The present chapter is extension of the work on antibiotics, here the second generation antibiotics of fluoroquinolones: ofloxacin, ciprofloxacin and norfloxacin have been selected. These drugs are used in bacterial infections, bone and joint infections, intra - abdominal infections, diarrhoea, respiratory tract infections, skin infections, typhoid fever and urinary tract infections [Gece *et al*.(2011) and Oliphant *et al.*(2002)]. Besides this, their applications as corrosion inhibitors are also well recognized [Wright *et al.*(2000)]. These drugs are free from S, P, metal and contain quinoline and piperazine moieties with different functionalities along with number of triboactive elements like N, O and methyl groups which might be useful in lubrication through adsorption. The antiwear property of fluoroquinolone, is solely based on its chemical structure, presence of hetero atoms/polar molecules (active elements) which have ability to interact with metal surface at working temperatures forming tribochemical film [Rastogi *et al.*(2002)]. Thus, it is desirable to formulate such low SAPS containing additives which are environment friendly and have performance comparable to those of multifunctional additives.

4.1. Materials & methods

4.1.1. Chemicals

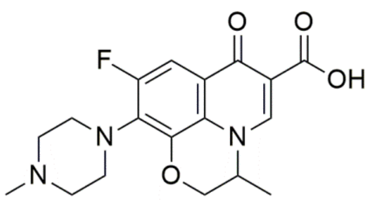
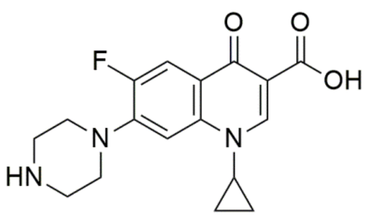
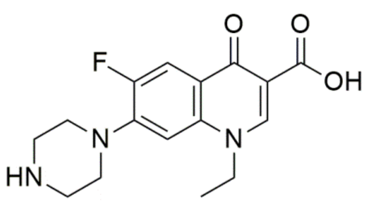
The fluoroquinolones antibiotics ofloxacin, ciprofloxacin and norfloxacin were obtained from Cipla Limited, Mumbai, Maharashtra, India. The chemical structures and names of these tested antibiotics have been mentioned in Table 4.1.

4.1.2. Sample preparation

The suspensions of paraffin oil with fluoroquinolones at different concentrations 0.00, 0.25, 0.50 and 1.00% (w/v) were made by stirring for one hour on magnetic stirrer.

These were further sonicated for half an hour at room temperature. The entire testing was carried out at an optimized additive concentration, 0.25% w/v.

Table 4.1. Molecular structures and commercial names of the tested antiwear lubricant additives

Structure	IUPAC name	Commercial name
	9-fluoro-3-methyl-10-(4-methylpiperazin-1-yl)-7-oxo-3,7-dihydro-2H-[1,4]oxazino [2,3,4]quinoline-6-carboxylic acid	Ofloxacin
	1-cyclopropyl-6-fluoro-4-oxo-7-(piperazin-1-yl)-1,4-dihydroquinoline-3-carboxylic acid	Ciprofloxacin
	1-ethyl-6-fluoro-4-oxo-7-(piperazin-1-yl)-1,4-dihydroquinoline-3-carboxylic acid	Norfloxacin

4.2. Results and discussion

4.2.1. Antiwear studies

At first the additive concentration for the all tribological tests, has been optimized. Figure 4.1 reveals that all the additives in paraffin oil efficiently reduced the MWD values at each concentration. As the additive concentration increased from 0.25% to 1.0% w/v, the value of MWD increased up to 0.5% and thereafter, it decreased. Overall, the extent of reduction in MWD values at 1.0% is found to be similar to that observed for 0.25% w/v. Thus, 0.25% w/v has been chosen as an optimized additive concentration. The outcome of the ASTM D4172 test results is summarized in Figure 4.2. This figure represents variation of MWD and COF together for all the tested additives in paraffin oil. It can be noted that the MWD and coefficient of friction (COF) values are large in case of paraffin oil alone while in case of additives, these values are significantly reduced. The values of MWD and COF have been observed to be smallest in case of ofloxacin followed by ciprofloxacin and the norfloxacin. The order of antiwear efficiency of these tested additives is as follows:

Ofloxacin > Ciprofloxacin > Norfloxacin

The tribological behavior of these additives may be explained on the basis of their chemical structures. Figure 4.3 shows the variation of COF with a function of sliding time at 392N applied load. In presence of additives, the COF values are reduced with the expense of time and later on these are stabilized in each case. In case of paraffin oil, the observed unusual trend may be due to absence of tribofilm.

