QUANTUM CHEMICAL INVESTIGATION OF EXPIRED PHARMACEUTICAL DRUGS AS CORROSION INHIBITORS FOR MILD STEEL IN HYDROCHLORIC ACID SOLUTIONS

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ABSTRACT

Inhibition performance and adsorption behavior of Expired Pharmaceutical drugs on metals were studied by quantum chemical calculations, this method very useful in determining molecular structure and to study compounds reactivity. Expired Pharmaceutical drugs corrosion inhibition properties determine by using MOPAC 2016 with Parameterized Model 3 (PM3), Quantum chemical calculations were down. Quantum chemical methods nowadays have become common practice to carry out virtual determinations in corrosion inhibition studies. Quantum chemical parameters such as energy levels of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), energy gap(ΔE), global hardness (η), global s softness (S), absolute electro negativity (χ), and electrophilicity index (ω) electronic density is virtually identified. Structure and activity of compounds can be readily screened, employing computational methodology with help of set of mathematical equations that are capable of representing accurately the chemical phenomenon under study. Present study elucidates inhibition efficiency of Expired Pharmaceutical drugs in acidic media. This research was performed using quantum chemical calculations by means of MOPAC 2016 with PM3 method to find correlation between molecular structures of compounds and their behavior as corrosion inhibitors. Results showed that Expired Pharmaceutical drugs (Ofloxacin, Ciprofloxacin, Norfloxacin and Gentamicin) inhibit efficient and effective corrosion of mild steel in hydrochloric acid media.

Keywords: *Quantum chemical parameters, Parameterized model, Corrosion inhibition, Mild Steel, Hydrochloric Acid media, Expired Pharmaceutical drugs,*

I. INTRODUCTION

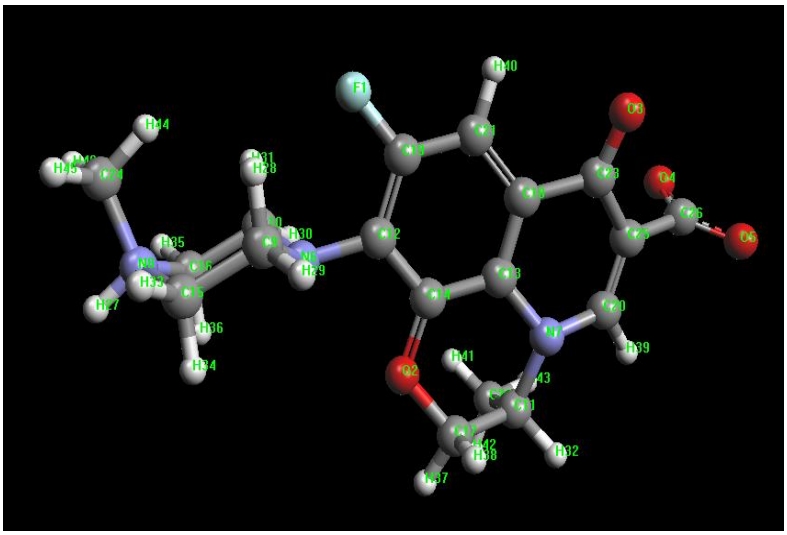
Many metals are extensively used in industries, get corroded when exposed to varies industrial environments. Acid solutions are widely used in industries as pickling agents, oil well acidizing and acid cleaning, etc. Use of corrosion inhibitors is one of the most common method for protection against corrosion, especially in hydrochloric acidic media. Many reviews on corrosion inhibitors tells that a large portion of the inhibitors are organic compounds N, O and S atoms or with polar groups of N- hetero cyclic compounds. They have essential properties with high electron density, making them the reaction centers, these block the dynamic corrosion destinations by adsorption on the metallic surface and the majority of them are exceedingly poisonous to the individuals and in addition the environment [1]. Inhibitors are chemical compounds added to corrosive environment with aim of adsorbing on the metal surface and reducing corrosion rate. Developments in software, contribute to use of computational methods to extend in many fields, one of which is the application of quantum chemical calculations (QCCS) in the corrosion inhibition studies also [2-6]. From QCCS calculations, it could be possible to characterize inhibitors molecular structure by calculated geometrical and electronic parameters analyses inhibition mechanism and also interactions of inhibitors with metal. The aim of present investigate study obtain information on inhibition mechanism using computational analysis of inhibitor structure [7-14].

