Fluoroquinolones as Corrosion Inhibitors for Mild Steel in Acidic Medium; Experimental and Theoretical Studies

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The inhibition of the corrosion of mild steel in H_2SO_4 by some fluoroquinolones is studied using experimental and theoretical methods. Results obtained from the gravimetric method indicate that ciprofloxacin (CFC), norfloxacin (NFC), ofloxacin (OFC) and sparfloxacin (SFC) are good corrosion inhibitors. The adsorption of the inhibitors on mild steel surface is consistent with Langmuir adsorption isotherm. Physical adsorption mechanism is proposed from the calculated thermodynamic parameters for all the compounds studied. Quantum chemical studies indicate that the inhibition potentials of these compounds correlate well with the dipole moment (μ) of the molecules and the fraction of electron transferred from the inhibitor to the metal (δ) and the energy gap (E_{LUMO-HOMO}). Fukui functions, electrostatic potentials and frontier molecular orbitals show the inhibitor absorption preferences. Correlation between the inhibition efficiencies of the compounds indicated that quantitative structure activity relationship (QSAR) can adequately be used to study the inhibition potentials of CFC, NFC, OFC and SFC. Theoretical values of inhibition efficiency (%IE) obtained from QSAR calculations correlated strongly with the experimental %IE. The local reactivity is analyzed through the Fukui function and condensed softness indices in order to compare the possible sites for nucleophilic and electrophilic attacks.

Keywords: Corrosion inhibitors, fluoroquinolones, DFT, fukui functions.

1. INTRODUCTION

A number of heterocyclic compounds containing N, O and S either in the aromatic or long chain carbon system have been reported to be effective inhibitors [1-4]. These inhibitors have

extended π -electron systems and functional groups (such as -C=C-, -OR, -OH, -NR₂, -NH₂ and -SR). The functional groups provide electrons that facilitate the adsorption of the inhibitor on the metal surface [5-10]. Some drugs (such as ampicillin, ampiclox, cloxacillin, tetracycline, methocarbamol, orphenadrine, penicillin G, azithromycin, etc) have been found to be good inhibitors for the corrosion of metals. Many authors generally agree that drugs are inhibitors that can compete favourably with green corrosion inhibitors and that most drugs can be synthesised from natural products. The choice of some drugs used as corrosion inhibitors is based on the following: (a) drug molecules contain oxygen, nitrogen and sulphur as active centres, (b) drugs are reportedly environmentally friendly and important in biological reactions and (c) drugs can be easily produced and purified [11-15].

It has been established that corrosion inhibitors usually promote the formation of a chelate on the metal surface, which include the transfer of electrons from the organic compounds to the metal, forming a donor-acceptor bond during the chemical adsorption process [16-22]. In this adsorption, the metal acts as an electrophile while the inhibitor acts as a nucleophile [23]. Considering the charge transfer characteristics of the adsorption, the wide use of quantum chemical calculations to study this process is justified [24].

The fluoroquinolones are a family of synthetic, broad spectrum antibacterial agents with bactericidal activity. The newer fluoroquinolones have a wider clinical use and a broader spectrum of antibacterial activity including gram-positive and gram-negative aerobic and anaerobic organisms. This constant need for new antimicrobials has produced a variety of newer fluoroquinolones termed / classified as I, II, III and IV generations as well as a handful of relatively similar compounds. The I generation fluoroquinolones include nalixidic acid, oxolinic acid, cinoxacin acid, pipedemic acid and flumequine; the II generation include norfloxacin, ciprofloxacin, enoxacin, fleroxacin, lomefloxacin, ogloxacin, levofloxacin and rufloxacin; the III generation include sparfloxacin, tosufloxacin, gatifloxacin, pazufloxacin and grepafloxacin while the IV generation include trovafloxacin, clinofloxacin, sitafloxacin, moxifloxacin and gemifloxacin. The classifications are based on their chemical structure and their important biological/pharmacological properties [25].

Several investigations of the corrosion inhibitory potentials of fluoroquinolones have lead to the establishment of important trends. For example, ciprofloxacin (CFC) and norfloxacin (NFC) were used as corrosion inhibitor for the protection of 304 stainless steel in 1.5% NaCl solution. The inhibition effect of these compounds was investigated by using electrochemical techniques such as open circuit potential (OCP) and potentiodynamic polarization.

The results obtained reveal that these compounds are very good corrosion inhibitors and show their best performance at a concentration of 1800 ppb. Potentiodynamic curves indicated that these compounds are anodic type of inhibitors [26]. The corrosion inhibition of mild steel in 3.4% NaCl solution by various concentrations of fluoroquinolones, namely, ofloxacin (OFC), amifloxacin, enoxacin, pefloxacin, CFC, and NFC was also investigated by Acharya *et al.* [27].

The inhibition efficiency of these inhibitors was evaluated by weight loss and electrochemical polarization techniques. Morphology of the mild steel specimens was examined using SEM in the presence and absence of the inhibitors. The inhibition efficiency of these compounds increased as the concentration of inhibitors was increased.

In the present study, we investigate the corrosion inhibition activity of CFC, NFC, OFC [II generation type] and sparfloxacin (SFC) [III generation type] by using gravimetric methods. We also explore correlations between advanced quantum chemical concepts and inhibition efficiency.

2. EXPERIMENTAL TECHNIQUES

2.1. Materials

Materials used for the study were mild steel sheet of composition (wt %); Mn (0.6), P (0.36), C (0.15) and Si (0.03) and the rest Fe. The sheet was mechanically pressed cut into different coupons, each of dimensions $5 \times 4 \times 0.11$ (in cm).

Inhibitor	Chemical structure	Formula	Molar mass (g/mol)
1-cyclopropyl- 6-fluoro- 4- oxo-7-piperazin-1-yl- quinoline- 3-carboxylic acid (ciprofloxacin) (CFC)	HO NH	C ₁₇ H ₁₈ FN ₃ O ₃	337.346
1-ethyl-6-fluoro-4-oxo-7- piperazin-1-yl-1 <i>H</i> - quinoline-3-carboxylic acid (norfloxacin) (NFC)		C ₁₆ H ₁₈ FN ₃ O ₃	319.331
7-fluoro-2-methyl-6-(4- methylpiperazin-1-yl)-10-oxo- 4-oxa-1-zatricyclo [7.3.1.0] trideca-5(13),6,8,11-tetraene- 11-carboxylic acid (Ofloxacin) (OFC)		$C_{18}H_{20}FN_{3}O_{4}$	361.368
5-amino-1-cyclopropyl-7- [(3 <i>R</i> ,5 <i>S</i>)3,5-dimethyl piperazin-1-yl]-6,8-difluoro-4- oxo-quinoline-3-carboxylic acid (Sparfloxacin) (SFC)	HO NH2 F WWWW	C ₁₉ H ₂₂ FN ₄ O ₃	392.410

Table 1. Chemical structure and properties of CFC, NFC, OFC and SFC

Each coupon was degreased by washing with ethanol, dipped in acetone and allowed to dry in air before they were preserved in a desicator. All reagents used for the study were Analar grade and double distilled water was used for their preparation.

The inhibitors listed in Table 1 were obtained from Aldrich Chemicals and were used without further purification. The concentrations of the inhibitors used for the study were 0.1 g/l to 0.5 g/l. For all the methods used in the study, each of these inhibitors was dissolved in a 1L solution of 0.1M H_2SO_4 .

2.2. Gravimetric method

In the gravimetric experiment, a previously weighed metal (mild steel) coupon was completely immersed in 250 mL of the test solution in an open beaker. The beaker was inserted into a water bath maintained at 303 K. After every 24 hours, the corrosion product was removed by washing each coupon (withdrawn from the test solution) in a solution containing 50% NaOH and 100g/l of zinc dust. The washed coupon was rinsed in acetone and dried in air. The difference in weight for a period of 168 hours was taken as total weight loss. From the weight loss results, the inhibition efficiency (%IE) of the inhibitor and degree of surface coverage (θ) were calculated using equations 1 and 2 [25];

$$\% IE = (1 - W_1 / W_2) \times 100$$
 (1)

$$\theta = 1 - W_1 / W_2 \tag{2}$$

where W_1 and W_2 are the weight losses (g) for mild steel in the presence and absence of the inhibitor in H_2SO_4 solution and θ is the degree of surface coverage of the inhibitor.

