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Eco-Friendly Corrosion Inhibitor: Experimental Studies on the Corrosion Inhibition Performance of Creatinine for Mild Steel in HCl Complemented with Quantum Chemical Calculations

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The power of Creatinine as inhibitor, for metals in 1 Molar corrosive acid solution (hydrochloric acid) has been investigated utilizing a weight loss technique. Impact of temperature and thermodynamic parameters were explored. Results demonstrated that the inhibition happens through adsorption of the creatinine molecules on the surface of the metal and the efficiencies were improved with an increment in creatinine concentration and diminished at higher temperature degrees. Scanning electron microscopy was done for the metal surface to examine it. The highest occupied molecular orbital energy, lowest unoccupied molecular orbital energy and dipole moment was theoretically calculated utilizing Density Function theory.

Keywords: Corrosion inhibitor, creatinine, weight loss, DFT

1. INTRODUCTION

The employments of acids, alkaline and salt solutions in industrial applications causes extensive severe corrosion in surface of metal, which prompts tremendous financial misfortunes. These issues had welcomed the consideration of researchers to look for control the corrosion and they found that the utilization of corrosion inhibitors is a recognizable strategy to control the corrosion. Inhibitor molecules absorbed by metal surface [1,2]. The excellent anticorrosion potential for metal surface were

the chemical compounds having in their structure atoms with unoccupied electron pair like Phosphorous, Sulfur, Nitrogen or Oxygen incorporated in an resonance system and groups with electron efficiency that push electron by inductive effect. Recently, researchers have been working on green inhibitors (environmental friendly) to stay away from the harmful impact of prepared inhibitors [3-5]. These inhibitors are found to be extremely active in corrosive solutions moreover they are financial valuable and eco-friendly [6-11]. For the same reason, different plant extracts are also investigated. To this end, the utilization of eco-friendly organic materials with atoms having unpaired electron pairs or conjugated pi-system as inhibitors to reduce corrosion attack has gotten definite consideration [12-15]. Weight loss technique was used to examine the inhibitory characteristics of the creatinine mild steel inundated in one molar of hydrochloric acid. The new concentrated inhibitor demonstrated inhibitory characteristics dependent on hetro-atoms. The most noteworthy inhibition efficiency was affirmed by scanning electron microscopy.

2. RESULTS AND DISCUSSION

2.1. Weight Loss Method

2.1.1. Effect of Concentration

CR (Corrosion Rate) and IE (Inhibition Efficiency) values that estimated from weight loss techniques in in the corrosive media having different concentrations of creatinine at different temperatures degrees 303, 313, 323 and 333 K are demonstrated in Figures 1 and 2.

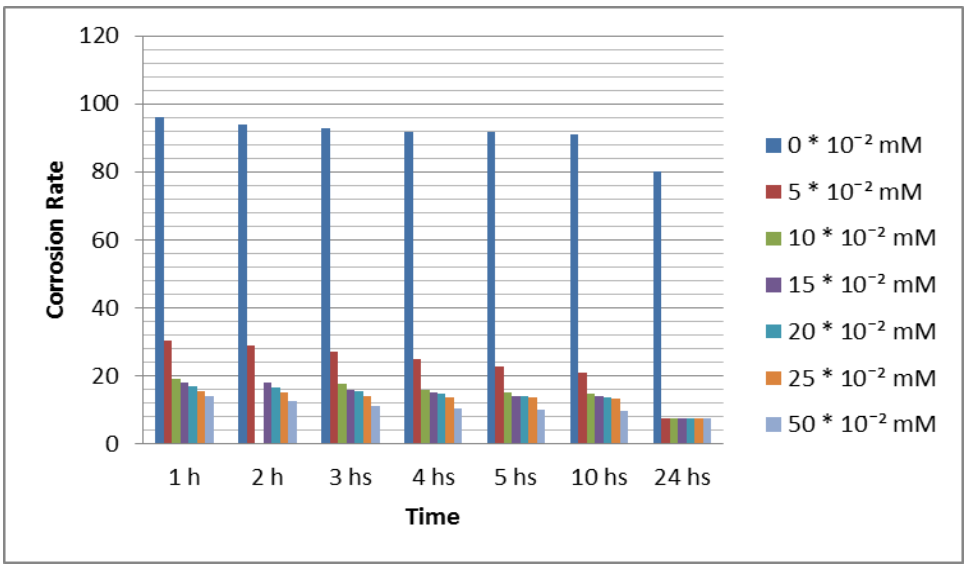


Figure 1. Different concentrations *vs* different immersion periods time for creatinine CR of metal.