II. MATERIALS AND METH ODS

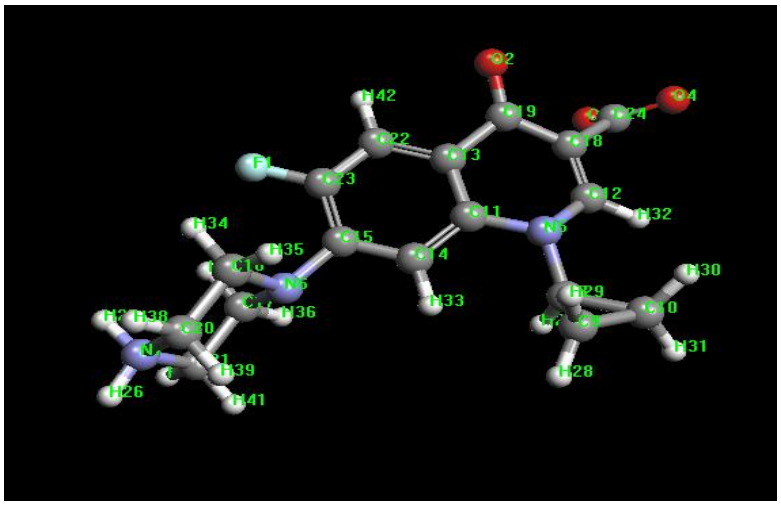
1. Molecular Structures

3-Dimensional (3D) Structures of Expired Pharmaceutical drugs (Ofloxacin, Ciprofloxacin, Norfloxacin and Gentamicin) were taken from structural database and optimized taken as input for the quantum chemical studies. The 3-Dimensional (3D) structures were Showed in **Fig. 1**

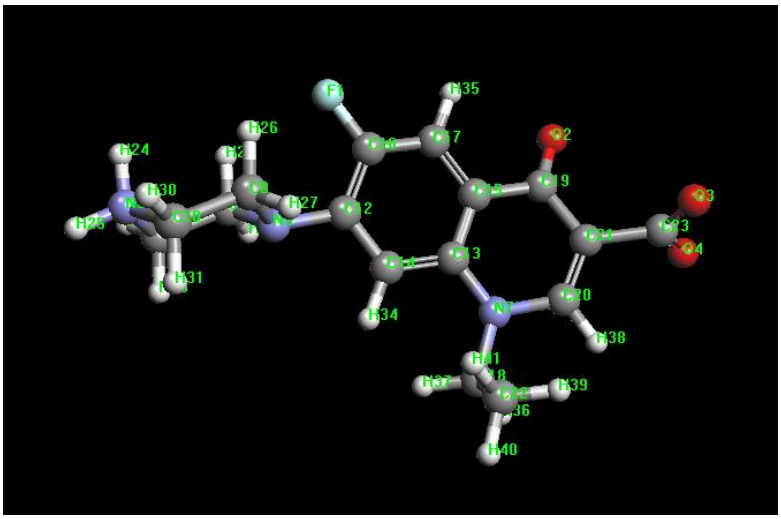
Fig.1 Molecular Structures Ofloxacin, Ciprofloxacin, Norfloxacin and Gentamicin