2.3. Computational technique

Full geometry optimization of the four molecules is carried out at different levels of theory, including Restricted Hartree-Fock (RHF), AM1 semi-empirical, and Density Functional Theory (DFT). The RHF and AM1 calculations are performed using the MOPAC 2000 software of CS ChemOffice software package version 8 for Windows [29] on an IBM compatible Intel Pentium IV 2.8 GHz computer. The DFT calculations are carried out using both the DMol³ of Accelrys Materials Studio software suite [30] and the Gaussian 03 computational chemistry software package [31]. For the DMol³ calculations, we employ the generalized gradient corrected BLYP functional [32] and the double numerical basis set with polarization functions on hydrogen atoms (DNP) [33]. For the Gaussian 03 calculations, we employ the hybrid B3LYP exchange-correlation functional [34] and the double- ζ 6-31G** basis set [35].

Statistical analyses were performed using SPSS program version 15.0 for Windows. Non-linear regression analyses were performed by unconstrained sum of squared residuals for loss function and estimation methods of Levenberg-Marquardt using SPSS program version 15.0 for Windows.

2.4. Quantum chemical parameter definitions

From the values of total electronic energy, the ionization potential (IP) and electron affinity (EA) of the inhibitors are calculated using equations 3 and 4.

$$IP = E_{(N-1)} - E_{(N)}$$
(3)

$$EA = E_{(N)} - E_{(N+!)}$$
 (4)

where $E_{(N-1)}$, $E_{(N)}$ and $E_{(N+1)}$ are the ground state energies of the system with N-1, N and N+1 electrons respectively. The global softness is evaluated as S = 1/(IP - EA), as follows [36]:

$$S = 1/[(E_{(N-1)} - E_{(N)}) - (E_{(N)} - E_{(N+1)})]$$
(5)

From the finite difference approximation for 0.1 electrons equation 5 is modified to:

$$S = 0.1 / [(E_{(N+0.1)} - E_{(N)}) - (E_{(N)} - E_{(N-0.1)})],$$
(6)

where $E_{(N+0.1)}$, $E_{(N)}$) and $E_{(N-0.1)}$ are the ground state electronic energies of the system with charge of +0.1 lel, 0.0 lel, and -0.1 lel, respectively. Wave function and total electronic energy calculations using partial charges are only possible in DMol³.

The fraction of electron transferred, δ can be evaluated using the following equation:

$$\delta = (\chi_{\rm Fe} - \chi_{\rm inh})/2(\eta_{\rm Fe} + \eta_{\rm inh}), \qquad (7)$$

where χ_{Fe} and χ_{inh} are the electronegativity values of the inhibitor and Fe, respectively. The electronegativity χ is calculated as $\chi = (IP + EA)/2$. η_{Fe} and η_{inh} are the global hardness of Fe and the inhibitor, respectively. In this study, we use the theoretical value of $\chi_{Fe} = 7.0$ eV and $\eta_{Fe} = 0$ for the computation of δ [37, 38].

Fukui functions which can be expressed using the finite difference approximation, as follows:

$$f_x^+ = q_{(N+1)} - q_{(N)}$$
 (8)

$$f_x = q_{(N)} - q_{(N-1)}$$
 (9)

where $q_{(N+1)}$, $q_{(N)}$ and $q_{(N-1)}$ are the Mulliken or Hirshfeld charge of the atom with N+1, N and N-1 electrons. In the finite difference approximation, the condensed Fukui functions [39] of atom *x* in a molecule that contains N electrons are defined in equations 10 and 11.

$$f_x^{+} = 10 [q_x(N+0.1) - q_x(N)] \qquad (for nucleophilic attack) \qquad (10)$$

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$$f_x = 10 [q_x(N) - q_x(N-0.1)]$$
 (for electrophilic attack) (11)

From the viewpoint of the simplest molecular orbital theory model, additional electrons would occupy the lowest unoccupied molecular orbital (LUMO), whereas upon ionization electrons would be removed from the highest occupied molecular orbital (HOMO). Thus, it would be expected to some extent that f_N^+ and f_N^- be related the LUMO and HOMO, respectively. However, the Fukui function includes information not only about the frontier molecular orbitals but also about the orbital relaxation, which is the change in the orbital shape that accompanies the addition and removal of electrons from the system.

The local softness, S_x for atom x is the product of the condensed Fukui function (f_x) and the global softness (S), as shown in equations 12 and 13;

$$S_x^+ = (f_x^+) S$$
 (12)

$$\mathbf{S}_{\mathbf{x}}^{-} = (\mathbf{f}_{\mathbf{x}}) \mathbf{S} \tag{13}$$

It is important to note that of all methods tested; only the DFT implemented in the DMol³ software allows calculation wave functions for systems with non-integer charges and advanced quantum chemical functions by using the finite difference approximation. More details on reactivity indices are available elsewhere [40].

3.0. RESULTS AND DISCUSSION

3.1. Adsorption and inhibition studies

Fig. 1 shows the variation of weight loss with time for the corrosion of mild steel in 0.1M H₂SO₄ containing 0.5 g/l of each fluoroquinolone used as inhibitors listed in Table 1.

From the plots, it can be seen that the weight loss of mild steel (for the blank solution) increases as the time elapsed is increased, indicating that the rate of corrosion of mild steel also increases as the contact period is increased. Values of inhibition efficiency of various concentrations of CFC, NFC, OFC and SFC are presented in Table 2. Table 2 shows indicate that inhibition efficiencies increase as the inhibitor concentration is increased and follow the order, NFC \approx OFC \approx CFC > SFC. The mean %IE for NFC, OFC and CFC are very close or nearly the same.

For adsorption inhibitors, the inhibition efficiency of the inhibitor tends to increase as the concentration is increased [26]. The observed trend for the decrease in inhibition efficiency differs from the trend obtained by Acharya *et al.* [27]. In their study, the inhibition efficiencies were found to follow the order, OFC > amifloxacin > enoxacin > pefloxacin > CFC > NFC. The difference could be due to the studied media. Acharya *et al.* [27] used NaCl as the aggressive environment, different from H_2SO_4 used in the present study.

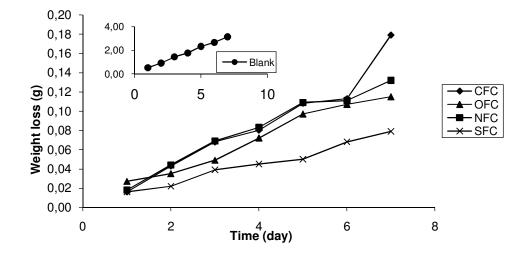


Figure 1. Variation of weight loss with time for the corrosion of mild steel in 0.1 M H₂SO₄ containing 0.5g/l of each fluoroquinolone used as inhibitors at 303 K (Insert is plot for the blank)

Conc. (g/l)	CFC	NFC	OFC	SFC
0.1	91.12	94.32	92.62	79.68
0.2	91.89	92.21	94.2	80.20
0.3	92.62	95.83	94.68	92.66
0.4	94.36	97.56	95.67	94.65
0.5	95.74	98.94	96.31	97.47
Mean	93.15	95.77	94.70	88.93

Table 2: Experimental Inhibition efficiency (%IE) of the inhibitors at 303K.

The adsorption behaviour of the inhibitors was studied by fitting the experimental data obtained for the degree of surface coverage (equation 2) into different adsorption isotherms namely, Langmuir, Temkin, Flory-Huggins, Bockris-swinkel, El Awardy et al., Frumkin and Freundlich isotherms. The tests revealed that the adsorption characteristics of the inhibitors are best described by the Langmuir adsorption isotherm.

The Langmuir adsorption isotherm equation can be written as follows:

 $\log(C/\theta) = \log C - \log K \tag{14}$

where C is the concentration of the inhibitor in the bulk electrolyte, θ is the degree of surface coverage of the inhibitor and K is the equilibrium constant of adsorption. From equation 14, plots of log(C/ θ) versus logC were linear as shown in Fig. 2 for the compounds studied.

