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Adsorption and Corrosion Inhibition of Mild Steel in Acidic Media by Expired Pharmaceutical Drug

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Abstract The effectiveness of the anti-Assam *Theophylline* (TD), expired drug, as corrosion inhibitor for mild steel in 0.5M HCl was investigated by weight loss method. Data obtained from weight loss studies were analyzed, and the Results show that the used TD drug was a good inhibitor. The inhibition efficiency increases with increasing the concentration of TD inhibitor and reached a maximum value of 73% at 30 ^{o}C and 100 ppm of the used inhibitor. The adsorption isotherm of TD obeyed Langmuir and Temkin adsorption isotherm. Quantum chemical calculations based on denisity function theory, DFT, were performed on TD drug. Calculated parameters such as the highest occupied molecular orbital energy (E_{HOMO}), the lowest unoccupied molecular orbital energy (E_{LUMO}), energy gap (ΔE), dipole moment (μ), electronegativity (χ), electron affinity (A), global hardness (η), softness (σ) and ionization potential (I), were calculated and correlated to the experimental data.
Keywords: Corrosion, mild Steel, acidic medium, Weight Loss, inhibition efficiency, expired drug, DFT calculation.

إدمصاص وتثبيط تأكل الحديد الصلب في الوسط الحمضي باستخدام مركب لدواء منتهي الصلاحية

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الملخص: تم التحقق من فعالية عقار ثيوفيلين (TD, *Theophylline* drug) كمثبط لتآكل الحديد لصلب في (0.5 M) حمض الهيدروكلوريك بواسطة طريقة فقدان الوزن. تم تحليل البيانات التي تم الحصول عليها من دراسات فقدان الوزن، وان النتائج تظهر أن الدواء المستخدم كان مثبط جيد لتآكل الحديد الصلب في (0.5M) حمض الهيدروكلوريك. كما أظهرت النتائج ان كفاءة التثبيط تزداد مع زيادة تركيز المثبط، وكفاءة تثبيط تصل إلى 73 % عند تركيز 100 جزء في المليون من المانع المستخدم وعند درجة حرارة 30 درجة مئوية. وبدراسة منحنيات الإدمصاص تبين ان إدمصاص الدواء المثبط يخضع لمنحنيات الإدمصاص لانجمويز (Langmuir adsorption isotherm) وتمكن (Temkin adsorption isotherm). أجريت الحسابات الكيميائية الكمية لجزئية عقار ثيوفيلين (TD) على أساس نظرية الكثافة الالكترونية (DFT). وعلى هذا الاساس تم قياس طاقة كل من المدارات الجزئية الرابطة والغير رابطة (E_{HOMO} & E_{LUMO}) وفجوة الطاقة بين المدار الرابط والغير الرابط (ΔE) وعزم ثنائي القطب (μ) والسالبية الكهربائية (χ) والميل الإلكترون (A) والصلابة (η) ليونة (σ) وجهد التأين (I). وتم ربط نتائج الحسابات النظرية ومقارنتها وربطها بالبيانات التجريبية.
الكلمات المفتاحية: التآكل، الحديد الصلب، الاوساط الحمضية، فقدان الوزن، كفاءة تثبيط، نظرية الكثافة الالكترونية، الداء المنتهي الصلاحية.

Introdution

The metals corrosion is a basic industrial and academic worry that has received a broad attention. Corrosion is identified as the attack of metals or alloy by chemical or electrochemical reaction [1]. Steel alloys are the most widely used materials in variety of industries, frequently exposed to the acids action as acid cleaning, acid de-scaling [2-4]. Consequently, it needs to protect their structures against corrosion attack. Inhibitors are extensively used, especially in the acidic medium [5]. Inhibitor is a substance that, when added in small concentration to an environment, decreases the corrosion rate [6]. Most acidic inhibitors are organic compounds containing nitrogen, sulfur and oxygen [7-11].