From Figures1 and 2, it can be demonstrated that creatinine decreased the corrosion of metal in corrosive media substantially. The IE increased when creatinine concentration increased and become highest IE at 0.5mM. The increment in IE with the increment in creatinine concentration is suggestive of the increase in the range of protection efficiency of creatinine.

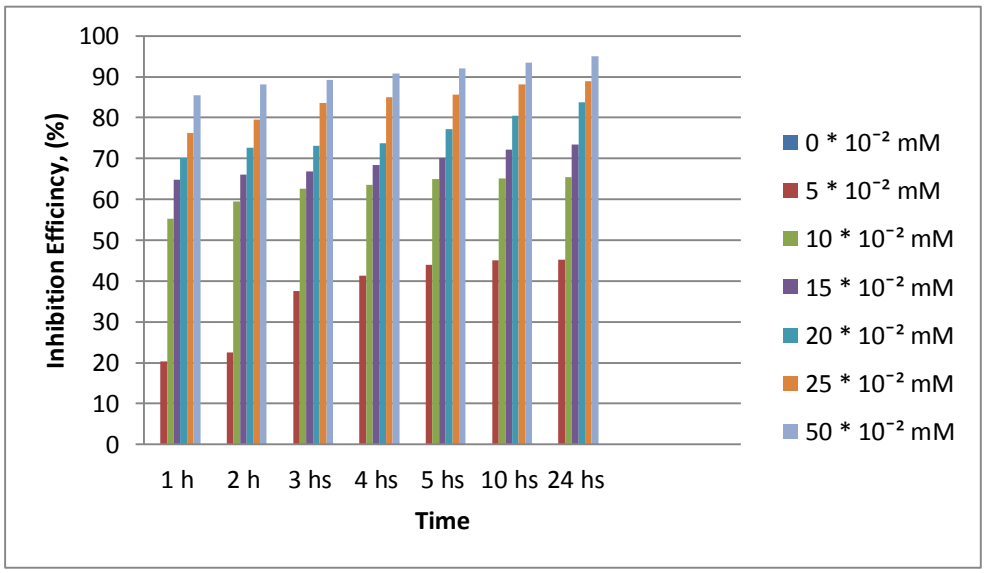


Figure 2. Different conc. *vs* different immersion periods time for creatinine IE of metal at 303K.

2.1.2. Effect of Temperature.

Figure 3 shows the correlation of the IE on metal in corrosive solution with and without of different concentrations of creatinine at of different temperatures. It can be demonstrated that IE improved with an increment in creatinine concentrations and diminished with an increment in temperature. The heat of adsorption is generally negative and this indicated an exothermic process. This is the cause that the IE, diminish at a raise of temperature.