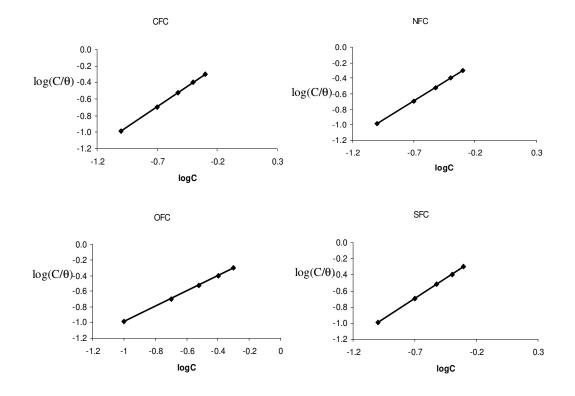


Figure 2. Langmuir isotherm for the adsorption of CFC, NFC, OFC and SFC on mild steel surface

Inhibitor	logK	Slope	ΔG _{ads} (kJ/mol)	\mathbf{R}^2
CFC	-0.001	0.967	-10.09	0.99
NFC	0.014	0.971	-15.89	0.99
OFC	0.010	0.977	-15.90	0.99
SFC	-0.029	0.861	-9.93	0.99

Table 3. Langmuir parameters for the adsorption of CFC, NFC, OFC and SFC on mild steel surface

Values of Langmuir adsorption parameters obtained from the plots are recorded in Table 3. The results indicate that the slopes and R^2 values were very close to unity indicating strong adherence of

adsorption data to the Langmuir isotherm model. Our results agree with an earlier study carried out in 1M HCl medium by Pang et al. [28].

The equilibrium constant of adsorption (K) obtained from the intercept of the Langmuir plots is related to the free energy of adsorption (ΔG_{ads}) as follows [29];

$$\Delta G_{ads} = -2.303 \text{RT} \log (55.5 \text{K})$$
 (15)

where 55.5 is the molar concentration of water in solution. Values of ΔG_{ads} calculated from equation 15 are recorded in Table 3. The absolute values of ΔG_{ads} decrease in the order NFC ~ OFC > CFC > SFC. These values indicate that the inhibitor adsorption on mild steel surface is spontaneous and the interaction between the inhibitor and the mild steel surface is strong. Generally, values of ΔG_{ads} around -20 kJ/mol are consistent with the electrostatic interaction between the charged molecules and the charged metal (physical adsorption) whereas those more negative than -40 kJ/mol involves charge sharing or transfer from the inhibitor's molecule to the metal surface leading to the formation of a donor-acceptor bond (chemical adsorption). For the compounds investigated in this study, ΔG_{ads} values ranged from -9.93 to -15.90 kJ/mol, indicating that the adsorption of the inhibitors is physical [30].

3.2. Global reactivity

In Table 4, we list the values of selected quantum chemical parameters calculated for these inhibitor molecules by using DFT methods.

Parameters	CFC	NFC	OFC	SFC
E _{HOMO} (eV)	-5.57 (-4.92) ^a	-5.72 (-4.89)	-5.25 (-4.45)	-5.04 (-4.72)
E _{LUMO} (eV)	-1.34 (-2.13)	-1.25 (-2.10)	-1.20 (-2.08)	-1.13 (-2.03)
E _{L-H} (eV)	4.23 (2.79)	4.47 (2.79)	4.05 (2.37)	3.91 (2.69)
μ (Debye)	8.16 (10.27)	9.68 (10.38)	9.81 (10.60)	7.71 (6.21)
TEE (Ha)	-1148.381 (-1148.463)	-1110.309 (-1110.394)	-1262.934 (-1263.027)	-1381.595 (-1381.715)
IP (eV)	7.20 (4.93)	7.21 (4.92)	6.42 (4.46)	6.81 (4.70)
EA (eV)	-0.31 (2.16)	-0.34 (2.13)	-0.05 (2.11)	-0.43 (2.05)
χ (eV)	3.44 (3.54)	3.43 (3.53)	3.19 (3.28)	3.19 (3.38)
η (eV)	7.51 (2.77)	7.55 (2.79)	6.47 (2.35)	7.24 (2.65)
$S(Ha^{-1})$	3.62 (9.80)	3.61 (9.75)	4.20 (11.53)	3.76 (10.26)
δ	0.24 (0.62)	0.24 (0.62)	0.29 (0.79)	0.26 (0.68)

Table 4. Quantum chemical parameters of the inhibitors calculated using Gaussian 99/B3LYP/6-31G** (DMol³/DNP/BLYP)^a.

According to Eddy *et al.* [44], the adsorption power and hence the inhibition efficiency of an inhibitor increases as the value of the dipole moment (μ) decreases. Our results, indicate that the value of μ for the studied inhibitors increases according to the trend, SFC < CFC < NFC < OFC, in

agreement with the increase orders of both the inhibition efficiency and the adsorption energy. The values of the fraction of electrons transferred (δ) suggest that the inhibitor electron donor strength increases in the same order as the dipole moment [45, 46]. The value of δ showed inhibition effect resulting from electrons donation which agrees with the study by Lukovits *et al.* [45] which reported that if $\delta < 3.6$ (as obtained in this study), the inhibition efficiency increased as the electron donating ability at the metal surface increases. In this study therefore, the fluoroquinolones are the electron donors and the mild steel surface was the acceptor thereby binding the fluoroquinolones to the mild steel resulting in inhibition adsorption layer against corrosion.

The HOMO energy (E_{HOMO}) is often associated with the electron donating ability of the molecule, whereas the E_{LUMO} indicates the ability of the molecule to accept electron. Therefore, high values of the E_{HOMO} indicate an increased tendency of the inhibitor to donate electron to the vacant d orbital of Fe in mild steel. According to Wang *et al.* [42], high values of the E_{HOMO} facilitate adsorption and enhance inhibition efficiency by influencing the transport process through the adsorbed layer. The molecular orbital energies (and the functions derived from these) obtained by using Gaussian 03 and DMol³ differ substantially but the trends are quite similar. The highest E_{HOMO} values are obtained for OFC and SFC, which are the strongest and the weakest inhibitor, respectively. This suggests that substantial differences in the inhibitor structure could be having strong effects on the orbital energies and occupancies. In fact, SFC differs from the rest in containing an extra F atom bonded to the quinoline moiety and is a III generation type fluoroquinolone. Large values of the energy gap ($E_{L-H} = E_{LUMO} - E_{HOMO}$) implies increased electronic stability and low reactivity, while low values render good inhibiting efficiency because the energy to remove an electron from the last occupied orbital will be low [32]. The inhibitor energy gap increases in the order OFC < SFC < CFC < NFC, indicating that that least stable molecule is the strongest inhibitor.

The values of IP, EA and S calculated from the above equations are recorded in Table 4. As expected, there are some similarities in the trends between the above parameters and frontier orbital molecular energies. The global softness S increases in the order SFC < NFC ~ CFC < OFC, as calculated by using Gaussian 03, suggesting that softer molecules are stronger inhibitors. The trend obtained by using DMol³ differs in the position of the SCF inhibitor.

In Fig. 3, we present the optimized structures and the HOMO and LUMO diagrams of CFC, NFC, OFC and SFC obtained by using DMol³. The spatial distribution of the HOMO and the LUMO are important for understanding the adsorption preferences of the inhibitors. Considering that the inhibitors would be electron donors with respect to the steel surface, the HOMO distribution would be of particular importance. The HOMO distribution maps of CFC and NFC are very similar and show localization near the O2 site and the carboxyl groups, suggesting that these sites could be involved in adsorption. The HOMO of OFC is localized on the piperazine moiety, suggesting strong docking to the N2 site. The HOMO of SFC is localized on the benzene ring of quinoline and the amine group. The LUMOs of all four inhibitors have very similar spatial distributions.

In Fig. 4, we show the electrostatic potentials (ESP) and Fukui functions of CFC, NFC, OFC and SFC mapped on the electron density surfaces. In these maps, the minima and maxima are shown in blue and red colours, respectively. For the ESP maps, the negatively charged blue regions are near heteroatoms. These electron-rich areas would be preferred sites for adsorption to metal surfaces. The

maxima of the nucleophilic Fukui functions f^+ indicate the preferred sites for adsorption of nucleophilic agents.