The variation of MWD values with different sliding time intervals at 392N load has been displayed in Figure 4.4. For each 15 min. of time interval up to 90 min., the MWD values progressively increase. These MWD values have been used to calculate mean wear volume with the help of linear regression model, Figure 4.5. With the help of mean wear volume running-in and steady-state wear rates have been calculated Figure 4.6 and Figure 4.7 and mentioned in Table 4.2. On comparing running-in and steady-state wear rates, the steady-state is found to be lowest in all cases which is directly related to the machine life.

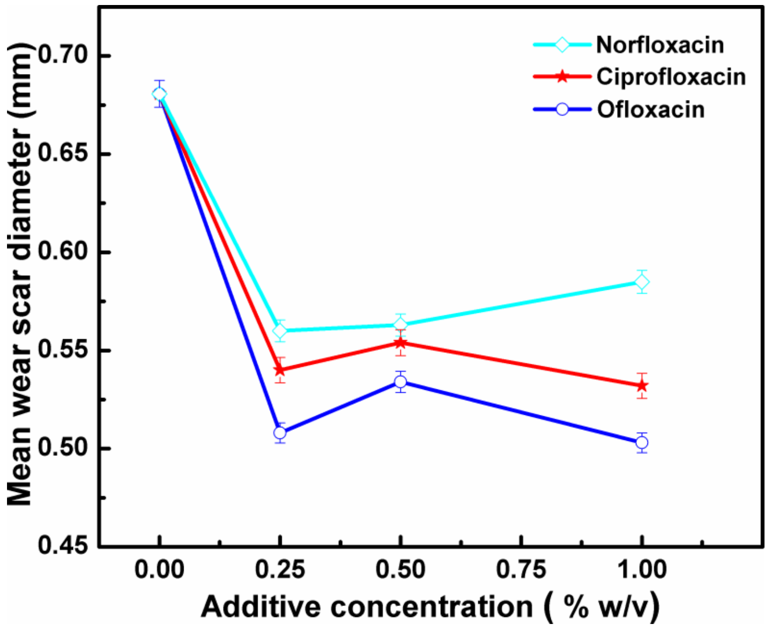


Figure 4.1. Variation of mean wear scar diameter in absence and presence of different additive concentrations in paraffin oil at 392N applied load and 60 min duration