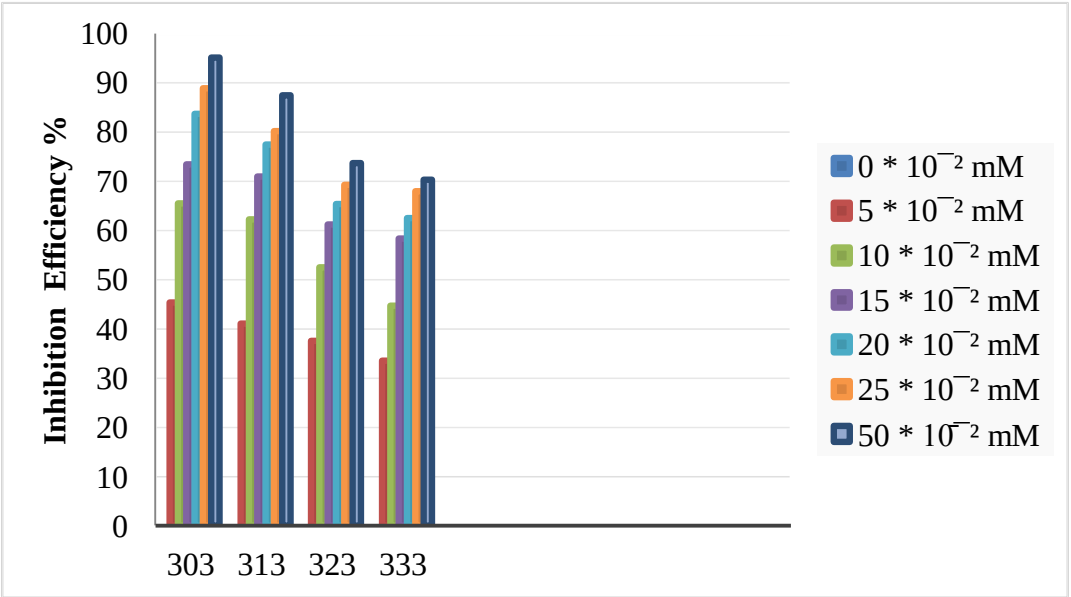


Figure 3. Impact of temperature on IE of creatinine at various concentrations

2.2. Scanning Electron Microscopy (SEM) Analysis.

Metal surface suffer from corrosive solutions, which was initially clean and smooth, got to be rough. The corrosion was carried out by 1 molar HCl. From Figure 4, a and b, it can be demonstrated that the inundation of metal in 1 molar HCl for 5 hs at 303 K that the surface did not suffer serious corrosion after added the inhibitor with concentration of 0.5 mM. Creatinine makes preservation to the metal surface from the corrosion created by acid through the absorption of creatinine particles by the mild steel surface.

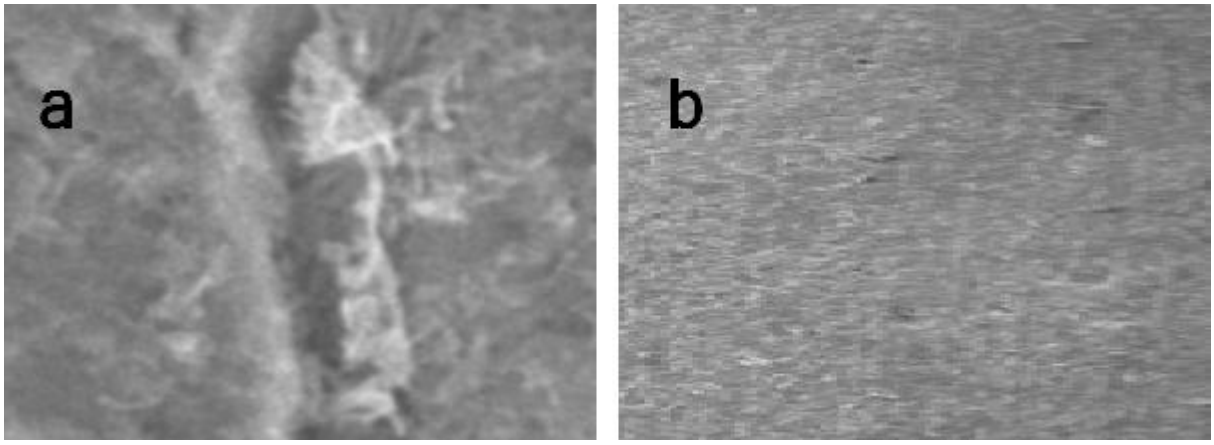


Figure 4. The SEM micrographs 5000X, for metal in 1.0 M HCl. (a, with creatinine; b, without creatinine).

2.3. Adsorption Isotherm

Creatinine adsorped by the mild steel surface. Thus decrease the corrosion rate. Primarily adsorption influenced by the nature and electronic properties of mild steel surface.The adsorption mechanism of natural or organic chemical compounds on mild steel surface can be clarified through the investigation of adsorption isotherm and adsorptive conduct [16]. The most frequently utilized adsorption isotherms are Langmuir, Temkin, Frumkin, and Freundluich isotherms [17].