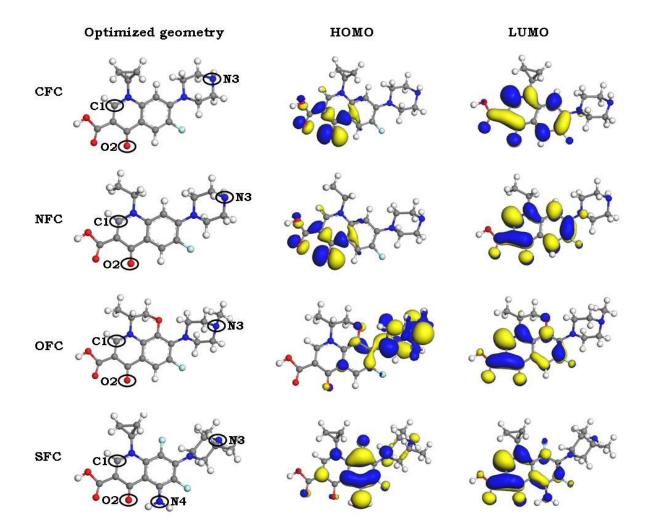


Figure 3. Optimized geometry and schematic diagrams of the HOMO and the LUMO of CFC, NFC, OFC and SFC.

The maxima of the electrophilic Fukui functions f indicate the preferred sites for adsorption of electrophilic agents, such as metal surfaces. For CFC and NFC, the f maxima are near site O2, whereas for OFC the maxima are delocalized near the piperazine moiety and the methyl group. For SFC, the f maxima show the largest extent of delocalization, which can be correlated with low inhibition efficiency. The definition of f suggests that it is related to the HOMO. However, the f also contains information on orbital relaxation upon addition of a fraction of an electron and is considered more informative than the HOMO [40, 47].

It is noteworthy that not only the π electron of the inhibitors enter unoccupied orbitals of Fe but the π^* orbital can also accept the electrons of d-orbitals of metallic Fe to form π -back bonds. In order to establish the formation of a feedback bond, a linear regression analysis was performed on the average inhibition efficiency versus the HOMO energy (E_{HOMO}) and LUMO energy (E_{LUMO}) of the inhibitors and the following equation was obtained;

$$\% IE = 0.006 E_{HOMO} - 0.009 E_{LUMO} + 1.1153$$
(16)

The implication of equation 16 is that inhibition efficiency increases as the values of E_{HOMO} increase but decreases as the values of E_{LUMO} decrease. The positive coefficient of E_{HOMO} and the negative coefficient of E_{LUMO} suggest that the formation of a feedback bond is dependent on the ability of the inhibitor to offer electrons.

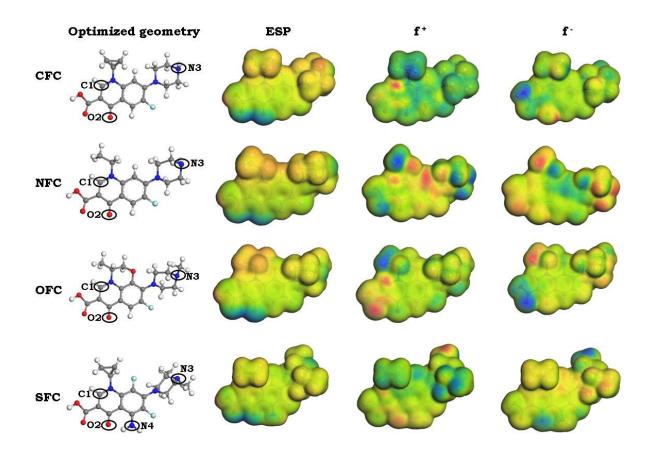


Figure 4. Electrostatic potential (ESP) and Fukui functions of CFC, NFC, OFC and SFC mapped on the 0.017 e/Å³ electron density surface calculated by using the DMol³/PBE/DNP method. The ESP, f^- , and f^+ minima to maxima values are mapped in blue to red colours, respectively.

3.3. Local reactivity

The local reactivity can be analysed using the atomic charges, condensed Fukui functions and local softness that enable us to distinguish each part of the molecule on the basis of its distinct chemical behaviour due to different substituent functional groups. The Fukui function is motivated by

the fact that if an electron δ is transferred to an N electron molecule, it will tend to distribute so as to minimize the energy of the resulting N + δ electron system [40].

Table 5.(part I) Optimized geometry, atomic charges (q), condensed (atomic) Fukui functions (f+ and f-) and local softness indices (s+ and s-) for **CFC** calculated by using the Mulliken (M) and Hirshfeld (H) population analysis methods and DMol³/DNP/BLYP.

Atom	#	X (Å)	Y (Å)	Z (Å)	q(M)	q(H)	f-(M)
С	1	-3.498	0.421	-0.197	0.119	0.023	0.028
0	2	-3.407	-3.187	0.081	-0.418	-0.263	0.178
Ν	3	5.307	0.113	-0.060	-0.407	-0.163	0.057
С	4	4.849	-1.196	0.414	-0.027	-0.018	-0.016
С	5	3.390	-1.211	0.869	-0.028	-0.022	-0.023
Ν	6	2.514	-0.688	-0.197	-0.393	-0.061	0.040
С	7	2.915	0.651	-0.631	-0.045	-0.021	-0.027
С	8	1.146	-0.965	-0.111	0.170	0.038	0.013
С	9	0.165	0.039	-0.159	-0.176	-0.077	0.021
С	10	-1.206	-0.270	-0.132	0.217	0.037	0.020
С	11	-1.639	-1.608	-0.045	-0.075	-0.026	0.019
С	12	-0.662	-2.617	0.004	-0.106	-0.044	0.008
С	13	0.673	-2.302	-0.035	0.336	0.075	0.027
Ν	14	-2.178	0.747	-0.176	-0.333	0.006	0.008
С	15	4.386	0.642	-1.065	-0.020	-0.018	-0.015
С	16	-3.996	-0.860	-0.122	-0.138	-0.045	0.013
С	17	-3.073	-2.002	-0.021	0.304	0.099	0.034
С	18	-5.459	-1.052	-0.145	0.480	0.173	0.025
0	19	-6.145	0.158	-0.163	-0.460	-0.183	0.023
0	20	-6.063	-2.108	-0.150	-0.386	-0.252	0.049
С	21	-1.780	2.135	-0.329	-0.003	0.019	-0.024
Н	22	4.481	0.019	-1.969	0.095	0.038	0.029
Н	23	4.693	1.663	-1.335	0.083	0.042	0.039
Н	24	5.357	0.761	0.731	0.171	0.095	0.027
Н	25	5.496	-1.524	1.240	0.086	0.045	0.039
Н	26	4.973	-1.916	-0.411	0.097	0.038	0.028
Н	27	3.276	-0.583	1.778	0.060	0.021	0.043
Н	28	3.083	-2.231	1.125	0.130	0.036	0.025
Н	29	2.282	0.948	-1.479	0.100	0.041	0.026
Н	30	2.775	1.397	0.182	0.059	0.020	0.042
Н	31	0.476	1.079	-0.191	0.102	0.032	0.029
Н	32	-0.995	-3.655	0.043	0.130	0.058	0.032
Н	33	-4.175	1.267	-0.278	0.129	0.048	0.037
Н	34	-7.084	-0.111	-0.192	0.266	0.163	0.034
С	35	-2.532	3.214	0.400	-0.186	-0.064	0.002
Н	36	-2.706	4.147	-0.135	0.110	0.055	0.027
Н	37	-3.340	2.915	1.067	0.122	0.055	0.010
С	38	-1.131	2.862	0.823	-0.171	-0.069	-0.004
Н	39	-1.018	2.308	1.755	0.118	0.052	0.007
Н	40	-0.317	3.552	0.596	0.105	0.051	0.020
Н	41	-1.417	2.368	-1.333	0.109	0.050	0.024
F	42	1.582	-3.321	-0.049	-0.324	-0.082	0.028