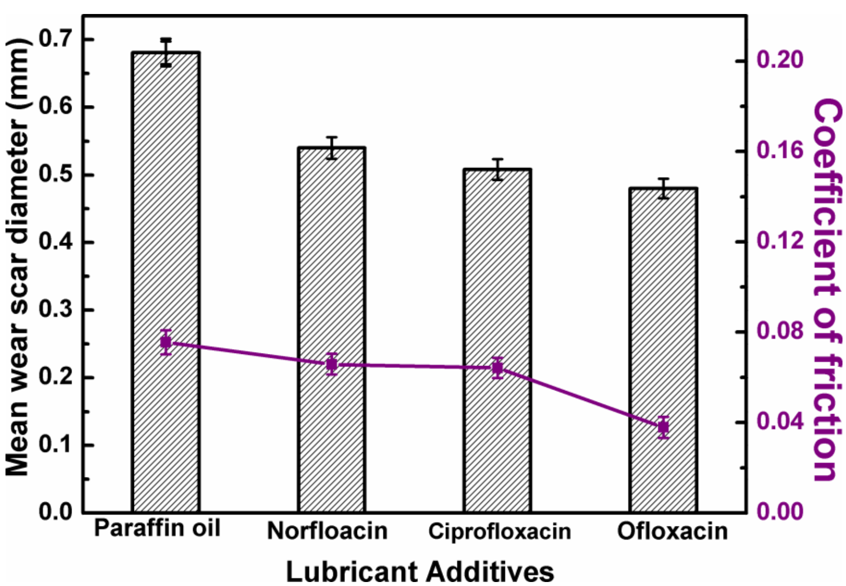


Figure 4.2. Comparison of MWD and average COF values of steel balls lubricated with different additives in paraffin oil at 392N; rotating speed: 1200 rpm, temperature: 75°C, test duration: 60 min., concentration: 0.25% w/v of additives

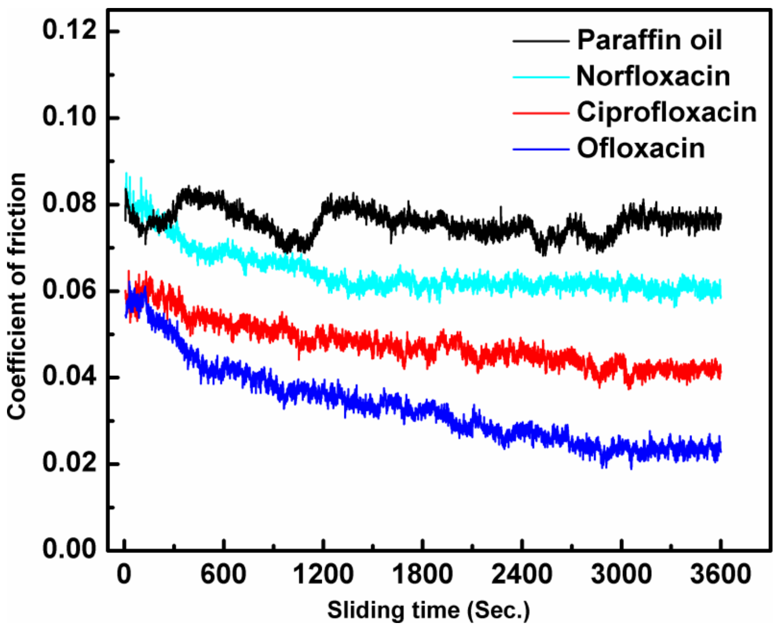


Figure 4.3. Variation of COF with sliding time in presence and absence of additives in paraffin oil at 392N; rotating speed: 1200 rpm, temperature: 75°C, test duration: 60 min., concentration: 0.25% w/v of additives

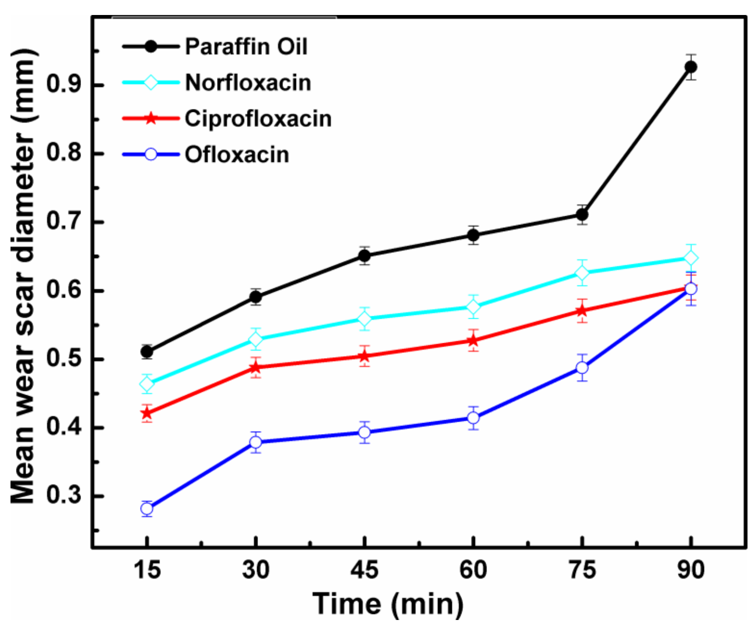


Figure 4.4. Variation of mean wear scar diameter with time in paraffin oil containing fluoroquinolone antibiotics at 392N applied load