The adsorption process is affected by structure of inhibitor, charge distribution, nature of surface and media that was utilized [18,19]. The estimations of (surface coverage) for the distinctive concentrations of the creatinine have been utilized to clarify the best adsorption.

$$\theta = \frac{\text{IE \%}}{100} \quad (1)$$

In this work, θ was computed from the equation 1, utilizing the IE estimated from the weight loss method [20].

$\frac{C_{inh}}{\theta}$ *vs* C_{inh} yield a straight line with an approximately unit-slope, showing that creatinine obeys the Langmuir adsorption isotherm [21], as showing in equation (2)

$$\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh} \quad (2)$$

where C_{inh} is concentration of creatinine while K_{ads} obtained from the intercept of the straight line and represent the adsorption constant that.

Standard free energy, ΔG°_{ads}, that associated with K_{ads} was given in equation 3;

$$\Delta G^{o}_{ads} = -RT ln[55.5\ K_{ads}] \quad (3)$$

where T is the absolute temperature and R is the gas constant.55.5 represents the value of the molar concentration of water in solution.

The estimated of k_{ads} and ΔG^{o}_{ads} was computed in proportion to Figure 5, and the estimated ΔG^{o}_{ads} was −33.41kJ mol^{-1}. The negative value of ΔG0ads shows the adsorption of the creatinine on the metal surface and the good interaction between the creatinine compound and metal surface. In references the researchers prove the if ΔG0ads around −20 kJ/mol is consistent with physical adsorption, where as if ΔG^{o}_{ads} equal or more than −40 kJ/mol indicate that chemical adsorption occurring with the sharing or transfer of electrons from inhibitor as a ligand to the metal surface [22]. ΔG0ads for creatinine is −33.41 kJ/mol and this indicated that the adsorption process is more likely to be physical adsorption.

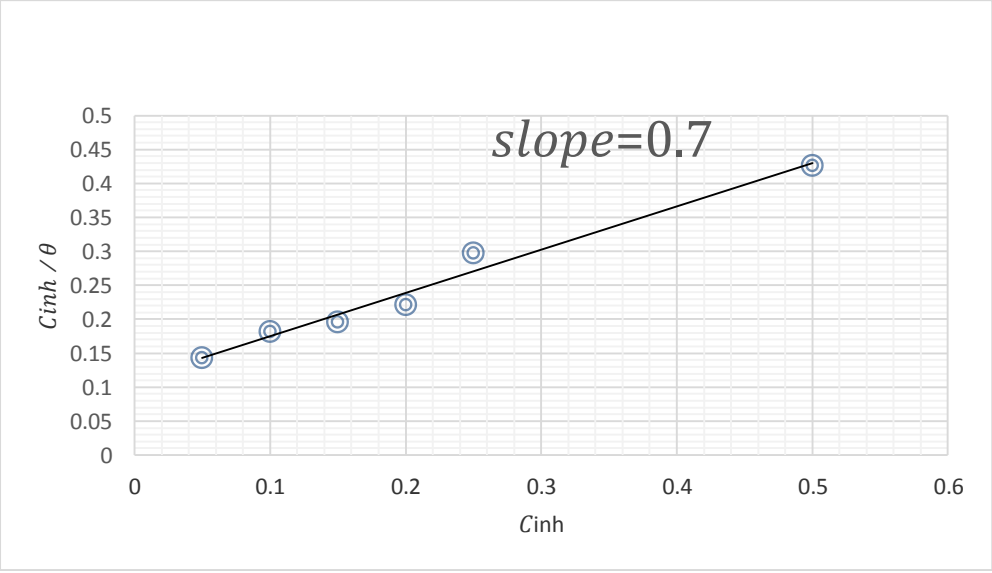
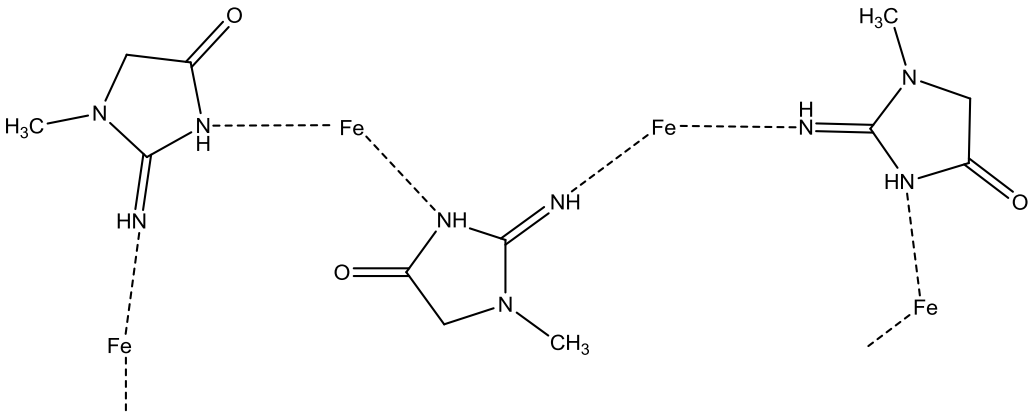