Table 5.(j	part II)
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Atom	#	f-(H)	f+(M)	f+(H)	s-(M)	s-(H)	s+(M)	s+(H)
С	1	0.028	0.131	0.109	2.770	2.770	12.961	10.784
0	2	0.173	0.075	0.074	17.611	17.117	7.421	7.322
Ν	3	0.057	0.015	0.012	5.640	5.640	1.484	1.187
С	4	0.014	-0.007	0.006	-1.583	1.385	-0.693	0.594
С	5	0.014	-0.022	0.006	-2.276	1.385	-2.177	0.594
Ν	6	0.044	0.018	0.019	3.958	4.353	1.781	1.880
С	7	0.013	-0.024	0.004	-2.671	1.286	-2.375	0.396
С	8	0.020	0.029	0.035	1.286	1.979	2.869	3.463
С	9	0.023	0.051	0.045	2.078	2.276	5.046	4.452
С	10	0.019	0.008	0.012	1.979	1.880	0.792	1.187
С	11	0.026	-0.004	0.009	1.880	2.572	-0.396	0.890
С	12	0.017	0.050	0.047	0.792	1.682	4.947	4.650
С	13	0.026	0.041	0.045	2.671	2.572	4.057	4.452
Ν	14	0.019	0.008	0.035	0.792	1.880	0.792	3.463
С	15	0.014	-0.007	0.007	-1.484	1.385	-0.693	0.693
С	16	0.020	0.021	0.045	1.286	1.979	2.078	4.452
С	17	0.039	0.044	0.044	3.364	3.859	4.353	4.353
С	18	0.017	0.036	0.032	2.474	1.682	3.562	3.166
0	19	0.035	0.013	0.023	2.276	3.463	1.286	2.276
0	20	0.053	0.065	0.063	4.848	5.244	6.431	6.233
С	21	0.000	-0.037	0.000	-2.375	0.000	-3.661	0.000
Н	22	0.015	0.015	0.008	2.869	1.484	1.484	0.792
Н	23	0.020	0.025	0.012	3.859	1.979	2.474	1.187
Н	24	0.022	0.010	0.008	2.671	2.177	0.989	0.792
Н	25	0.020	0.025	0.013	3.859	1.979	2.474	1.286
Н	26	0.015	0.013	0.007	2.770	1.484	1.286	0.693
Н	27	0.022	0.027	0.012	4.254	2.177	2.671	1.187
Н	28	0.011	0.009	0.005	2.474	1.088	0.890	0.495
Н	29	0.012	0.009	0.003	2.572	1.187	0.890	0.297
Н	30	0.021	0.022	0.010	4.155	2.078	2.177	0.989
Н	31	0.014	0.036	0.020	2.869	1.385	3.562	1.979
Н	32	0.018	0.043	0.027	3.166	1.781	4.254	2.671
Н	33	0.021	0.055	0.042	3.661	2.078	5.442	4.155
Н	34	0.025	0.038	0.026	3.364	2.474	3.760	2.572
С	35	0.012	-0.004	0.014	0.198	1.187	-0.396	1.385
Н	36	0.014	0.036	0.019	2.671	1.385	3.562	1.880
Н	37	0.007	0.012	0.009	0.989	0.693	1.187	0.890
С	38	0.008	0.000	0.014	-0.396	0.792	0.000	1.385
Н	39	0.004	0.013	0.008	0.693	0.396	1.286	0.792
Н	40	0.010	0.034	0.018	1.979	0.989	3.364	1.781
Н	41	0.010	0.044	0.018	2.375	0.989	4.353	1.781
F	42	0.029	0.036	0.037	2.770	2.869	3.562	3.661

In Tables 5 to 8, we present the calculated values of the atomic charges, f_x^+ and f_x^- for CFC, NFC, OFC and SFC. The largest negative atomic charges are calculated for O2, N2, N3, and the carboxyl group atoms. As a rule, the preferred site for an attack by an electrophillic and nucleophillic agents will be the place where the value of f_x^- or f_x^+ is maximum.

Table 6.(part I) Optimized geometry, atomic charges (q), condensed (atomic) Fukui functions (f+ and f-) and local softness indices (s+ and s-) for **NFC** calculated by using the Mulliken (M) and Hirshfeld (H) population analysis methods and DMol³/DNP/BLYP.

Atom	#	X (Å)	Y (Å)	Z (Å)	q(M)	q(H)	f-(M)
С	1	3.450	0.491	0.012	0.103	0.021	0.032
0	2	3.346	-3.126	-0.143	-0.420	-0.264	0.183
Ν	3	-5.350	0.194	0.100	-0.407	-0.163	0.051
С	4	-4.444	0.818	-0.865	-0.019	-0.018	-0.014
С	5	-2.966	0.781	-0.458	-0.047	-0.021	-0.026
Ν	6	-2.562	-0.594	-0.165	-0.393	-0.061	0.035
С	7	-3.423	-1.223	0.856	-0.027	-0.022	-0.021
С	8	-1.194	-0.880	-0.120	0.171	0.038	0.017
С	9	-0.210	0.122	-0.064	-0.174	-0.077	0.019
С	10	1.162	-0.187	-0.067	0.215	0.037	0.021
С	11	1.588	-1.531	-0.108	-0.075	-0.025	0.019
С	12	0.610	-2.537	-0.169	-0.106	-0.043	0.008
С	13	-0.725	-2.218	-0.183	0.336	0.076	0.025
Ν	14	2.136	0.826	-0.003	-0.348	0.006	0.007
С	15	-4.890	-1.159	0.430	-0.028	-0.018	-0.014
С	16	3.943	-0.796	-0.035	-0.138	-0.047	0.018
С	17	3.019	-1.935	-0.101	0.306	0.098	0.035
С	18	5.405	-0.990	-0.017	0.479	0.172	0.029
0	19	6.094	0.219	0.035	-0.464	-0.185	0.019
0	20	6.008	-2.046	-0.044	-0.387	-0.253	0.050
С	21	1.697	2.237	0.049	-0.039	0.007	-0.017
Н	22	-5.031	-1.791	-0.462	0.097	0.039	0.026
Н	23	-5.524	-1.567	1.229	0.086	0.045	0.036
Н	24	-5.375	0.759	0.954	0.171	0.095	0.023
Н	25	-4.752	1.862	-1.024	0.083	0.043	0.036
Н	26	-4.559	0.290	-1.826	0.095	0.038	0.027
Н	27	-2.811	1.446	0.421	0.059	0.020	0.039
Н	28	-2.346	1.159	-1.283	0.100	0.041	0.024
Н	29	-3.115	-2.263	1.001	0.130	0.036	0.021
Η	30	-3.293	-0.691	1.823	0.060	0.021	0.040
Η	31	-0.538	1.155	0.008	0.088	0.034	0.031
Н	32	0.944	-3.574	-0.228	0.131	0.058	0.032
Н	33	4.146	1.321	0.063	0.141	0.045	0.039
Н	34	7.033	-0.055	0.041	0.266	0.163	0.037
С	35	2.809	3.271	0.126	-0.272	-0.086	-0.011
Н	36	3.468	3.244	-0.751	0.110	0.048	0.012
Н	37	2.343	4.265	0.159	0.102	0.053	0.028
Н	38	1.039	2.346	0.925	0.113	0.044	0.021
Н	39	1.082	2.423	-0.846	0.113	0.044	0.021
Н	40	3.419	3.161	1.032	0.110	0.048	0.012
F	41	-1.635	-3.228	-0.301	-0.323	-0.082	0.030

Table 6.(part II)