Despite the wide range of available organic compounds, most of the inhibitors that have been tested are very expensive and toxic in nature. There is a big concern in replacing environmental unsafe inhibitors with effective non-toxic alternatives. Expired drugs (non-toxic characteristics) were used as corrosion inhibitors for metal alloys. Most of the chemical drugs are more expensive than the organic inhibitors that used in industries. Thus, expired drugs which are of no use can be investigated as corrosion inhibition. By this way, the environmental and

economical problems concern the pollution with pharmaceutically active expired drug can be solved [12]. So drugs represent a promising class of inhibitors [13, 14]. In light of the above observation, we aimed to investigate the corrosion inhibition properties of expired drug namely *Theophylline TD* (Scheme. 1) on mild steel in 0.5M HCl solution, as part of undertaken investigation in our laboratory on the corrosion inhibiting behaviour of mild steel. *Theophline,* a drug used was selected as a corrosion inhibitor based on its molecular structure that has O, N active center atoms. The corrosion inhibition behaviour of TD and was studied using weight loss and DFT techniques.

Scheme 1. Inhibitor molecule of *Theophylline* (*TD*)

2. Experimental method

2.1. Material

Tests were performed on a freshly prepared cylinder of mild steel (specimens were collected from Musrata steel factory). Specimens used in the weight loss experiment were mechanically cut into 4.0 cm length and 1cm diameter, then abraded with SiC abrasive papers 400-1200 grit, respectively, washed in absolute ethanol and acetone, dried in room temperature and stored in a moisture free desiccators before their use in corrosion studies.

2.2. Solutions

The aggressive solutions of 0.5 M HCl were prepared by dilution of analytical grade 37% of HCl, with distilled water. The concentration range of *Theophylline* (TD) prepared and used in this study was 50 - 500 ppm. The inhibitor was prepared by dissolving the appropriate amount in DMSO.

2.4. Gravimetric measurements

In this study, weight loss technique was used to investigate the inhibition characteristic of *Theophylline* (*TD*). Typically, a previously weighed mild steel coupon was completely immersed in 50 mL of the test solution in an open beaker. The beaker was inserted into a water bath maintained at 313 K. The coupons were retrieved after 90 min interval, rinsed severally in deionized water, cleaned, dried in acetone, and re-weighed. The weight loss, in milligrams, was taken as the difference in the weight of the mild steel coupons before and after immersion in different test solutions. The corrosion rate (R_{corr}) in mg cm^{-2} min^{-1} was calculated from the following equation:

$$R\,(mg\,cm^{-2}min^{-1}) = (W/At) \quad (1)$$

where W, is the average weight loss of three mild steel cylinder; A, is the total area of one mild steel specimen, and t, is the immersion time (90 min). From the weight loss results, the inhibition efficiency (%I) of the inhibitor and degree of surface coverage (ϴ) were calculated using equation 2 & 3: , respectively

$$I\% = \left(1 - \frac{R_{inh}}{R_0}\right) \times 100 \quad (2)$$

$$\theta = \left(1 - \frac{R_{inh}}{R_0}\right) \quad (3)$$

where R_{inh} and R_0 are the corrosion rate for mild steel in the presence and absence of the inhibitor in the acidic solutions,

2.5. Computational details

The molecular geometry, HOMO and LUMO orbitals, and the overall electronic structure of drug inhibitor was calculated at the DFT (Density Function Theory) level with DMol[3] using the Materials Studio suite of programs (version 5.5). Structure optimization calculations were performed using a generalized gradient approximation (GGA) function [15, 16] and a hybrid exchange–correlation function (Becke-Lee-Yang-Parr) BLYP [17, 18] with a double numeric plus polarization (DNP) basis set to map the orbital structure of the compound.

Highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO) and the energy gap between them (ΔE) are used to predict the reactivity of molecules. According to Koopman's theorem [19-21], the energies of the HOMO and the LUMO orbitals of the molecule are related to the ionization potential, (I), and the electron affinity, (A), respectively, by the following equations:

$$\Delta E = E_{LUMO} - E_{HOMO} \quad (4)$$

$$I = -E_{HOMO} \quad (5)$$

$$A = +E_{LUMO} \quad (6)$$

Absolute electronegativity, (x) and global hardness, (η), Softness, (σ), of the inhibitor molecule are given by Pearson [21].

$$x = \frac{I + A}{2} \quad (7)$$

$$\eta = \frac{I - A}{2} \quad (8)$$

$$\sigma = \frac{1}{\eta} \quad (9)$$

3. Results and discussion

The gravimetric method is probably one of the most widely used method of inhibition examination. The simplicity and reliability of the measurement offered by the weight loss method is such that the technique forms the baseline method of measurement in many corrosion-monitoring programmers.