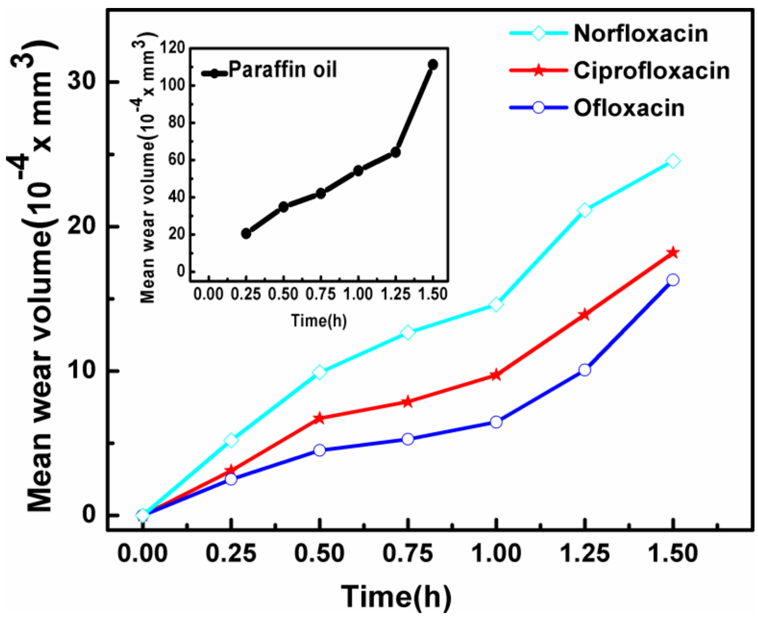


Figure 4.5. Variation of mean wear volume with time (h) in paraffin oil containing fluoroquinolone antibiotics at 392N applied load

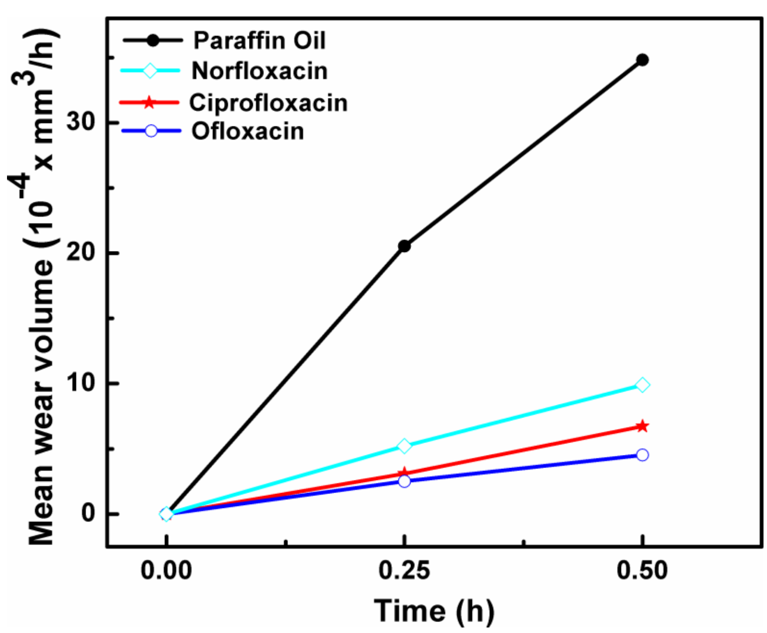


Figure 4.6. Determination of running-in wear rate by varying mean wear volume with time (h) for paraffin oil containing fluoroquinolone antibiotics at 392N applied load

