The effect of some green inhibitors on the corrosion rate of Cu, Fe and Al metals

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Abstract

Inhibition of metal corrosion is a very important and challenging issue environmentally. The use of corrosion inhibitors is an effective method to reduce the corrosion rate of several metals. In this regard, researchers have used a wide range of corrosion inhibitors for several decades to minimize the damages arising in corrosive environments. Density functional theory (DFT) calculations with B3LYP/6-31G* (d,p) level have been performed on APDTC, CMI, HPMA, PASP and PESA as a green source of environmentally friendly corrosion inhibitors for Cu, Fe and Al metals. Global quantum parameters of inhibitors and thermodynamic Gibbs function (ΔG_{ads}) of adsorption of metals have been calculated and used to investigate the efficiency of each corrosion inhibitor. Our results showed that APDTC exhibits the highest anti-corrosion efficiency among all compounds with Cu, Fe and Al metals showing remarkable inhibition efficiency with Cu comparing with Fe and Al. APDTC exhibit the highest electrophilicity index (ω) values compared to other inhibitors and its effect on the metals in the order: Cu > Fe > Al. The distinguished corrosion inhibition of APDTC is explained by its unique high electrophilicity power and Gibbs free energy of adsorption value on metal surface (ΔG_{ads}). The HOMO and LUMO gap (ΔE_{gap}) of the inhibitors increases in polymers in the order: HPMA > CMI > PESA > PASP > APDTC. These results show excellent agreement with recent published work.

Keywords: DFT, metals, green inhibitors, APDTC.

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Introduction

Metals are incorporated in a wide variety of products of manufacturing, from steel and iron used in building materials and automobile parts, to aluminum used in packaging, to titanium used in electronic parts. Chosen of such metals related to their durability, strength,

resistance to weather, *etc.* and examples of such metals; copper, iron and aluminum that have their unique characteristics like copper which is good corrosion resistance, high electrical and thermal conductivity [1]. These characteristics of copper give it wide applications in production of wire, sheets and pipelines, in electronic industries, marine industries, power stations, heat exchangers and cooling towers [2]. Aluminum is a very light metal with a specific weight of 2.7 g/cm^3 , also it is physically, chemically and mechanically stable in addition to conduct electric current. Such metals may suffer corrosion based on the environment of use such as presence of oxygen and some aggressive anions (Cl^- and SO_4^{2-}) [3]. This corrosion has its negative effect on the performance of systems that constructed based on these metals leads finally to reduce the efficiency of the industrial tools resulting in huge economic losses [4]. According to widespread use of such metals in different industries, the issue of corrosion and corrosion protection of metals has attracted a lot of attention and many studies have been conducted to date on this issue and are still ongoing.

Inhibition of metal corrosion is very important and challenging issue. The use of corrosion inhibitors is an effective method to reduce the corrosion rate of several metals. In this regard, researchers have used wide range of corrosion inhibitors for several decades to minimize the damages arising in corrosive environments [5, 6]. Generally, inhibitors act to reduce the anodic or the cathodic reaction or both of them in the metal environment [7]. Corrosion inhibitors are classified into two main categories; inorganic and organic. Molybdates MoO_4^{2-} and tetra borates $\text{B}_4\text{O}_7^{2-}$ are examples of inorganic inhibitors that provide weak corrosion inhibition efficiency, while organic corrosion inhibitors and their derivatives are widely used due to their high corrosion inhibition efficiency [8]. The efficiency of corrosion inhibitors depends on their chemical composition, structure, electronic properties, nature of metal and environmental properties. The majority of known corrosion inhibitors are organic compounds containing electronegative functional groups and π -electrons in triple or conjugated double bonds [9] particularly, heterocyclic compounds containing nitrogen, sulfur or oxygen atoms [10]. The efficiency of the heterocyclic corrosion inhibitors rises in order of O, N then S due to their increasing tendency to form a coordinate bond [11]. Recent researches are mainly focused on using environmental friendly corrosion inhibitor of metals such as ammonium pyrrolidine dithiocarbamate (APDTC) [12, 13], carboxymethylinulin biopolymer (CMI), hydrolyzed polymaleicanhydride (HPMA), polyaspartic acid (PASP) [14,15] and polyepoxysuccinic acid (PESA) polymers.