3.1. Inhibition characteristic of *Theophline*

The corrosion rate of mild steel in the absence and presence of (TD) at 303 K was studied using the weight loss method. Table 1 and figure 1 show the calculated values of corrosion rates (mg $cm^{-2}min^{-1}$), and inhibition efficiency (I%) for dissolution of mild steel in 0.5 M HCl in the presence and absence of (TD).

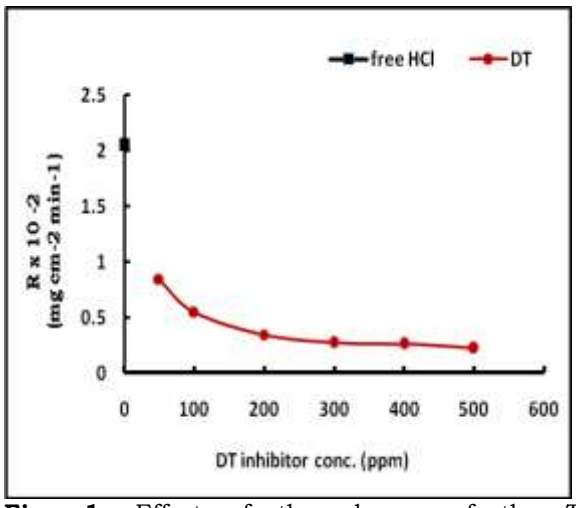


Figure1. Effect of the change of the T**D** concentration on the inhibition of mild steel in 0.5M HCl at 30°C.

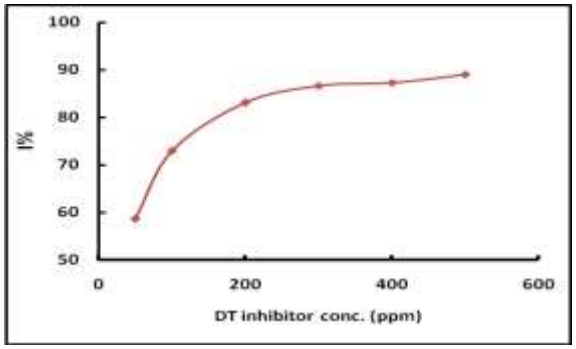


Figure2. The inhibition efficiency of **TD** at 30 °C

From the values obtained, it is obvious that there is a decrease in the corrosion rate of mild steel in the presence of (TD) when compared to the blank.

Table 1 Corrosion rate and inhibition efficiency of TD in the absence and presence of HCl at 30°C.

TD Conc. (ppm)	R x 10 $^{-2}$ (mg cm^{-2} min^{-1})	I%
0	2.048	
500	0.2242	89.05
400	0.2609	87.26
300	0.2729	86.67
200	0.3463	83.09
100	0.5529	73.002
50	0.8474	58.63

3.2. Adsorption isotherms

Basic information on the interaction between the inhibitor and the mild steel surface can be provided by the adsorption isotherm. The adsorbed layer hinders the action of the acid solution and enhances the protection of metal surface [22]. When there is insufficient Fe-$(Inh)_{ads}$ to cover the metal surface (if the inhibitor concentration was low or the adsorption rate was slow), metal dissolution would take place at sites on the mild steel surface which were free of Fe-$(Inh)_{ads}$. With high inhibitor concentrations, compact and coherent inhibitor over-layer is formed on the mild steel surface, reducing chemical attack of the metal [22, 23].