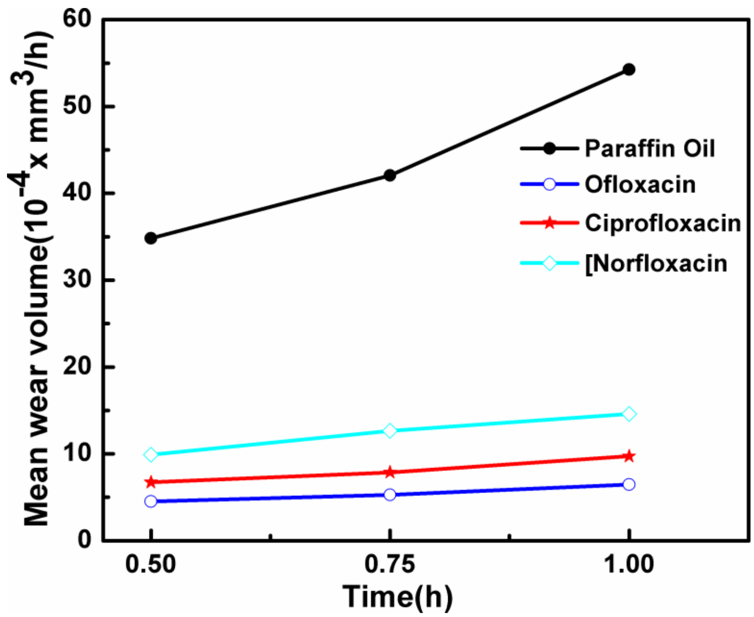


Figure 4.7. Determination of steady-state wear rate by varying mean wear volume with time (h) for paraffin oil containing fluoroquinolone antibiotics at 392N applied load

Table 4.2. Wear rate for paraffin oil in the presence and absence of fluoroquinolones (0.25 % w/v) for 90 minute test duration at 392 N applied load

S.N.	Lubricants	Wear rate (10^{-4} x mm^3/h)	
		Running-in	Steady-state
1	Paraffin oil	69.99	38.88
2	Norfloxacin	19.80	09.40
3	Ciprofloxacin	13.46	05.99
4	Ofloxacin	09.02	03.90

4.2.2. Effect of load

The effect of applied load on the MWD in presence and absence of additives has been studied and the obtained results are mentioned in Figure 4.8. In case of paraffin oil alone, it bears the load up to 490N only, however, in case of all tested additives the load carrying ability has been increased up to 686N. The ability of these additives towards significant reduction in MWD and COF values is ascribed to the presence of triboactive elements in their molecular structures. The quinoline and piperazine moieties are common in all the tested additives, therefore, all of them are highly active. Among these additives, the best tribological behaviour is shown by ofloxacin. This may be attributed to the presence of additional six-membered heterocyclic ring along with methyl groups which enhance the adsorption of the additive on the sliding surface. On the other hand, ciprofloxacin and norfloxacin behave similarly containing cyclopropyl and ethyl groups, respectively. Under tribostress conditions these active elements such as N, O and F have tendency to get adsorbed on the metal surface to form tribochemical film on the steel-steel interfaces thereby reducing friction and wear [Rastogi *et al*.(2014)].

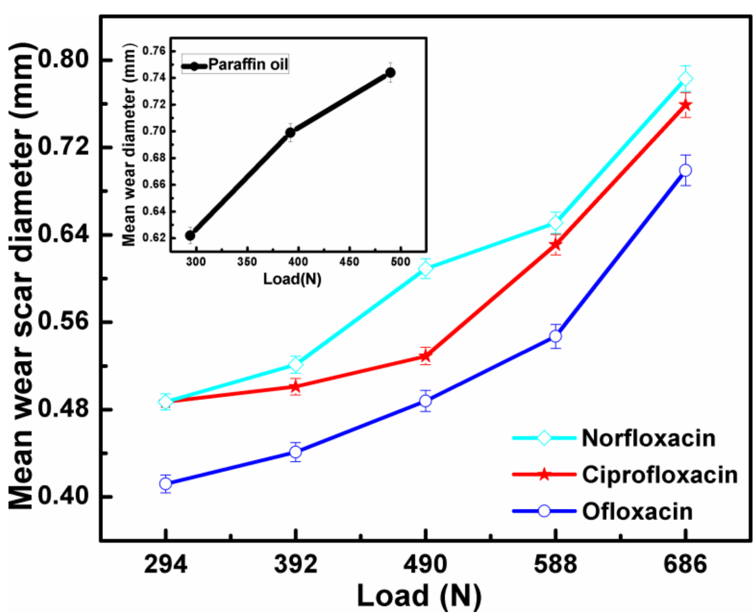


Figure 4.8. Variation of mean wear scar diameter with applied load for paraffin oil containing 0.25% w/v of different additives for 30 min. test duration