Recently, most of researchers who concern corrosion inhibitors in their studies utilized quantum chemistry calculations in order to enhance the efficiency of the used corrosion inhibitors. Density functional theory (DFT) has proven to be an important tool in modern quantum chemistry because of its ability to include some effects of electron correlation at a greatly reduced computational cost [16]. In recent studies, DFT methods have been applied to corrosion inhibitor in order to analyze the characteristics of the

inhibitor/surface mechanism and to describe the structural nature of the inhibitor in corrosion process [17]. DFT also has provided a very useful framework for developing new criteria for rationalize predicting, and eventually understanding many aspects of chemical processes [18]. In 2012, I.B. Obot *et al.* studied the corrosion inhibition efficiency of sulphathiazole (STZ) on mild steel in 0.5 M HCl at 303–333 K using gravimetric and quantum chemical methods. They also used the density functional theory (DFT) at the BLYP/6-31G(d) basis set to correlate the structural and electronic properties such as E_{HOMO} , E_{LUMO} , energy gap, Mulliken charges, HOMO and LUMO orbitals with the inhibitive action of STZ. It's found that STZ acts as a good inhibitor for the corrosion of mild steel in 0.5 M HCl and the quantum chemical calculations (DFT) show that STZ adsorbed mainly as molecular species on the steel surface using nitrogen, oxygen and some carbons atoms as its active centers [19]. In 2013, B. Semire and A.O. Odunola proved the electronic structure and the efficiency of (2-phenylimidazo[1,2-*a*]pyridine (2PIP) and 2-(*m*-methoxyphenyl)imidazo[1,2-*a*]pyrimidine (2MPIP) as inhibitors of mild steel corrosion using DFT [20]. Saranya with his team prepared a corrosion inhibitor of (3*E*)-3-{[4-(phenylsulfonyl)]imino}-3,4-dihydroquinoxalin-2(1*H*)-one (PSDQO) which has inhibiting action on the corrosion of mild steel in sulfuric acid. As a result of this study, the inhibitor molecule PSDQO shows very high inhibition efficiency for mild steel in 1 M H_2SO_4 . Quantum chemical calculations (DFT) were employed to give further insight into the mechanism of inhibitive action of the synthesized inhibitor (PSDQO) were found to be in good agreement with the experimental results [11]. P. Udhayakala applied DFT calculations on a series of azalactone corrosion inhibitors. The results of his study proved that inhibition efficiency increases with an increase in E_{HOMO} and a decrease in energy gap (ΔE) for the studied azalactone corrosion inhibitor [18]. N. Wazzan and F. Mahgoub carried out computational calculations by means of DFT/B3LYP/6-31 + G(d,p) level of theory. These calculations involved the parameters of E_{HOMO} , E_{LUMO} , energy gap (ΔE_{LH^-}), dipole moment (μ), ionization energy (I), electron affinity (A), absolute electronegativity (χ), absolute hardness (η), absolute softness (σ), the fraction of electron transferred (ΔN), and the total energy (E_{tot}). The results showed success of DFT calculations in predicting the inhibition efficiency of corrosion inhibitor [9]. Benzoin (BN), benzil (BL), benzoin-(4-phenylthiosemicarbazone) (BN4PTSC) and benzil-(4-phenylthiosemicarbazone) (BL4PTSC) are corrosion inhibitors used for mild steel in acidic medium. F. Kayadib and his group performed density functional theory (DFT) calculations to investigate the mechanism and the efficiency of these corrosion inhibitors [21]. In the present work, DFT combined with global quantum parameters have been used to explain the mechanism of corrosion inhibition. These methods have proved to be very important and cost effective tools for studying the corrosion inhibition mechanism [22–27]. DFT model has emerged as an attractive tool to investigate the efficiency of APDTC, CMI, HPMA, PASP and PESA compounds (Figure 1) as corrosion inhibitors of Cu, Fe and Al metals.