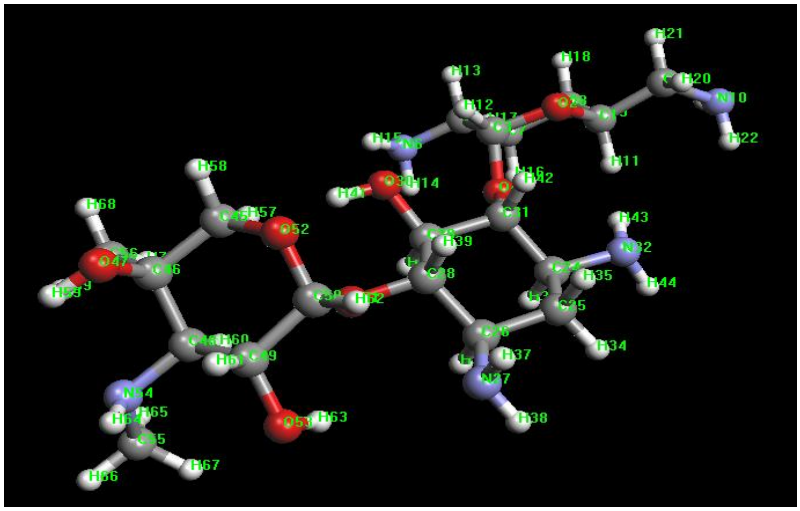
Molecular Structure of Ofloxacin



Molecular Structure of Ciprofloxacin



Molecular Structure of Norfloxacin



Molecular Structure of Gentamicin

2. Software

By MOPAC2016 (Molecular Orbital package 2016) software using PM3 (Parameterized Model number 3) method, the computational analysis of molecular structures of Expired Pharmaceutical drugs were done. This software can perform calculations on small enzymes and molecules using PM3 method based on semi-empirical prosier for the quantum calculation of molecular electronic structure in computational chemistry [15-16]. PM3 was parameterized using experimental and high-level ab initio reference data, augmented by a new type of reference data intended to better define the structure of parameter space. MOPAC2016 software based on employed for analysis. Mulliken atomic charges were performed with the semi-empirical Parametric Method 3 (PM3) parameterization. In Argus Lab (tm) Positive and negative regions in HOMO and LUMO orbitals of compounds were computed [17].

3. Quantum Chemical Calculations

To obtained to inhibitor molecular reactivity from molecular properties like energy of highest occupied molecular orbital (E_{HOMO}), energy of lowest unoccupied molecular orbital (E_{LUMO}), chemical hardness (η), chemical potential (μ) and electrophilicity index (ω) of the inhibitor molecules. Electronegativity is measure of power of an electron or group of atoms to attract electrons towards it is called electronegativity [18]. Chemical potential is negative of electronegativity [19].

$$\mu = - \chi$$

According to Koopmans's theorem [20] which relates to the energy of HOMO and LUMO, belong to the reactivity and selectivity of the inhibitors the molecular properties like ionization potential (I), electron affinity (A), electronegativity (χ), global hardness (η) and softness (σ) were estimated. Ionization potential is the amount of energy required to remove an electron from outer most cell of a molecule, easier to remove an electron from a molecule if lower the Ionization potential. High Ionization energy indicates chemical inertness, high stability and small ionization energy high reactivity of the atoms and molecules [21]. It can be related to the energy of the E_{HOMO} through the equation:

$$I = -E_{HOMO}$$

Electron affinity (A) can be related to ELUMO through the equation:

$$A = -ELUMO$$

Electronegativity (χ) and global hardness (η) can be determined from the values of I and A. The chemical hardness fundamentally signifies the resistance towards the polarization of the electro cloud or deformation of the atoms, ions or molecules under small perturbation of chemical reaction. A soft molecule has high tendency to react while hard molecule least tendency to react. A soft molecule has a small energy gap and hard molecule has a large energy gap. Absolute electronegativity (χ) and absolute chemical hardness (η) of the inhibitor molecule can be given [22] as

$$\chi = I+A /2$$

$$\eta = I-A /2$$

The measure of the capacity of an atom or group of atoms to receive electrons is called as Electron polarizability or chemical softness(σ) was estimated by using the equation [23].

$$\sigma = 1/\eta$$

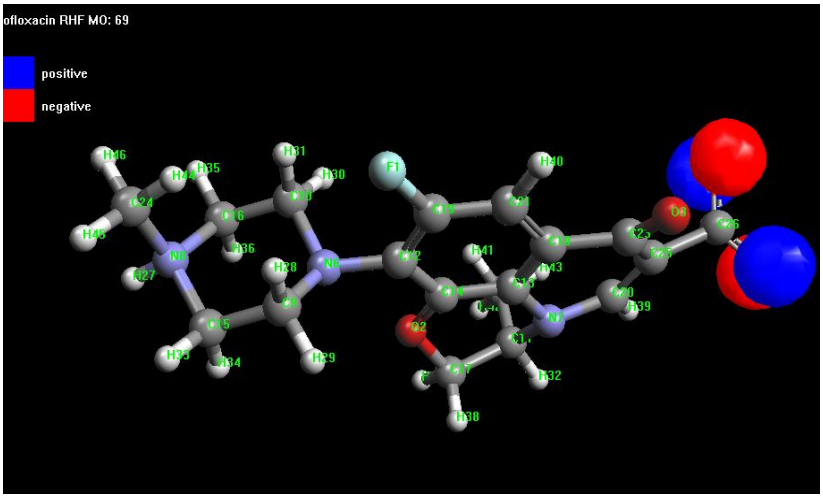
The nucleophilic or electrophilic nature of the molecule depends on the electrophilicity values. A high electrophilicity value shows that the molecule has a high tendency to act as an electrophile while a low value of electrophilicity shows that the molecule has a high tendency to act as a nucleophile [24]. This index measures the propensity of chemical species to accept electrons. Mulliken population analysis determines the nucleophilic and electrophilic reaction centers in the compounds. The absolute electrophilicity index (ω) [25] can be calculated by the equation.

