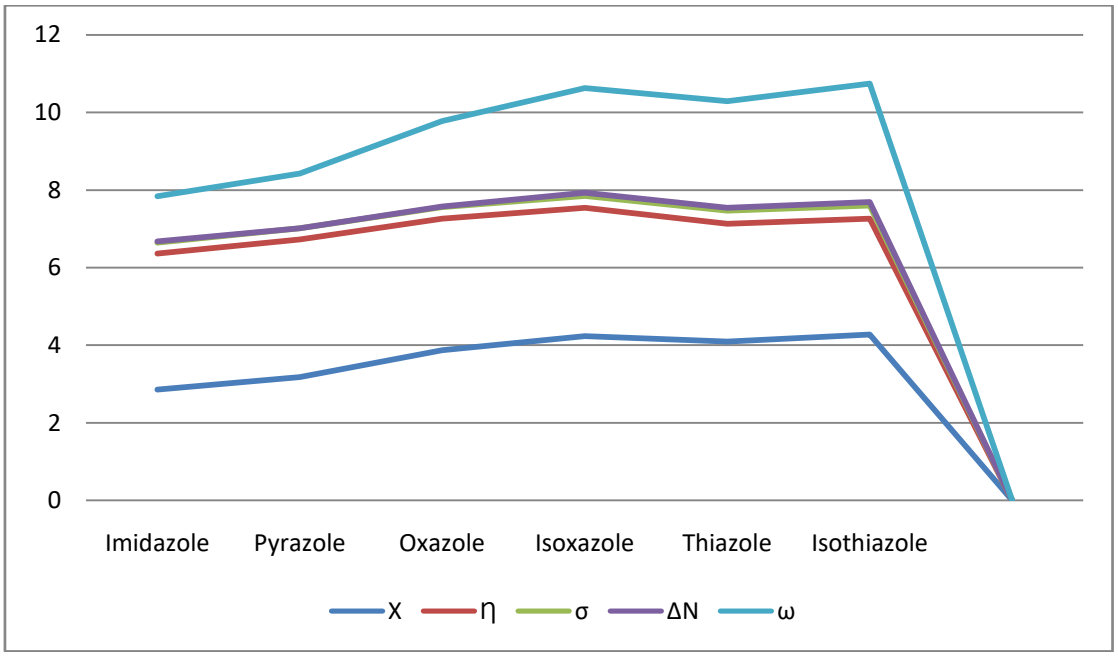


Fig. 2. Quantum parameter values of inhibitors

Soft molecules have small ΔEgap whereas hard molecules have large ΔEgap based on (Hard-Soft-Acid-Base) hypothesis (HSAB) [26,27]. The most effective inhibitor for the metals is classified as a soft base [28]. As a result, the Isothiazole with the shortest Egap and highest softness (σ) is predicted to have the best. Calculating the inhibitor's softness (σ) and thus its reactivity confirms this result. Table 3 shows that the isothiazole has the highest value compared to the others. In addition, it can be observed (Table 3) that the hardness (η) of the Isot Thiazole has the smallest value of all fragments. This tendency is the reverse of what has been obtained for the softness (σ). Consequently, the Isothiazole is the best inhibitor. The electrophilicity index (ω) indicates the ability of the inhibitor to accept electrons from Aluminum.

Compounds that can donate electrons to the metal surface's vacant orbitals to make coordinated covalent bonds, as well as absorb free electrons from the metal surface to establish bonds using their antibonding orbitals, are efficient corrosion inhibitors

4. CONCLUSIONS

Theoretical calculations gave a good picture of the compounds as aluminum corrosion inhibitors, and isothiazole showed greater inhibition efficiency compared to other inhibitors, as they were found to have higher values (ω) due to lower values of E_{LUMO}, which indicates their high acceptability. Electrons from aluminum.