Figure 5. Metal surface adsorption isotherm at various conc. of creatinine

2.4. Creatinine as Inhibitor- Action Mechanisms

Generally inhibitors are adsorbed on the mild steel and structures a coating film or a synthetic bonds structure by response of inhibitor and metal and form inorganic complex (free electrons of inhibitor-ligand with the unoccupied d-orbital for the metal). The action mechanism of creatinine as inhibitor can move ahead by means of interaction. Interaction of Creatinine and metal electrostatically or interaction of unpaired electrons of hetro-atoms of creatinine with metal. IE of creatinine can be demonstrated to the hetro-atoms, charge, size, stereo-hindrance and ability of formation of metallic insoluble complex. Creatinine act as bi-dentate ligand unpaired electrons of oxygen and nitrogen to form coordinated bonds with metal (Scheme 2).



Scheme 2. The suggested mechanism of creatinine as corrosion inhibitor

2.5. Theoretical Studies.

2.5.1. Isomers of Creatinine

Concerning the imine group, creatinine may exist as *amie* or *imin* structures as in Figure 6.

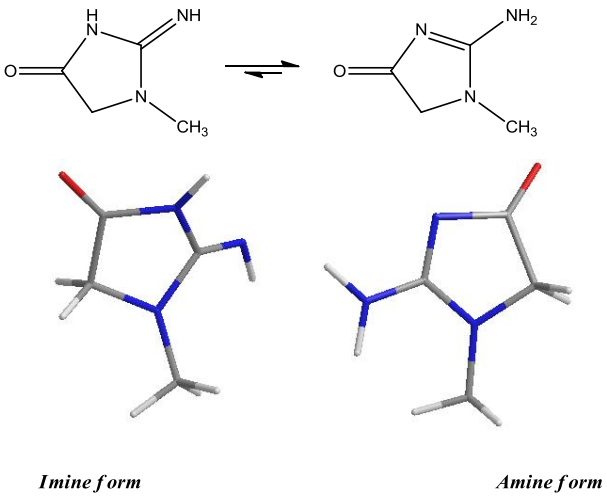


Figure 6. Structure of creatinine

DFT utilizing B3LYP system with 6–31G set was conducted to find energy computing. Estimations showed a little variety in energy that equal to −4.459 cal/mol, according to amine and imine conformers. Accordingly, we reasoned that the creatinine was acquired as imine structure. Creatinine the isomers imino isomer and the amino isomer, as demonstrated in Figure 6. The stability of these structures from the computing of quantum utilizing the DFT indicated in Table 1, the imino structure being more steady than the amino structure, which is prove by the estimation of the total energy that figured for them. Imine form energy is greater than the amine one at −4.459 cal/mol, and the isomerization conversions between the two forms were elucidated in Figure 6. It would appear, the estimations of the HOMO for the two groups demonstrate that the imino form isomer is more steady than the amino structure isomer. Band gap refers to the energy variations between LUMO and HOMO and this is equivalent to the energy needed to free an external shell electron from its orbit about the nucleus to turn into a versatile charge transporter, ready to move freely within the solid material. Energy gap estimations of the two structures imino form isomer and amino form isomer, are 10.501 eV and 9.280 eV, separately, and this demonstrates that molecules in the gas phase are insulators for the electrical conductivity. Figure 7 demonstrates the HOMO electronic distribution for the two forms. Different records of wavelength for highest absorption (kmax) of the two forms, imino form isomer amino form isomer, are 399 and 364 nm, separately, with the imino form having a wavelength longer than the amino form due to the imine double bond. The two forms have no symmetry at all.