$$\omega = \mu^2/2\,\eta$$

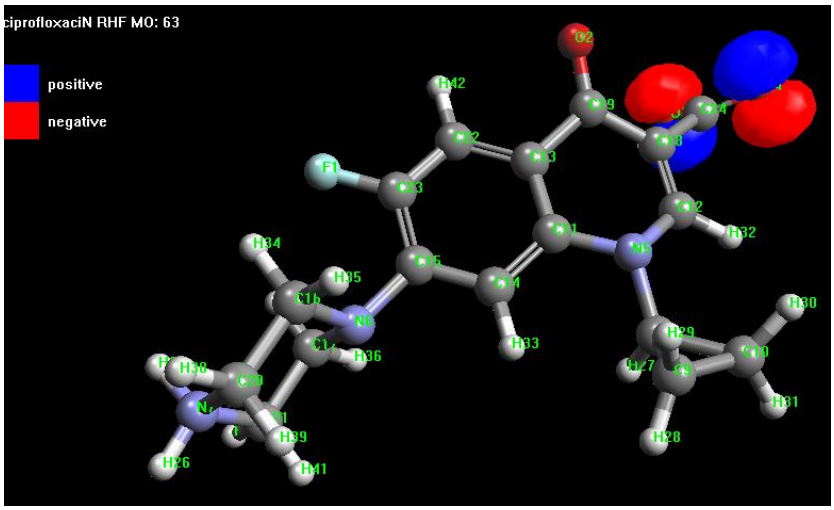
III. RESULTS AND DISCUSSIONS

The structures are sketched with ACD chemsketch and structural geometries were optimized to obtain a stable structure. Quantum chemical methods is a very powerful tool for studying inhibition property of corrosion on metals [26]. By using MOPAC2016 with PM3 method, the HOMO density distribution and the LUMO density distribution for molecules were executed. In the Argus Lab, Positive and negative regions on HOMO and LUMO orbitals of the molecules were computed. E_{HOMO} and E_{LUMO} are important so as to find the electronic properties of the compounds theoretically using PM3 method. The positive and negative phases of the orbital are represented by two coolers, the blue regions represent an increase in electron density and the red region represents a decrease in electron density [27]. E_{HOMO} measures electron donating ability of a compound to an appropriate acceptor molecule with LUMO. An inhibitor with higher E_{HOMO} can easily provide electrons for metallic substrate to adsorb on its surface [28-30]. E_{LUMO} reveals tendency of a molecule to receive electrons. A molecule with lower LUMO energy would be a better electron acceptor from a donor molecule [33], It has been reported that inhibitor molecules can be adsorbed not only by donating electrons from their HOMO orbitals of Fe, but also by receiving electrons from metals to their LUMO molecular orbitals leading to create a feedback bond. Electrophilic attacks were shown to correlate with atomic sites having high density of the HOMO orbital, whereas nucleophilic attacks correlated well with atomic sites having high density of the LUMO orbital [31-33]. Energy gap ΔE is an important parameter as a function of reactivity of inhibitor molecule towards adsorption on metallic surface as ΔE decreases, reactivity of molecule increases, leading to increase of inhibitor efficiencies if ΔE increases, the reactivity of molecule decreases, leading to decreases of inhibitor efficiencies. [34]. The HOMO and LUMO orbitals shown in **(Fig. 2 and Fig. 3).**