The inhibition efficiency is increased due to the saturation and adsorption process on the aluminum surface, so the resulting inhibition efficiency order is

Oxazole > Pyrazole > Imidazole >> Isoxazole Thiazole> Isothiazo

COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES

1. Oguzie EE. Corrosion inhibition of aluminium in acidic and alkaline media by Sansevieria trifasciata extract. Corros. Sci. 2007;49:1527–1539.
2. Sherif EM, Park SM. Effects of 1,4-naphthoquinone on aluminum corrosion in 0.50 M sodium chloride solutions. Electrochim. Acta 2006;51:1313–1321.
3. Osório WR, Cheung N, Peixoto LC, Garcia, A. Corrosion Resistance and Mechanical Properties of an Al 9wt% Si Alloy Treated by Laser Surface Remelting. Int. J. Electrochem. Sci. 2009;4:820–831.
4. El-Shafei AA, Moussa MNH, El-Far AA. Inhibitory effect of amino acids on Al pitting

corrosion in 0.1 M NaCl. J. Appl. Electrochem. 1997;27:1075–1078.
5. Xhanari K, Finsgar M. Organic corrosion inhibitors for aluminium and its alloys in acid solutions: A review. RSC Adv. 2016;6:62833–62857.
6. El-Meligi AA. Corrosion Preventive Strategies as a Crucial Need for Decreasing Environmental Pollution and Saving Economics. Recent Pat. Corres. Sci. 2010;2:22–33.
7. Nnaji NJN, Ujam OT, Ibisi NE, Ani JU, Onuegbu TO, Olasunkanmi LO, Ebenso EE. Morpholine and piperazine based carboxamide derivatives as corrosion inhibitors of mild steel in HCl medium. J. Mol. Liq. 2017;230:652–661.
8. Umoren SA, Eduok UM. Application of carbohydrate polymers as corrosion inhibitors for metal substrates in different media: A review. Carbohydr. Polym. 2016;140:314–341.
9. Popoola LT, Grema AS, Latinwo GK, Gutti B, Balogun AS. Corrosion problems during oil and gas production and its mitigation. Int. J. Ind. Chem. 2013;4:35.
10. Dewar MJS, Thiel W. J. Am. Chem. Soc. 1977;99:4899-4907.
11. Pearson RG. Inorg. Chem. 1988;27: 734-740.
12. Parr RG, Szentpaly LV, Liu S, J. Am. Chem. Soc. 1999;121:1922-1924.
13. Lukovits I, Kalman IE, Zucchi EF, Corrosion F. 2001;57: 3-8.
14. Parr RG, Szentpaly LV, Liu SJ. Am. Chem. Soc. 1999;121:1922-1924.
15. Pearson RG, Inorg Chem.1988;27: 734-740.
16. Humpola PD, Odetti HS, Fertitta AE, Vicente JL, J. Chil. Chem. Soc. 2013;58:1541-1544.
17. Gece G, Bilgic S, Corros Sci. 2009;51:1876-1878.
18. Lide DR, CRC Handbook of Chemistry and Physics, 88th ed., 2007- 2008.
19. Lide DR, CRC Handbook of Chemistry and Physics, 88th ed., 2007- 2008.
20. Martinez S,Mater.Chem.Phys. 2002;77:97.
21. Musa AY, Kadhum AH, Rohoma AB, Mesmari H, J.Mol.Struct. 2001;969:233.
22. Gece G, Bilgic S, Cooros. Sci. 2009;51: 1876.
23. Klopman G, J. Am. Chem. Soc. 1968;90:233.
24. Arslan T, Kandemirli F, Ebenso EE, Love I, Alemu H, Corros. Sci., 2009;51:35.
25. Li S, Deng H, Fu T, Li. Electrochim. Acta, 2009;54:4089.
26. Al-Mazaideh GM, Ejlidi WB, Khalil SM, Inter. Res. J. Pure & Appl. Chem. 2016;12(4):1.
27. Al-Mazaideh GM, Al-Zereini WA, Al-Mustafa AH, Khalil SM. Adv. Envi. Biol., 2016;10(8):159.
28. Li X, Deng S, Fu H, Li T. Electrochem. Acta. 2009;54(16):4089.

Peer-review history:
The peer review history for this paper can be accessed here:
https://www.sdiarticle5.com/review-history/83870