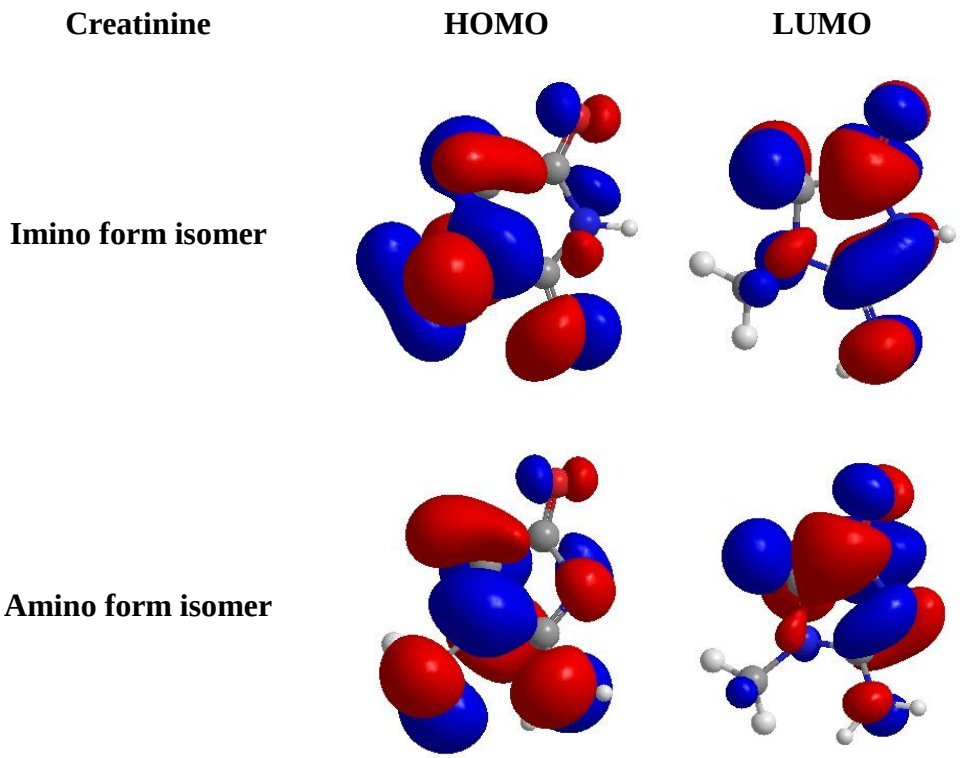


Figure 7. The distribution of electron density of high occupied molecular orbital (HOMO) for creatinine isomers