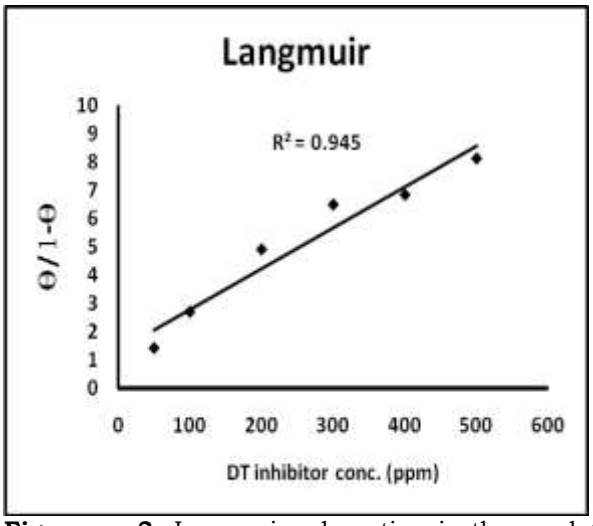
The adsorption of an organic adsorbate on the surface of a metal is regarded as a substitution adsorption process between the organic compound in aqueous phase $Org_{(aq)}$ and the water molecules adsorbed on the electrode surface $H_2O_{(s)}$ [22].

$$org_{(aq)} xH_2O_{(ads)} \rightarrow org_{(ads)} xH_2O_{(aq)} \qquad (1)$$

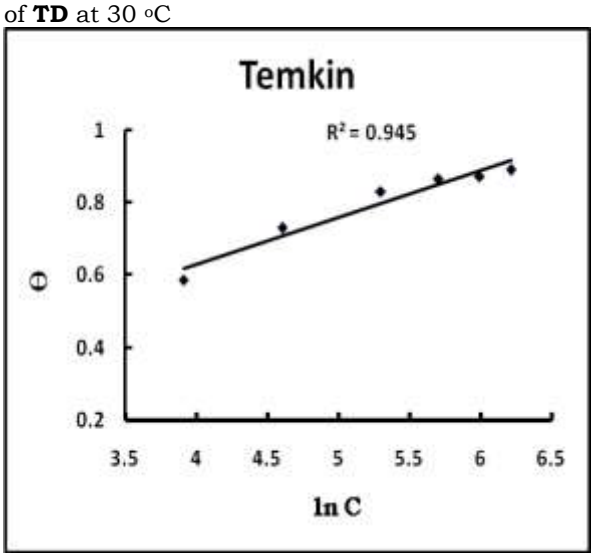
Where *x* is the size ratio, which is the number of water molecules replaced by one molecule of organic inhibitor. In order to obtain the adsorption isotherm, the degree of surface coverage (θ) for various concentrations of the inhibitor has been calculated using equation 3. Attempts were made to fit the θ values to Langmuir and Temkin adsorption isotherm. Langmuir isotherm is given by the expression:

$$\frac{\theta}{1-\theta} = K_{ads}\, C_{inh} \qquad (10)$$

where K_{ads} is the equilibrium constant for the adsorption process. The plot of (θ */ 1* - θ) against C is shown in Figure 3. Linear plots were obtained with very good correlation coefficients, indicating multilayer and physisorption character.



Figureure 3. Langmuir adsorption isotherm plot of **TD** at 30 °C



Figureure 4. Temkin adsorption isotherm plot of (■TD) at 30 °C

In addition, Temkin adsorption isotherm was tested for its fit to the experimental data. The isotherm equation is given by:

$$\theta = \frac{1}{-2\alpha}\ln C + \frac{1}{-2\alpha}\ln K \qquad (11)$$

α is the interaction factor. The plot of ɵ versus inhibitor concentration lnC would give a straight line slope equal to α and intercept equal to ln K (Figure 4).

Table 2. parameters from thermodynamic–kinetic model and Langmuir isotherm for (TD) & (TD+KI) at 30 °C

parameter	α	K_{ads}	ΔG^{o}_{ads}
TD	-3.876	4.675 x10^3	-103.649

The equilibrium constant of the adsorption process is related to the standard free energy of adsorption, ΔG^{o}_{ads}, by:

$$\Delta G^{o}_{ads} = -R\,ln(55.5\,K_{ads}) \qquad 12$$

were ΔG^{o}_{ads} is the free energy of the adsorption, R is the gas constant and T is the temperature of the system. Generally, ΔG^{o}_{ads} values up to -20 kJ mol^{-1} are compatible with the electrostatic interaction between the charged molecules and charged metal (physical adsorption), while those more negative than -40 kJ mol^{-1} involve charged pairs or organic molecule transfer onto the metal surface, so as to form a type of coordinated bond (chemical adsorption) [24, 25] Calculated values of the free energies are also presented in Table 2.