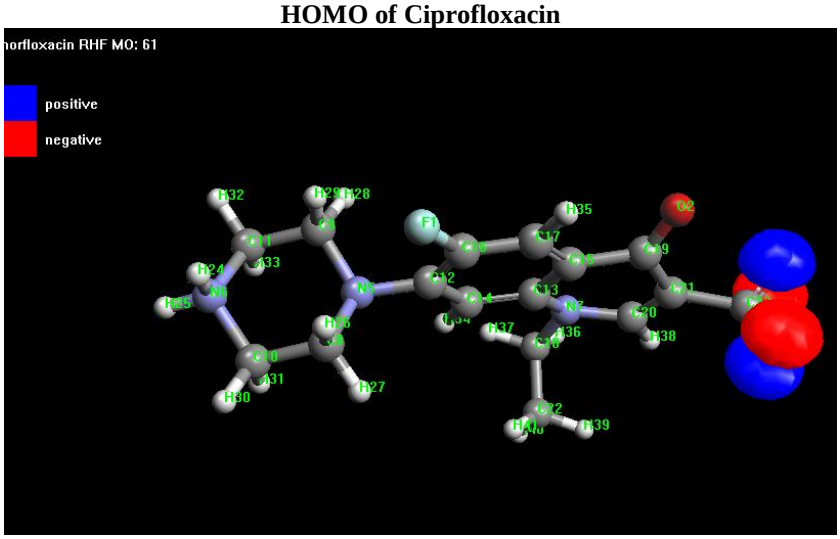
Fig. 2 HOMO of Ofloxacin, Ciprofloxacin, Norfloxacin and Gentamicin