Atom	#	f-(H)	f+(M)	f+(H)	s-(M)	s-(H)	s+(M)	s+(H)
С	1	0.031	0.119	0.101	3.140	3.042	11.677	9.911
0	2	0.185	0.085	0.078	17.958	18.154	8.341	7.654
Ν	3	0.051	0.014	0.013	5.005	5.005	1.374	1.276
С	4	0.013	-0.008	0.007	-1.374	1.276	-0.785	0.687
С	5	0.012	-0.025	0.005	-2.551	1.178	-2.453	0.491
Ν	6	0.038	0.019	0.021	3.435	3.729	1.864	2.061
С	7	0.013	-0.025	0.006	-2.061	1.276	-2.453	0.589
С	8	0.022	0.031	0.038	1.668	2.159	3.042	3.729
С	9	0.023	0.056	0.050	1.864	2.257	5.495	4.907
С	10	0.019	0.009	0.014	2.061	1.864	0.883	1.374
С	11	0.024	-0.007	0.011	1.864	2.355	-0.687	1.079
С	12	0.016	0.057	0.053	0.785	1.570	5.593	5.201
С	13	0.027	0.042	0.046	2.453	2.650	4.121	4.514
Ν	14	0.022	0.006	0.032	0.687	2.159	0.589	3.140
С	15	0.012	-0.008	0.006	-1.374	1.178	-0.785	0.589
С	16	0.023	0.015	0.041	1.766	2.257	1.472	4.023
С	17	0.042	0.046	0.045	3.435	4.121	4.514	4.416
С	18	0.020	0.032	0.028	2.846	1.963	3.140	2.748
0	19	0.033	0.018	0.026	1.864	3.238	1.766	2.551
0	20	0.057	0.064	0.059	4.907	5.593	6.280	5.790
С	21	0.007	-0.034	0.008	-1.668	0.687	-3.336	0.785
Н	22	0.014	0.014	0.007	2.551	1.374	1.374	0.687
Н	23	0.019	0.026	0.013	3.533	1.864	2.551	1.276
Н	24	0.020	0.012	0.008	2.257	1.963	1.178	0.785
Н	25	0.019	0.026	0.013	3.533	1.864	2.551	1.276
Н	26	0.014	0.015	0.008	2.650	1.374	1.472	0.785
Н	27	0.019	0.023	0.011	3.827	1.864	2.257	1.079
Н	28	0.012	0.009	0.004	2.355	1.178	0.883	0.393
Н	29	0.011	0.010	0.004	2.061	1.079	0.981	0.393
Н	30	0.020	0.029	0.013	3.925	1.963	2.846	1.276
Н	31	0.015	0.039	0.024	3.042	1.472	3.827	2.355
Н	32	0.018	0.045	0.029	3.140	1.766	4.416	2.846
Н	33	0.020	0.048	0.037	3.827	1.963	4.710	3.631
Н	34	0.025	0.036	0.026	3.631	2.453	3.533	2.551
С	35	0.007	-0.015	0.009	-1.079	0.687	-1.472	0.883
Н	36	0.007	0.015	0.009	1.178	0.687	1.472	0.883
Н	37	0.016	0.039	0.021	2.748	1.570	3.827	2.061
Н	38	0.010	0.034	0.017	2.061	0.981	3.336	1.668
Н	39	0.011	0.036	0.017	2.061	1.079	3.533	1.668
Н	40	0.007	0.016	0.009	1.178	0.687	1.570	0.883
F	41	0.029	0.036	0.038	2.944	2.846	3.533	3.729

Table 7.(part I) Optimized geometry, atomic charges (q), condensed (atomic) Fukui functions (f+ and f-) and local softness indices (s+ and s-) for **OFC** calculated by using the Mulliken (M) and Hirshfeld (H) population analysis methods and DMol³/DNP/BLYP.

Atom	#	X (Å)	Y (Å)	Z (Å)	q (M)	q(H)	f-(M)
С	1	3.446	1.852	0.127	0.101	0.020	0.009
0	2	1.324	4.783	0.305	-0.416	-0.261	0.043
N	3	-4.367	-2.474	0.369	-0.412	-0.099	0.120
С	4	-3.278	-2.431	1.349	0.003	-0.020	-0.030
С	5	-1.942	-1.925	0.783	-0.017	-0.024	-0.024
N	6	-2.159	-0.614	0.168	-0.419	-0.061	0.063
С	7	-3.213	-0.612	-0.858	-0.022	-0.021	-0.020
С	8	-1.171	0.368	0.144	0.133	0.022	-0.018
С	9	0.213	0.100	0.046	0.218	0.042	0.035
С	10	1.167	1.139	0.118	0.175	0.016	0.016
С	11	0.755	2.484	0.194	-0.072	-0.026	0.024
С	12	-0.617	2.769	0.245	-0.123	-0.056	0.016
С	13	-1.526	1.738	0.243	0.342	0.075	0.014
N	14	2.542	0.844	0.089	-0.338	-0.002	-0.005
С	15	-4.515	-1.159	-0.265	-0.012	-0.020	-0.031
С	16	3.128	3.193	0.182	-0.141	-0.046	0.013
С	17	1.719	3.615	0.234	0.305	0.099	0.009
С	18	4.226	4.176	0.194	0.478	0.172	0.010
0	19	5.477	3.564	0.195	-0.464	-0.185	0.008
0	20	4.129	5.388	0.199	-0.387	-0.253	0.025
С	21	2.944	-0.582	0.115	-0.010	0.037	-0.010
Н	22	-4.869	-0.451	0.501	0.097	0.035	0.057
Н	23	-5.287	-1.225	-1.046	0.078	0.041	0.062
Н	24	-3.142	-3.436	1.775	0.075	0.039	0.062
Н	25	-3.588	-1.758	2.165	0.089	0.034	0.059
Н	26	-1.529	-2.653	0.060	0.081	0.019	0.053
Н	27	-1.214	-1.820	1.597	0.096	0.037	0.054
Н	28	-3.366	0.409	-1.221	0.114	0.037	0.051
Н	29	-2.891	-1.227	-1.721	0.074	0.024	0.052
Н	30	-0.930	3.809	0.326	0.128	0.056	0.031
Н	31	4.488	1.553	0.111	0.136	0.046	0.021
Н	32	6.100	4.317	0.197	0.267	0.163	0.018
F	33	-2.851	2.037	0.358	-0.320	-0.082	0.011
С	34	-4.271	-3.580	-0.580	-0.061	-0.062	-0.038
Н	35	-4.251	-4.529	-0.025	0.078	0.038	0.056
Н	36	-5.166	-3.582	-1.218	0.080	0.039	0.055
Н	37	-3.385	-3.563	-1.247	0.049	0.017	0.062
0	38	0.598	-1.214	-0.131	-0.470	-0.102	-0.006
С	39	1.906	-1.351	-0.690	0.102	0.016	-0.015
Н	40	2.885	-0.929	1.161	0.122	0.044	0.011
С	41	4.343	-0.837	-0.430	-0.255	-0.087	-0.003
Н	42	4.459	-0.434	-1.445	0.107	0.047	0.011
Н	43	5.126	-0.408	0.207	0.116	0.051	0.015
Н	44	4.518	-1.920	-0.466	0.102	0.052	0.015
Н	45	1.905	-1.000	-1.737	0.093	0.041	0.019
Н	46	2.126	-2.424	-0.674	0.101	0.055	0.020

Table 7.(part II)