The aim of this work is to predict the systematic way for the analysis of the inhibitor on the metals' surface interaction. The chemical reactivity of the inhibitor is a function of

interaction between highest occupied molecular orbital E_{HOMO} , the lowest unoccupied molecular orbital E_{LUMO} and other parameters such as energy gap ΔE_{gap} , global hardness η , softness σ , electronegativity X , the fraction of electron transferred ΔN and electrophilicity index ω . Furthermore, the theoretical calculations have been used to predict inhibitors activity and the efficiency of each compound as a corrosion inhibitor of the studied metals.

Figure 1. The chemical structure of the inhibitors: carboxymethylulinulin biopolymer (CMI), hydrolyzed polymaleicanhydride (HPMA), poly(aspartic acid) (PASP) and polyepoxysuccinic acid (PESA) and ammonium pyrrolidine dithiocarbamate (APDTC).

Computational Work

Different inhibitors (APDTC, CMI, HPMA, PASP and PESA) were used to study their effect as corrosion inhibitors for metals. DFT calculations were performed in this work using B3LYP functional with 6-31G* (d, p) basis set. DFT-B3LYP was used to optimize the molecules by using Gaussian 09 (G09) [28]. The quantum parameters together with thermodynamic function of adsorption ΔG_{ads} of the metal were calculated of the studied inhibitors. The geometry structures were optimized under no constraint. Figure 2 shows the final structure of the potential inhibitors after a fully optimization and calculated HOMO and LUMO of the inhibitors in gas phase. It has been proved that the experimental data can be correlated very well with the results of quantum chemical parameters such as E_{HOMO} , E_{LUMO} , ΔE_{gap} , η , σ , X , ΔN and ω [22].

Figure 2a. The optimized structure of the investigated inhibitors. The colors of the atoms are as follows: yellow (S), dark blue (N), light blue (C), green (O), gray (H).

Figure 2b. Calculated HOMO and LUMO of the inhibitors in gas phase.

Frontier Molecular Orbital theory (FMO) of the inhibitors showed the adsorption ability of the molecule over metal surface [29]. In one hand the, E_{HOMO} indicates capability of a molecule to donate electrons to the appropriate acceptor of inhibitor with unoccupied d -orbitals of metal (Table 1). On the other hand, the E_{LUMO} indicates its ability to accept electrons. Therefore, the lower E_{LUMO} value shows the more ability of the molecule to accept electrons and this leads to a better inhibitor efficiency [30]. Therefore, when increasing HOMO and decreasing LUMO energy levels the binding capability of the inhibitor to the metal surface increases.

Table 1. Calculated energies of HOMO and LUMO of inhibitors.

	E_{HOMO} , eV	E_{LUMO} , eV
Al	-5.985^a	0.4328^a
Fe	-7.902^a	-0.151^a
Cu	-7.726^a	-1.235^a
APDTC	-0.080	4.390
PESA	-7.810	-2.170
HPMA	-7.670	-0.890
PASP	5.480	-0.610
CMI	-6.720	-0.410

^a [31]

The values of E_{HOMO} and E_{LUMO} for metals have been compared to the calculated values for inhibitors to determine the type of the interaction. $E_{\text{LUMO}} - E_{\text{HOMO}}$ (ΔE energy gaps) for the interaction between metal and inhibitors are given in Table 2. The theoretical

quantum calculations on neutral inhibitor structure might be a good approach to predict the inhibitor efficiency to explain experimental results [32, 33]. Herein, metals will act as a Lewis base while the inhibitors act as a Lewis acid. So, metal utilizes the HOMO to initiate the reaction with LUMO of inhibitor.

Strong covalent bond can be expected only if the $E_{\text{LUMO,inh}} - E_{\text{HOMO,Cu}}$ gap is approximately zero [34]. In this case, all inhibitors act as a cathodic inhibitor whereas no molecules act as anodic inhibitors.

Table 2. Calculated quantum chemical parameters of inhibitors ($X_{\text{Al}} = 3.209$, $\eta_{\text{Al}} = 2.776$, $X_{\text{Fe}} = 4.026$, $\eta_{\text{Fe}} = 3.875$, $X_{\text{Cu}} = 4.480$, $\eta_{\text{Cu}} = 3.250$) [35].