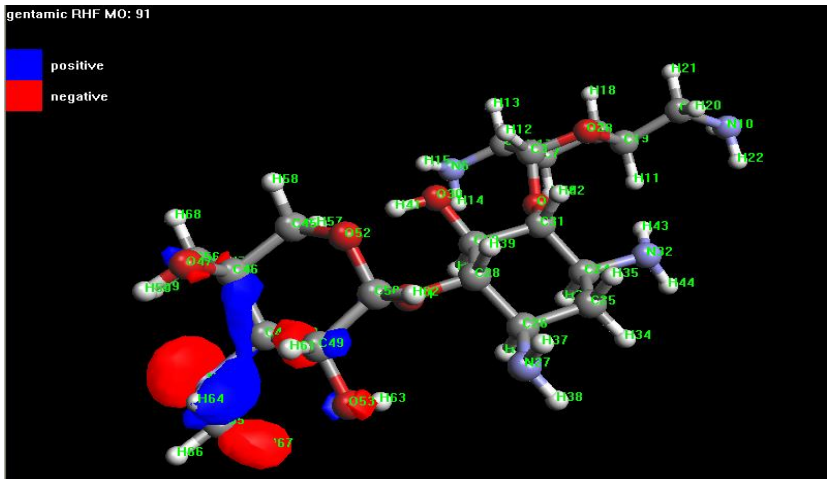
HOMO of Ofloxacin



HOMO of Ciprofloxacin

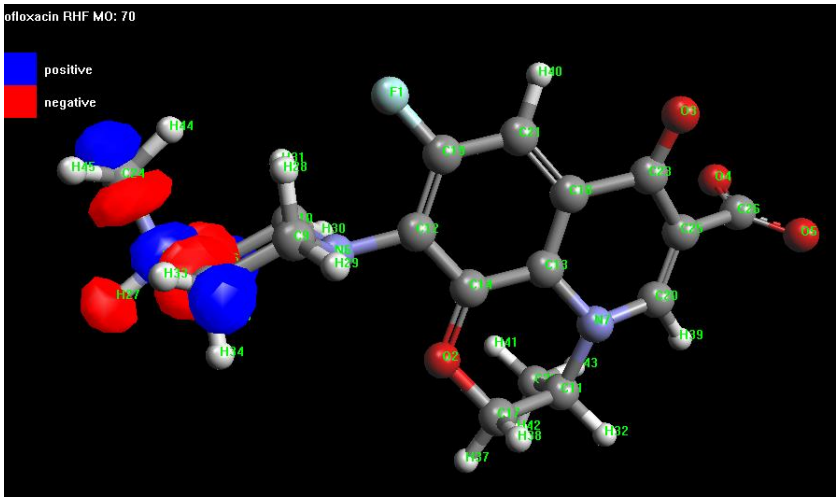


HOMO of Norfloxacin

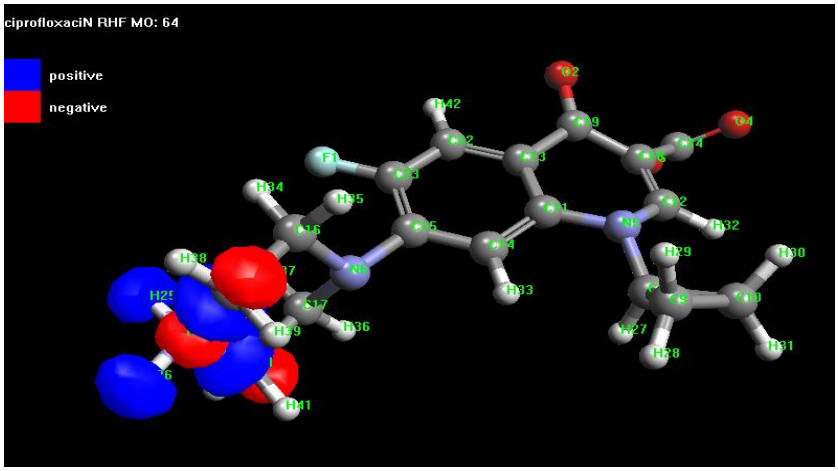


HOMO of Gentamicin

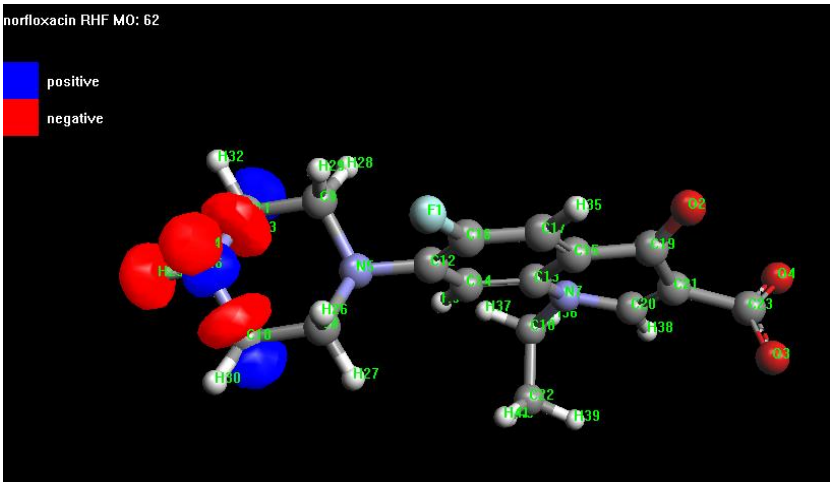
Fig. 3 LUMO of Ofloxacin, Ciprofloxacin, Norfloxacin and Gentamicin