Atom	#	f-(H)	f+(M)	f+(H)	s-(M)	s-(H)	s+(M)	s+(H)
С	1	0.013	0.146	0.116	1.046	1.511	16.971	13.484
0	2	0.040	0.073	0.070	4.998	4.650	8.486	8.137
Ν	3	0.126	0.009	0.007	13.949	14.646	1.046	0.814
С	4	0.026	-0.005	0.005	-3.487	3.022	-0.581	0.581
С	5	0.027	-0.019	0.003	-2.790	3.138	-2.209	0.349
Ν	6	0.061	0.014	0.017	7.323	7.091	1.627	1.976
С	7	0.026	-0.020	0.005	-2.325	3.022	-2.325	0.581
С	8	0.002	0.029	0.029	-2.092	0.232	3.371	3.371
С	9	0.021	0.044	0.032	4.068	2.441	5.115	3.720
С	10	0.014	0.004	0.010	1.860	1.627	0.465	1.162
С	11	0.029	0.005	0.010	2.790	3.371	0.581	1.162
С	12	0.020	0.032	0.035	1.860	2.325	3.720	4.068
С	13	0.011	0.040	0.043	1.627	1.279	4.650	4.998
Ν	14	0.002	0.007	0.039	-0.581	0.232	0.814	4.533
С	15	0.026	-0.005	0.004	-3.603	3.022	-0.581	0.465
С	16	0.015	0.021	0.048	1.511	1.744	2.441	5.580
С	17	0.013	0.037	0.038	1.046	1.511	4.301	4.417
С	18	0.009	0.045	0.042	1.162	1.046	5.231	4.882
0	19	0.012	0.017	0.028	0.930	1.395	1.976	3.255
0	20	0.023	0.076	0.074	2.906	2.674	8.834	8.602
С	21	0.003	-0.023	0.006	-1.162	0.349	-2.674	0.697
Н	22	0.030	0.009	0.005	6.626	3.487	1.046	0.581
Н	23	0.031	0.024	0.011	7.207	3.603	2.790	1.279
Н	24	0.031	0.023	0.012	7.207	3.603	2.674	1.395
Н	25	0.031	0.011	0.005	6.858	3.603	1.279	0.581
Н	26	0.029	0.020	0.009	6.161	3.371	2.325	1.046
Н	27	0.027	0.005	0.001	6.277	3.138	0.581	0.116
Н	28	0.026	0.008	0.003	5.928	3.022	0.930	0.349
Н	29	0.029	0.026	0.012	6.044	3.371	3.022	1.395
Н	30	0.016	0.040	0.023	3.603	1.860	4.650	2.674
Н	31	0.010	0.053	0.041	2.441	1.162	6.161	4.766
Н	32	0.013	0.039	0.028	2.092	1.511	4.533	3.255
F	33	0.013	0.035	0.037	1.279	1.511	4.068	4.301
С	34	0.030	-0.012	0.004	-4.417	3.487	-1.395	0.465
Н	35	0.031	0.017	0.008	6.509	3.603	1.976	0.930
Н	36	0.031	0.018	0.009	6.393	3.603	2.092	1.046
Н	37	0.042	-0.001	0.001	7.207	4.882	-0.116	0.116
0	38	0.004	0.024	0.024	-0.697	0.465	2.790	2.790
С	39	0.005	-0.013	0.010	-1.744	0.581	-1.511	1.162
H	40	0.005	0.042	0.019	1.279	0.581	4.882	2.209
C	41	0.006	-0.021	0.008	-0.349	0.697	-2.441	0.930
Н	42	0.006	0.021	0.008	1.279	0.697	1.627	0.930
Н	43	0.009	0.011	0.009	1.744	1.046	1.744	1.046
Н	44	0.009	0.019	0.021	1.744	0.930	4.533	2.441
Н	45	0.009	0.039	0.011	2.209	1.046	2.557	1.279
Н	46	0.009	0.022	0.020	2.325	1.046	4.417	2.325
	τu	0.007	0.050	0.020	2.323	1.040	7.71/	2.323

Table 8.(part I) Optimized geometry, atomic charges (q), condensed (atomic) Fukui functions (f+ and f-) and local softness indices (s+ and s-) for SFC calculated by using the Mulliken (M) and Hirshfeld (H) population analysis methods and DMol³/DNP/BLYP.

Atom	#	X	У	Z	q(M)	q(H)	f-(M)
С	1	4.065	0.832	0.140	0.122	0.026	0.012
0	2	4.200	-2.763	0.092	-0.477	-0.236	0.032
Ν	3	-4.661	0.203	0.221	-0.392	-0.161	0.056
Ν	4	1.785	-3.686	-0.154	-0.411	-0.157	0.080
С	5	-3.657	1.001	0.942	0.011	0.021	-0.017
С	6	-2.417	0.179	1.313	0.004	-0.025	-0.025
Ν	7	-1.880	-0.499	0.126	-0.417	-0.065	0.042
С	8	-2.861	-1.362	-0.535	0.002	-0.027	-0.026
С	9	-0.518	-0.804	0.085	0.130	0.021	0.013
С	10	0.431	0.249	0.088	0.268	0.044	0.064
С	11	1.810	0.032	0.017	0.179	0.024	0.027
С	12	2.310	-1.308	-0.008	-0.120	-0.043	0.034
С	13	1.377	-2.391	-0.065	0.175	0.042	0.017
С	14	0.006	-2.095	0.000	0.274	0.048	0.039
Ν	15	2.744	1.091	-0.032	-0.346	0.007	0.009
С	16	-4.094	-0.529	-0.921	0.019	0.022	-0.018
С	17	4.611	-0.422	0.268	-0.131	-0.048	0.030
С	18	3.749	-1.597	0.114	0.321	0.099	0.011
С	19	6.059	-0.550	0.515	0.478	0.172	0.015
0	20	6.709	0.676	0.447	-0.457	-0.182	0.010
0	21	6.676	-1.569	0.768	-0.391	-0.257	0.037
С	22	2.344	2.471	-0.297	0.020	0.013	-0.026
Н	23	-3.762	0.235	-1.646	0.088	0.031	0.025
Н	24	-3.328	1.791	0.246	0.094	0.031	0.022
Н	25	-2.699	-0.571	2.083	0.061	0.021	0.044
Н	26	-1.643	0.824	1.743	0.107	0.032	0.020
Н	27	-2.401	-1.797	-1.432	0.098	0.037	0.025
Н	28	-3.183	-2.197	0.118	0.069	0.018	0.040
Η	29	4.700	1.713	0.166	0.131	0.050	0.032
Н	30	7.641	0.456	0.646	0.267	0.164	0.025
С	31	3.192	3.320	-1.205	-0.190	-0.068	0.006
Н	32	3.325	4.366	-0.926	0.106	0.053	0.027
Н	33	4.063	2.868	-1.680	0.118	0.052	0.013
С	34	1.838	2.843	-1.659	-0.153	-0.072	-0.008
Н	35	1.820	2.052	-2.410	0.111	0.051	0.004
Н	36	1.004	3.542	-1.711	0.107	0.051	0.019
Н	37	1.881	2.961	0.560	0.115	0.046	0.019
F	38	-0.839	-3.175	0.048	-0.342	-0.080	0.028
F	39	-0.080	1.517	0.148	-0.332	-0.073	0.042
Н	40	2.799	-3.818	-0.023	0.263	0.090	0.029
Н	41	1.113	-4.418	0.044	0.205	0.118	0.037
С	42	-5.169	-1.398	-1.563	-0.217	-0.098	-0.011
Н	43	-6.041	-0.785	-1.826	0.095	0.039	0.028
Н	44	-4.794	-1.886	-2.473	0.081	0.039	0.020
Η	45	-5.500	-2.187	-0.869	0.071	0.033	0.018
С	46	-4.290	1.642	2.170	-0.218	-0.098	-0.009
Η	47	-3.574	2.298	2.686	0.080	0.039	0.017
Η	48	-5.166	2.237	1.880	0.095	0.040	0.027
Η	49	-4.619	0.876	2.890	0.071	0.033	0.018
Η	50	-5.081	-0.470	0.872	0.163	0.088	0.024

Table 8.(part II)