The value obtained from this research was −103.65 kJ mol^{-1} for the tested solution of TD which indicates that the adsorption mechanism of TD on mild steel in HCl solution at the studied temperatures is a combination of both physisorption and chemisorption [26]. The high value of K_{ads} for studied TD (Table 2) indicates stronger adsorption on the mild steel surface in HCl solution. It has been reported that the higher the K_{ads} value (>100), the stronger and more stable the adsorbed layer of the inhibitor on metal surface and consequently, the higher the inhibition efficiency [27, 28]. The value of the molecular interaction parameters 'α' obtained from Temkin adsorption isotherm is negative, which provide information on repulsive forces between the inhibitor molecules that prevail in the adsorptive layer.

3.3. Theoretical calculation

Quantum chemical calculations were performed to investigate the structural parameters that affect the inhibition efficiency of inhibitors. Geometric and electronic structures of the inhibitors were calculated by the optimization of their energy, bond length and angle. Corresponding to the global minimum optimized structure in the neutral form, the calculated bond lengths of TD molecules are in the normal range of single and double bond (Table 3). The optimized molecular structures with minimum energies obtained from the DFT calculations are given in Figure 5 a. The two rings on the Theophylline molecules are approximately in the same plan. As result, TD molecule being almost planar Figure 5 b. And the electronic density are distributed equally on the hole molecule.

Table 3: calculated bond lengths TD molecules

bond	length (Å)	bond	length (Å)
N2 - C3	1.397	O1- C1	1.25
N2 - C4	1.478	O2 - C3	1.244
N2 - C5	1.388	C4-C5	1.388
N3 - C4	1.37	N1 - C1	1.425
N3 - C6	1.342	N1 - C2	1.481
N4 - C6	1.361	N1 - C3	1.417
N4 - C5	1.39	N4 -H	1.009

Highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO) are used to predict the adsorption centers of the inhibitor molecule. The highest occupied molecular orbital (HOMO), and the lowest unoccupied molecular orbital (LUMO) were used to predict the adsorption active site of the inhibitor molecule. According to the frontier molecular orbital theory [29-33], the formation of a transition state of chemical inhibitor is due to an interaction between HOMO and LUMO of the reacting inhibitor. The energy of HOMO describes the electron donating ability of a molecule and characterizes the tendency of the molecule towards attack by electrophiles. High value of E_{HOMO} (-5.468 eV) indicates a tendency of the molecule to donate electrons to acceptor molecules with low energy molecular orbital or empty electron orbital [29, 32].

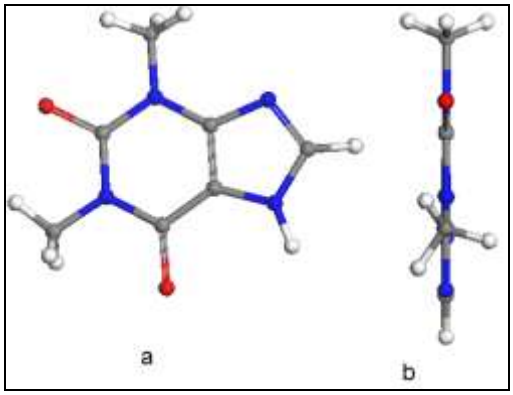


Figure5. (a) optimized inhibitor molecule by DFT, (b)planarity of drug molecules

However, the LUMO energy characterizes the electron accepting ability and the susceptibility of the molecule towards attack by nucleophiles. Low value of $E_{LUMO}(-1.879)$ indicates an electron accepting ability of an inhibitor molecule (the lowest value the higher the tendency of accepting electrons) [29].