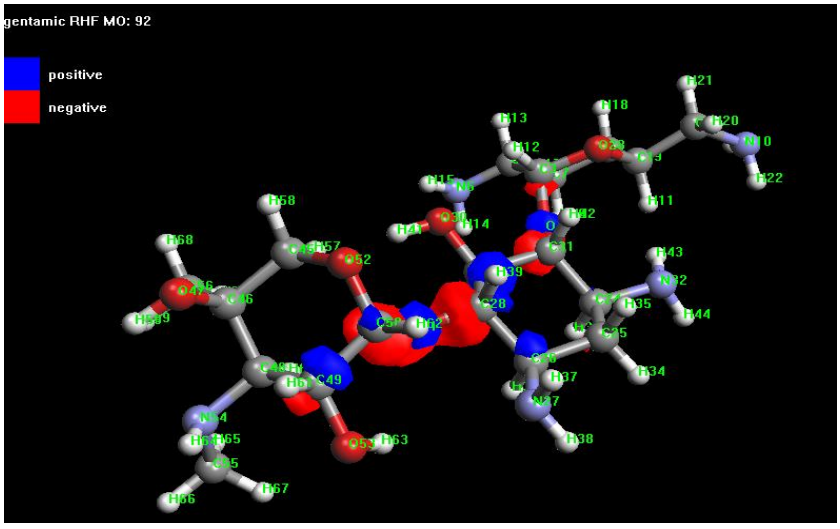
LUMO of Ofloxacin



LUMO of Ciprofloxacin



LUMO of Norfloxacin



LUMO of Gentamicin

The molecule with highest EHOMO value tends to give electrons to suitable acceptor molecule of low empty molecular orbital energy [35]. From the observations of quantum chemical calculations, it was clear that Ofloxacin had most elevated value of EHOMO - 6.818 (eV) and could be a better adsorbed on metal surface and be the best corrosion inhibitor. Energy gap (ΔE) gives data about overall reactivity of a molecule. As ΔE diminishes, reactivity of particle builds prompting increment in inhibition efficiency of molecule. Low values of ΔE gap will render great inhibition efficiencies since energy to expel an electron from last possessed orbital will be minimized [36]. EHOMO, ELUNO and ΔE are shown in Table 1. From the quantum chemical study, tendency for (ΔE) values takes after the order Ofloxacin < Ciprofloxacin < Norfloxacin< Gentamicin, which recommends that Ofloxacin had great reactivity in contrast with other compounds and would in this way likely interact strongly with metal surface. Mulliken populace examination is generally utilized for computation of charge distribution in a molecule [37]. These quantities are easy to get and could give at slightest a subjective understanding of structure and reactivity of molecule [38]. Quantum chemical parameters gotten from hypothetical calculations which are responsible for inhibition efficiency of compounds such as dipole moment (μ), electro negativity (χ), electron affinity (EA), global hardness (η), softness (S), ionization energy (IE) and electrophilicity (ω) are shown in **Table 2 and Table 3**. High IE shows great stability and chemical inertness and small ionization energy demonstrates greater reactivity of atoms and molecules [39]. Low ionization energy 6.318(eV) of the drug Ciprofloxacin shows great inhibition efficiency. Absolute hardness and softness are the most important properties to measure molecular stability and reactivity. A hard molecule has a huge energy gap and a soft molecule has a little energy gap [40]. For

simplest transfer of electron, adsorption could happen at portion of molecule where softness (S), which is a local property, has the greatest value [41]. Ofloxacin with softness value of 0.434 has the greatest inhibition efficiency. Ofloxacin with low hardness value 2.303 (eV) in contrast with other compounds has a low energy gap. Ordinarily, inhibitor with the least value of global hardness can be anticipated to have the highest inhibition efficiency [42].

Table 1Quantum Chemical Parameters for Ofloxacin, Ciprofloxacin, Norfloxacin and Gentamicin Using PM3

S.No	Compound	E_{HOMO} eV	E_{LUMO} eV	Energy gap(ΔE) eV
1	Ofloxacin	-6.751	-2.144	4.607
2	Ciprofloxacin	-6.818	-1.700	5.118
3	Norfloxacin	-8.507	-1.908	6.599
4	Gentamicin	-8.647	-0.492	8.155

Table 2 Quantum Chemical Parameters for Ofloxacin, Ciprofloxacin, Norfloxacin and Gentamicin Using PM3

S.No	Compound	IE eV	EA eV	EN eV
1	Ofloxacin	6.750721	2.144	4.447361
2	Ciprofloxacin	6.318267	1.700	4.009134
3	Norfloxacin	8.646982	1.908	5.277491
4	Gentamicin	8.507047	0.492	4.499524

Table 3 Quantum Chemical Parameters for Ofloxacin, Ciprofloxacin, Norfloxacin and Gentamicin Using PM3

S.No	Compound		Ŋ	S	μ	ω
1	Ofloxacin		2.303361	0.434148	-4.44736	4.293513
2	Ciprofloxacin		2.309134	0.433063	-4.00913	3.480343
3	Norfloxacin		3.369491	0.296781	-5.27749	4.132955
4	Gentamicin		4.007524	0.249531	-4.49952	2.525963

IV. CONCLUSIONS

Quantum chemical calculations presented for all intents and purposes accumulated major outcomes on properties that can't be figured in research facility. From results using the Semi empirical PM3 calculations, inhibition efficiency of observed compounds prompts the accompanying conclusions. Based on energy gap esteems, the reactivity order is as followed: Ofloxacin <Ciprofloxacin < Norfloxacin < Gentamicin. Among the broke down Expired Pharmaceutical medications Ofloxacin was found to have most astounding inhibitive reactivity in contrast with alternate compounds. It had most elevated inhibition efficiency because it possessed high EHOMO energy in examination with alternate medications and it was more fit for offering electrons. Parameters like softness (S), hardness (η), electron affinity (EA) ionization potential (IE), dipole moment (μ), and electro negativity (χ) affirm the inhibition efficiency of Ofloxacin. The analysis of LUMO, HOMO and partial atomic charges recommended that these focuses would be favored for nucleophilic or electrophilic attacks. Quantum chemical analysis proved that Norfloxacin, Ofloxacin, Gentamicin and Ciprofloxacin could fill in as compelling corrosion inhibitor against metal that could be demonstrated further with studies to build up these competitors as eco-friendly corrosion inhibitors.

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