Parameter	APDTC	PESA	HPMA	PASP	CMI
E_{HOMO}	−0.080	−7.810	−7.670	5.480	−6.720
E_{LUMO}	4.390	−2.170	−0.890	−0.610	−0.410
ΔE_{gap}	4.470	5.640	6.780	4.870	6.310
Dipole moment μ	9.930	3.300	5.590	5.480	8.590
$I = -E_{\text{HOMO}}$	0.080	7.810	7.670	5.480	6.720
$A = -E_{\text{LUMO}}$	−4.390	2.170	0.890	0.610	0.410
$\chi = (I + A)/2$	2.155	4.990	4.280	3.045	3.565
$\eta = (I - A)/2$	2.235	2.820	3.390	2.435	3.155
$\sigma = 1/\eta$	0.447	0.355	0.295	0.411	0.317
$\Delta N = (\chi_{\text{Al}} - \chi_{\text{inh}}) / 2(\eta_{\text{Al}} + \eta_{\text{inh}})$	0.105	0.159	0.087	0.016	0.030
$\Delta N = (\chi_{\text{Fe}} - \chi_{\text{inh}}) / 2(\eta_{\text{Fe}} + \eta_{\text{inh}})$	0.153	0.072	0.017	0.078	0.033
$\Delta N = (\chi_{\text{Cu}} - \chi_{\text{inh}}) / 2(\eta_{\text{Cu}} + \eta_{\text{inh}})$	0.212	0.042	0.015	0.126	0.071
$\omega_{\text{Al}} = \mu^2/2\eta$	2.303	1.823	1.520	2.115	1.632
$\omega_{\text{Fe}} = \mu^2/2\eta$	3.626	2.874	2.390	3.330	2.569
$\omega_{\text{Cu}} = \mu^2/2\eta$	4.490	3.559	2.960	4.121	3.181

According to the FMO, the interaction between HOMO and LUMO levels are mainly responsible for the chemical reactivity. The energy separation ΔE_{gap} is appropriate parameter and indicates the reactivity of the inhibitor towards the adsorption on metallic surface. So, as ΔE_{gap} decreases, the reactivity of the inhibitors increases and the inhibitor efficiency increases [36]. The ΔE_{gap} values of the three inhibitors (Table 2) increases in polymers in the order:

$$\text{HPMA} > \text{CMI} > \text{PESA} > \text{PASP} > \text{APDTC}$$

Other global reactivity parameters [22] were used to study the effectiveness of inhibitors. Such as: the global hardness (η), the electronegativity (X), the global softness (σ), the fraction of electron transferred (ΔN), and the electrophilicity index (ω) of the molecules are shown in Table 2. The binding tendency of the inhibitor towards metal can be used in terms of Hard-Soft-Acid-Base (HSAB) theory that helps to explain the inhibitor-metal stability. HSAB states that hard acids prefer to co-ordinate to bases with hard properties and soft acids prefer to co-ordinate to bases with soft properties. Consequently, atoms of metal classified as soft acids, because soft molecules have small ΔE_{gap} whereas hard molecules have high ΔE_{gap} [36]. Therefore, inhibitors which classified as soft bases will exhibit a pronounced effect on metals [37]. For this reason, APDTC which has the smallest ΔE_{gap} and the highest softness (σ) is expected to have good inhibitor efficiency as compared to other compounds. This result is confirmed by calculating softness (σ) of the inhibitor and so its reactivity is indicated in Table 2.

In addition, it can be observed that the hardness (η) of all compounds is the largest values than APDTC. This tendency is the reverse of what has been obtained for softness (σ). Consequently, the highest softness (σ) and smallest hardness (η) values of APDTC nominate him to be the best inhibitor, since soft molecule is more reactive than a hard one [38]. The fraction of transferred electrons (ΔN) is also results shows that most electrons transferred to the metals' surface come from the APDTC molecule when compared to other inhibitors. The electrophilicity index (ω) indicates the ability of the inhibitor to accept electrons from metals.