Table 4: Chemical reactivity parameters

Parameters	*quantities*
E_{HOMO}	-5.468
E_{LUMO}	-1.879
Energy band gap (ΔE)	-3.589
Ionization potential I(I)	5.468
Electroaffinity (A)	1.879
Electronegativity (χ)	3.6735
Global hardness(η)	1.7945
global softness (σ)	0.557258
dipole moment (μ) debye	5.125

Adsorption of Theophylline inhibitor at metal surfaces takes place (on the basis of donor–acceptor interactions) by electro transfer, through the loosely bound electrons of the π-bonds or the aromatic rings with the vacant *d*-orbitals of metal surface atoms [23] . The TD molecules may be adsorbed on the metal surface via the chemisorption mechanism involving the displacement of water molecules from the metal surface and the sharing of electrons between nitrogen, oxygen atoms and iron.

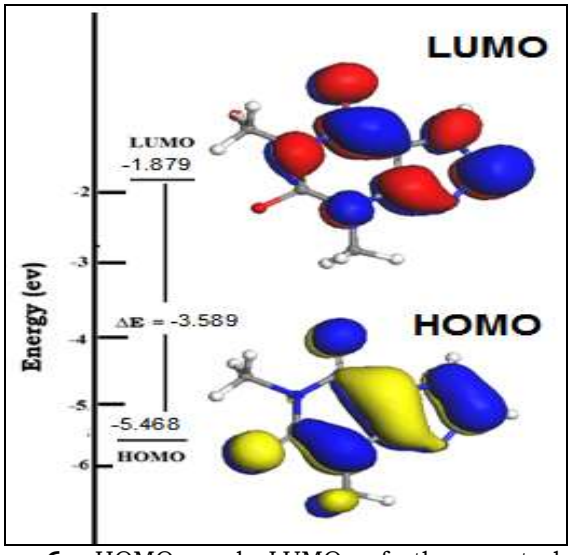


Figure6. HOMO and LUMO of the neutral inhibitor molecule by DFT

The Theophylline molecules can be adsorbed also on the metal surface on the basis of interactions between π-electrons of the aromatic ring and vacant *d*-orbitals of iron. Theophylline might be exist as protonated species in the acid medium as $\mathbf{NH_3^+}$. indicating that protonated inhibitor species may also be adsorbed due to the electrostatic interaction with the negatively charged mild steel surface ($FeCl_{ads}^-$) [34, 35]. The protonated TD molecules may adsorb through electrostatic interactions between the positively charged molecules and the negatively charged metal surface, i.e. Cl^- and protonated TD molecules.

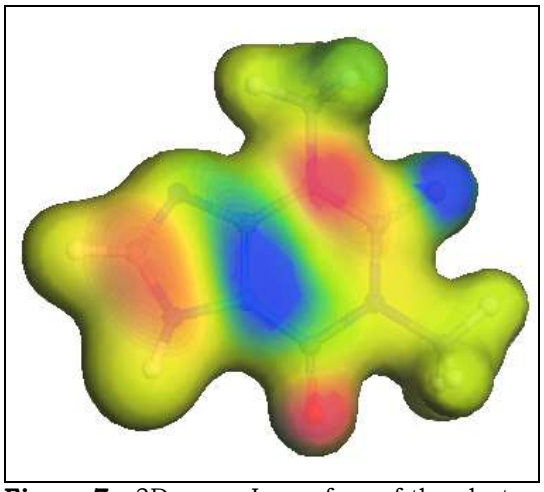


Figure 7. 3D maps Isosurface of the electrostatic potential in the studied TD inhibitor

In the case of a donor molecule, the HOMO density is critical to the charge-transfer (electrophilic attack). The Frontier molecular orbitals, FMO, diagram of the TD inhibitor indicates the dense electron cloud around CH-NH fragment on the five membered-ring and one of the two oxygen atoms in the six-membered ring (N and O) indicates the site of electrophilic attack as it appear in figure 7.

Conclusion

Phenyl Theophylline (TD) was found to be an inhibitor for mild steel corrosion in HCl. Inhibition efficiency increased with an increase in concentration of (TD). The adsorption of the (TD) can be fitted to the Langmuir and Temkin adsorption isotherms. The adsorption mechanism of TD on mild steel in HCl solution at the studied temperatures is a combination of both physisorption and chemisorption mechanism. Data obtained from quantum chemical calculations using DFT shows LUMO, HOMO distributed along of drug molecules. However, the oxygen (O) atom in the inhibitor molecules is only homo contributed.

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