2.5.2. Quantum Computations.

Mechanism of inhibition can be illustrate by DFT Density Functional Theory. This method has been discovered to be effective in giving experiences into the chemical reactivity and selectivity regarding of global parameters, electro-negativity, hardness and softness[23,24]. The utilizing of creatinine as a corrosion inhibitor was in view of some resonse such as, active centers (oxygene and nitrogen),creatinine can be easily found and extract from urine. Also, creatinine consider as environmental friendly compound. Moreover, creatinine is natural compound. Phenomenal inhibitors are generally chemical compounds offer electron pairs to abandoned orbitals of mild steel and reversely the inhibitor also accept unpaired electrons from the mild steel [25,26]. Quantum computations were utilized to researched the action of metal toward inhibitor [27]. HOMO, LUMO, Fukui function and additionally the total electron density of creatinine are introduced in Figure 8. HOMO, HOMO and Dipole Moment parameters are given in table 1. The HOMO areas for creatinine, which are the destinations that electrophiles represent active site with the most extreme capacity to react with the mild steel, has contributions from methylene, methyl and amine. Then again, LUMO may accept electrons from the mild steel utilizing hostile anti-bonding orbital to form bonds are saturated around the creatinine ring [28]. HOMO with high energy demonstrates the tendency of creatinine atoms to give electrons to a molecule with an unoccupied orbital, and in other hand the LUMO energy describes the power of molecule toward nucleophilic attack [29]. Low estimations energy of the gap ($E_{LUMO}-E_{HOMO}$) suggests that the energy to to expel an electron from the last possessed orbital will be minimized, relating to enhanced IE [30,31]. The value of EHOMO, don't shift notably for creatinine, which implies that any observed differences in the adsorption qualities would come about because of molecular size parameters as opposed to electronic structure parameters. The apparently high estimation of ΔE is as per the non-particular nature of the relation of molecule with mild steel. A relationship between the corrosion IE of the creatinine with the orbital energies of the HOMO and LUMO and in addition μ is demonstrated in Table 1.

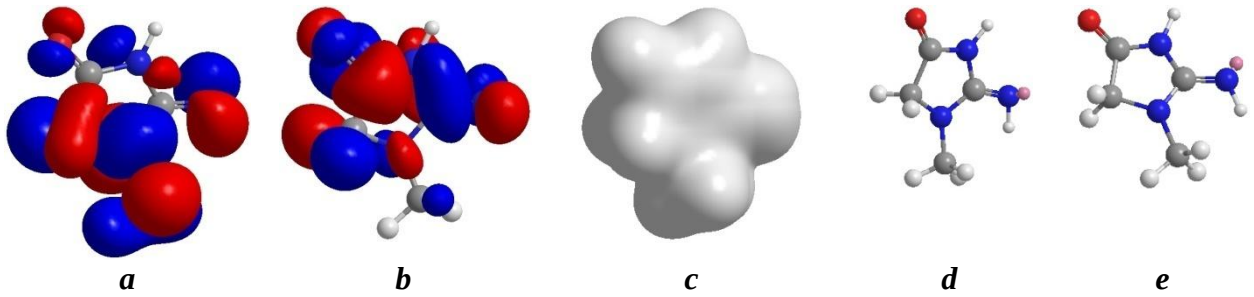


Figure 8. Creatinine electronic characteristics of a (high occupied molecular orbital); b (Lowest unoccupied molecular orbital); c (total electron density); d (Fukui (f−)function) and e (Fukui (f+) function).

As is plainly noted, IE increments with an increment in EHOMO (Figure 8a) values along with a decrease in ELUMO (Figure 8b) values. The polarity in a bond can be measured via dipole moment and is related to the distribution of electrons in a molecule. In spite of the fact that literature is

conflicting on the utilization of μ as an indicator of the direction of a creatinine reaction, it approved that the adsorption of polar compounds having high dipole moments on the mild steel ought to prompt to better IE. The data got from the this work demonstrate that the creatinine as an inhibitor has the estimation of μ = 1.421 and most highest IE (95.1%).

The information got from the present study demonstrate that the creatinine inhibitor has the estimation of μ = 1.421 and most astoundi μ is an alternate indicator of the electronic distribution inside a molecule. Many researchers show that the IE increments with increasing μ, which relies on upon the nature of molecules considered. In any case, there is an absence of assent in the references on the relationship between dipole-moment and inhibition effeciency, as sometime no correlation between these values has been distinguished [32-34].

Table 1. Quantum properties for stable conformation of creatinine.