APDTC exhibits the highest electrophilicity index (ω) values compared to other inhibitors and its effect on the metals is in the order: $\text{Cu} > \text{Fe} > \text{Al}$. This result is in a good agreement with the experimental published work [12, 13]. The electrochemical results showed that APDTC has a fast adsorption process and forms a thick protective film to cover the surface of Cu. The Cu–APDTC complex is produced due to the reaction between sulphur atoms and Cu sites which leads to prevent oxide formation. As a result, this observation confirms its high capacity to accept electrons from metals. That is, metals act as Lewis bases while all compounds act as Lewis acids (cathodic inhibitor). Metal will accept electrons from inhibitor to form a co-ordinated bond. In addition, the inhibitor can accept electrons from metal to form back-donating bond depending on the orientation of optimized structure of the inhibitor on the spatial. The inhibition efficiency will increase since donation and back-donation processes strengthen the adsorption of inhibitors onto the metal surface.

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

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

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

Where μ indicates the chemical potential, and is equal to the negative value of the absolute electronegativity (X) as in ref. [39]. The calculated values of ΔG_{ads} for inhibitors are given in Table 3 based on Equations 1 & 2.

Table 3. Calculated ΔG_{ads} (kJ mol^{-1}) of the investigated inhibitors.

Inhibitors	Cu		Fe		Al	
	Cathodic inhibitors	Anodic inhibitors	Cathodic inhibitors	Anodic inhibitors	Cathodic inhibitors	Anodic inhibitors
APDTC	−224.328		−180.524		−101.695	
PESA		49.208		107.581		171.84
HPMA	−19.297			39.0765		103.336
PASP	−138.4564		−80.0828		−15.82359	
CMI	−88.2840		−29.9104			34.3488

The adsorption of all inhibitors on Cu and Fe shows that all of them have negative ΔG_{ads} values except PESA with all metals, also HPMA with Fe and Al and CMI with Al. The magnitude of ΔG_{ads} depends on the type of adsorption whether it is chemical or physical [40]. ΔG_{ads} is classified as physical adsorption when the value falls in the range of 0 to $-40 \text{ kJ} \cdot \text{mol}^{-1}$, whereas the ΔG_{ads} is chemical adsorption when the value falls in the range of -40 to $-400 \text{ kJ} \cdot \text{mol}^{-1}$ [41].

As shown in Table 3, the suggested mechanism of inhibitors in the case of Cu is spontaneous chemical adsorption because ΔG_{ads} value falls in the chemical adsorption range (-40 to $-400 \text{ kJ} \cdot \text{mol}^{-1}$), and it is nonspontaneous physical adsorption with PESA. In case of Fe, all inhibitors showed spontaneous chemical adsorption except with HPMA, PESA (non-spontaneous physical adsorption). For Al, PASP has negative ΔG_{ads} values in the range of 0 to $-40 \text{ kJ} \cdot \text{mol}^{-1}$, which indicate spontaneous physical adsorption. APDTC has a negative ΔG_{ads} values in the range -40 to $-400 \text{ kJ} \cdot \text{mol}^{-1}$. Other inhibitors showed positive ΔG_{ads} values and this suggest a non-spontaneous adsorption. APDTC is found to be the best corrosion inhibitor for all metals especially Cu (Figure 3), due to its highest dipole moment, ΔN , and ω comparing with other inhibitors.

Figure 3. Interaction of Sulphur atoms and Cu sites (APDTC–Cu complex).

Conclusion

Theoretical calculations gave a good picture about the effect of some green inhibitors on the corrosion rate of metals. Our theoretical results showed the best adsorption of the APDTC inhibitor on the Cu, Al and Fe metal surfaces especially on Cu metal to make it one of the best candidates against corrosion attack. APDTC showed the inhibition efficiency, because it has low E_{LUMO} that enables it to form a strong interaction with Cu (more than Fe, Al) acting as cathodic inhibitor. More over the highest electrophilicity of APDTC as compared to the other compounds represents a measure of the electrophilicity power of the molecule. All inhibitors show spontaneous energy and APDTC has the highest value as compared to other compounds, which suggest that corrosion inhibition is mainly from APDTC. This result explained the experimental electrochemical measurements of the interaction of sulphur atoms from APDTC with Cu sites forming APDTC–Cu complex which avoided oxide formation.

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