Atom	#	f-(H)	f+(M)	f+(H)	s-(M)	s-(H)	s+(M)	s+(H)
С	1	0.021	0.143	0.114	1.228	2.149	14.635	11.667
0	2	0.034	0.065	0.062	3.275	3.480	6.652	6.345
Ν	3	0.048	0.011	0.008	5.731	4.912	1.126	0.819
Ν	4	0.081	0.029	0.033	8.187	8.290	2.968	3.377
С	5	0.008	-0.006	0.002	-1.740	0.819	-0.614	0.205
С	6	0.011	-0.014	0.004	-2.559	1.126	-1.433	0.409
Ν	7	0.042	0.011	0.013	4.298	4.298	1.126	1.330
С	8	0.012	-0.017	0.002	-2.661	1.228	-1.740	0.205
С	9	0.019	0.030	0.030	1.330	1.944	3.070	3.070
С	10	0.062	0.040	0.029	6.550	6.345	4.094	2.968
С	11	0.027	0.004	0.011	2.763	2.763	0.409	1.126
С	12	0.032	0.010	0.013	3.480	3.275	1.023	1.330
С	13	0.029	0.018	0.025	1.740	2.968	1.842	2.559
С	14	0.031	0.039	0.033	3.991	3.173	3.991	3.377
Ν	15	0.015	0.011	0.040	0.921	1.535	1.126	4.094
С	16	0.009	-0.006	0.003	-1.842	0.921	-0.614	0.307
С	17	0.030	0.014	0.047	3.070	3.070	1.433	4.810
С	18	0.014	0.042	0.039	1.126	1.433	4.298	3.991
С	19	0.015	0.048	0.043	1.535	1.535	4.912	4.401
0	20	0.017	0.021	0.031	1.023	1.740	2.149	3.173
0	21	0.035	0.077	0.074	3.787	3.582	7.880	7.573
С	22	-0.003	-0.032	0.002	-2.661	-0.307	-3.275	0.205
Н	23	0.011	0.006	0.003	2.559	1.126	0.614	0.307
Н	24	0.009	0.004	0.002	2.251	0.921	0.409	0.205
Н	25	0.022	0.026	0.011	4.503	2.251	2.661	1.126
Н	26	0.009	-0.003	0.000	2.047	0.921	-0.307	0.000
Н	27	0.011	0.004	0.002	2.559	1.126	0.409	0.205
Н	28	0.021	0.022	0.009	4.094	2.149	2.251	0.921
Н	29	0.016	0.056	0.042	3.275	1.637	5.731	4.298
Н	30	0.017	0.040	0.029	2.559	1.740	4.094	2.968
С	31	0.013	-0.006	0.013	0.614	1.330	-0.614	1.330
Н	32	0.015	0.037	0.019	2.763	1.535	3.787	1.944
Н	33	0.008	0.010	0.008	1.330	0.819	1.023	0.819
С	34	0.005	0.004	0.016	-0.819	0.512	0.409	1.637
Н	35	0.002	0.013	0.008	0.409	0.205	1.330	0.819
Н	36	0.009	0.037	0.019	1.944	0.921	3.787	1.944
Н	37	0.007	0.039	0.018	1.944	0.716	3.991	1.842
F	38	0.029	0.031	0.031	2.866	2.968	3.173	3.173
F	39	0.045	0.027	0.023	4.298	4.605	2.763	2.354
Н	40	0.024	0.016	0.014	2.968	2.456	1.637	1.433
Н	41	0.031	0.031	0.022	3.787	3.173	3.173	2.251
С	42	0.009	-0.004	0.005	-1.126	0.921	-0.409	0.512
Н	43	0.015	0.018	0.010	2.866	1.535	1.842	1.023
H	44	0.011	0.007	0.004	2.047	1.126	0.716	0.409
Н	45	0.009	0.010	0.006	1.842	0.921	1.023	0.614
С	46	0.009	-0.005	0.004	-0.921	0.921	-0.512	0.409
Н	47	0.010	0.004	0.003	1.740	1.023	0.409	0.307
Н	48	0.015	0.019	0.010	2.763	1.535	1.944	1.023
Н	49	0.010	0.011	0.006	1.842	1.023	1.126	0.614
Н	50	0.019	0.010	0.007	2.456	1.944	1.023	0.716

From the results, it is evident that the preferred sites for attack by nucleophilic agents in all four inhibitors are near carbon atom C1. The preferred sites for attack by electrophillic agents for CFC and NFC are near the O2 atom. The preferred sites for attack by electrophillic agents for OFC and SFC are near the N3 and O4 atoms, respectively. For SFC, it is particularly interesting to note that the maximum values of the condensed Fukui functions are substantially lower than these for the other three inhibitors, suggesting weaker adsorption. We note that the atoms with highest value of relative nucleophilicity and electrophilicity for the four inhibitors were similar to those obtained for the Fukui functions. The similarity is due to the fact that the condensed local softness indices are proportional to the condensed Fukui function indices, as expressed by equations 12 and 13.

It is particularly interesting to note that the atomic charges calculated by using the Hirshfeld and Mulliken population analysis methods differ substantially and even follow different trends. The charge calculation method also determines the condensed Fukui function trends. The main disadvantage of Mulliken population analysis-derived condensed Fukui functions is that nothing can be predicted about the sign of the f_x and f_x^+ . This is because the Mulliken weight factor to the electron density distribution is system dependent (i.e. depends on whether the system is neutral, cationic or anionic) [48]. Fuentealba *et al.* have stated that negative condensed Fukui functions are unphysical for ground state molecules in their equilibrium geometry [49]. This argument is not proven but having negative f_x^- and f_x^+ values is very unlikely. These authors also admit the local Fukui function does not have to be positive everywhere [49]. The problem of negative condensed Fukui function values becomes very serious if one attempts to calculate Fukui functions for cations and anions, i.e. using fill instead of partial charges.

3.4. Quantitative structure activity relationship (QSAR)

Attempts are made to correlate the calculated quantum chemical parameters with the experimental corrosion inhibition efficiencies of the inhibitors. The test reveals that there is no simple or direct relationship between the two set of parameters. This may be attributed to the complex nature of the interactions in the corrosion inhibition processes. Therefore, a composite index of more than one parameter which might affect the inhibition efficiency of a molecule may be correlated with its corrosion inhibition efficiency. Regression analysis was used to correlate inhibitor's concentration (C_i) and quantum chemical parameters with the average experimental inhibition efficiencies, IE (%).

The linear model approximates corrosion inhibition efficiency $(E_{cal} \%)$ as follows:

$$E_{cal} = Ax_i C_i + B \tag{17}$$

where *A* and *B* are constants obtained by regression analysis; x_j a quantum chemical index characteristic for the molecule *j*; C_i denotes the inhibitor-concentration. Such linear approach was found to be satisfactory for the correlation of the present results. Also, the non-linear model (NLM), proposed by Lukovits and co-workers for the study of the interaction of corrosion inhibitors with metal

surface in acidic medium, was derived from equation 17 based on the Langmuir adsorption isotherm to give the following relationship [41];

$$E_{Cal} = [(AE_{HOMO} + BE_{LUMO} + C\mu - D)C_{inh}]/(1 + (AE_{HOMO} + BE_{LUMO} + C\mu - D)C_{inh}$$
(18)

where A, B, C and D are regression coefficients. The plot of the correlation between theoretically calculated %IE (E_{Cal}) computed from equation 18 and the experimental %IE is presented in Fig. 5.

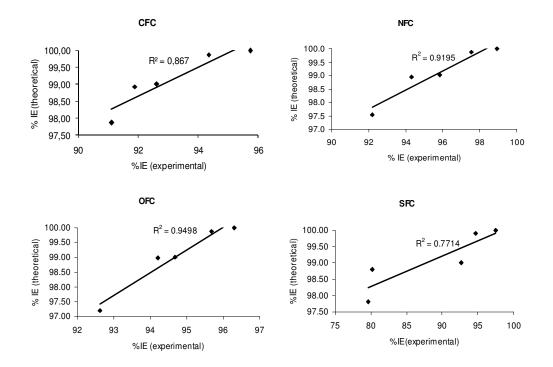


Figure 5. Plot of correlation between the theoretically calculated %IE and experimental %IE

These values correlated well with the experimental values of the inhibition efficiencies ($R^2 = 0.8676, 0.9195, 0.9498, 0.7714$ for CFC, NFC, OFC and SFC, respectively) indicating that the structures of the compounds have significant effect on the inhibition efficiencies.

4. CONCLUSIONS

From the results of the study we conclude the following:

1. The CFC, NFC, OFC and SFC are good adsorption inhibitors for the corrosion of mild steel in H₂SO₄. The adsorption of the inhibitors on mild steel surface favours a physical adsorption mechanism and is best described by Langmuir adsorption isotherm.

- 2. The dipole moment and the fraction of electrons transferred correlate very well with the experimental inhibition efficiency and adsorption energy orders. The LUMO-HOMO energy gap increases as the adsorption strength decreases, suggesting that the inhibitor that has the most stable electronic state is the least efficient. The electrostatic potential and Fukui function maps as well as the molecular orbital spatial distributions are highly informative for determination of the inhibitor adsorption configuration. Local reactivity indices allow quantitative comparison of adsorption preferences.
- 3. The inhibition efficiencies of CFC, NFC, OFC and SFC relate closely with some quantum chemical parameters/descriptors. Our analyses have shown that one quantum-chemically derived parameter is not sufficient in correlating the inhibition activities of these types of molecules. Hence, several parameters or a composite index of more than two or more quantum chemical parameters were taken into consideration to characterize the inhibition activity of the molecules. The theoretically calculated %IE was found to be close to experimental %IE but with different values of coefficient of correlation (R²) which may be improved significantly if a systematic change in the structure of the compounds is considered to avoid overlapping of structural effects. This QSAR approach is adequately sufficient to forecast the inhibitor effectiveness using the theoretical approach; it may be used to find the optimal group of parameters for predicting a molecule's suitability to be a corrosion inhibitor.

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