Function	Values
E_{HOMO}	-0.375 Hartree
E_{LUMO}	0.010 Hartree
E_{HOMO} - E_{LUMO}	-0.385 Hartree
f^{-}_{max}	0.116
f^{+}_{max}	0.098
Dipole Moment	1.421

FI (Fukui indices) to evaluate reactive districts regarding f+ (nucleophilic) and f− (electrophilic) conduct. Figure 8d demonstrates that the f− functions of molecule compare with high occupied molecular orbital locations, demonstrating sites through which the molecule can adsorb on mild steel, while f+ as shown in Fig. 8e relate with lowest unoccupied molecular orbital locations, indicating destinations through which the molecule could interact with the nonbonding electrons in the metal. High f^{-} values are qualities with hetro-atoms (in creatinine) functions molecule, while carbon atoms functions possess high f^{+} values. Density of electron as shown in Fig. 8***c*** is saturated over creatinine molecule, thus we ought to expect level-lying adsorption [30].

2.5.3. Mulliken charge

The electron in the outer shell orbital for nitrogen and oxygen can be effectively gives its electron to the unoccupied orbital of the metal [35]. It could be promptly watched that N, O and some C-atoms have negative charge and this negative electron density would be easy electrophiles attach [36]. Consequently, these atoms would be active centers have the very good ability to bonging with the metal. Alternately, atoms that carry positive charges, which are regularly destinations where nucleophiles can attach. So, Iron can accept unpaired electrons from creatinine and also accepted electrons from Iron. Many researchers reported that the good inhibitors offer electrons to the metal empty orbitals and also accept unpaired [37-42]. The data got indicate that the highest-charge in creatinie molecule is at [N(HN=CH-) -0.3235)] the next charge one is at [N(-N-CH_3) -0.285], [O -

0.2777], [N(-C-NH-) -0. 2509] and [C(-CH_2-) (-0.1602)].These data indicate clearly that these four atoms are very active toward reaction with the metal.

3. EXPERIMENTAL SECTION

3.1. Gravimetric Experiments

3.1.1. Mild steel specimens.

MS specimen composition was as follows: Carbon, 0.21; Aluminium, 0.01: Silicon, 0.38: Phosphorous, 0.09: Sulfur, 0.05: Manganese, 0.05 and Iron, 99.21. The specimen was cleaned according to procedure G1-03 that mentioned in reference [43].

3.1.2. Weight loss method

The MS utilized in our study was in rectangular-shape with dimensions $25*10^{-1}$ cm length; $20*10^{-1}$ cm width and $25*10^{-3}$ cm density. Specimen in duplicate was immersed in 200 mL of the examined solution, in presence and absence of creatinine of various conc. ($0*10^{-2}$mM, $5*10^{-2}$mM, $10*10^{-2}$mM, $15*10^{-2}$mM, $20*10^{-2}$, $25*10^{-2}$mM and $50*10^{-2}$mM), for 1, 2, 3, 4, 5, 10 and 24 h. Specimen weight was determined before suspended and also after suspended. IE of MS was determined utilizing the average of the duplicate value utilizing equation 4.

$$\text{Inhibition Efficiency (IE \%)} = \left[1 - \frac{w_2}{w_1}\right] \text{x } 100 \quad (4)$$

w_1 and w_2 are the weight loss of the MS in presence and absence of creatinine respectively.

The corrosion rate (CR) was calculated [44] from equation 5.

$$CR\ (mpy) = 87.6W / \rho\ A\ t \quad (5)$$

where w is the weight loss in mg, ρ is the density of mild steel in g/cm^3, A is the area of specimen and t is the time of immersion.

Specimen was also immersed in 200 mL of the examined solution in presence and absence of $50*10^{-2}$mM of creatinine for 1 h in the range of temperatures (30,40,50 and 60 °C). The specimen was washed, dried and weighed. IE was calculated using the equation 4.

4. CONCLUSIONS

The consequences of our work revealed that creatinine worked as a very-good inhibitor for mild steel in 1 Molar hydrochloric acid. The inhibition efficiency of creatinine has maximum IE equal

to 95.1% at the highest concentration of creatinine and also, diminishes with a rise in temperature, that mean creatinine is adsorbed over a metal complying with Langmuir adsorption isotherm. Creatinine is demonstrated as an efficient natural inhibitor having great inhibive properties because of presence of N and O atoms. Scanning electron microscopy analysis support formation of a protective-film by creatinine on the mild steel surface. The anticorrosion investigation of creatinine clearly revealed its role in the protection of MS in corrosive solution.

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