4.2.3. COF test

The coefficient of friction test has been performed according to ASTM D5183 standard also Figure 4.9. After the 60 min. of wear test, the paraffin oil shows sudden huge increase in COF value at 1078N load whereas abrupt increase in the COF values in case of ofloxacin, ciprofloxacin and norfloxacin have been observed at 2842, 2352 and 2352N, respectively in the step loading test. This test further supports that these additives are capable to bear high loads.

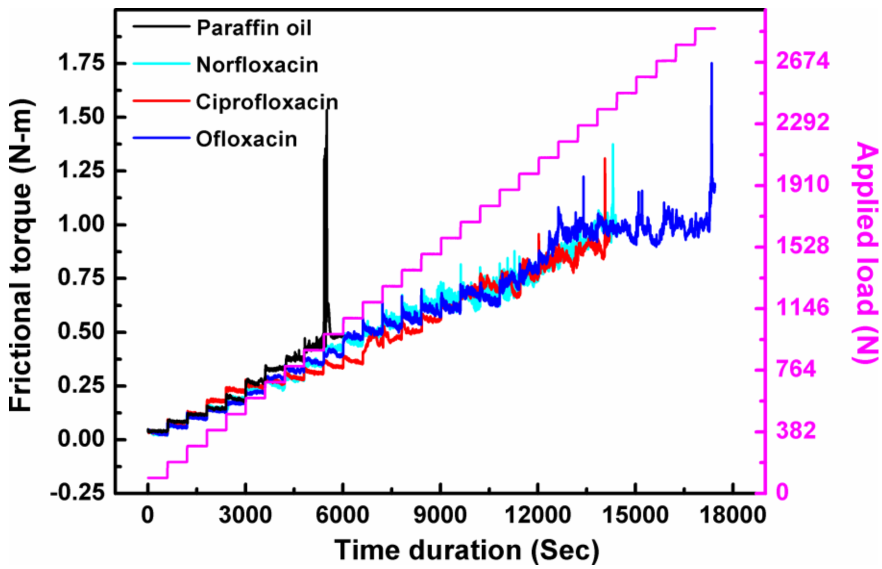


Figure 4.9. Variation of frictional torque as a function of step loading (with the increment of 98N load at every 10 min. of test run) and time for different additives; sliding speed: 600 rpm; temperature: 75 °C, additive concentration: 0.25% w/v

4.2.4. Surface Characterization

4.2.4.1. Surface morphology

Figure 4.10 shows the SEM micrographs of worn surfaces lubricated with paraffin oil and its blends with different fluoroquinolone additives at 392N load for 60 min time duration. In case of paraffin oil alone large MWD value with severe scuffing has been observed while in presence of tested additives drastic reduction in MWD values is obtained. Besides this, fluoroquinolone additives are prone to smoothen the tribosurface to a much greater extent than that of base oil. The SEM micrographs taken at higher load (686N) revealed that these additives have capability to resist severe increase in their MWD value under extreme conditions, Figure 4.11. However, paraffin oil alone sustains the load only up to 490N.

The 2*D* and 3*D*-AFM images of the worn surfaces supplemented with studied fluoroquinolones are shown in Figure 4.12 which shows that in case of paraffin oil alone the line (Rq) as well as area roughness (Sq) are very high but in presence of fluoroquinolones these values are extremely low. The bar diagram, Figure 4.13 has been constructed to show the variation of Rq, Sq and peak-valley height (Sy) of paraffin oil and the tested additives. These roughness parameters also support the results obtained from SEM and AFM studies. The 2*D* and 3*D*-AFM images of the worn surface supplemented with additives at higher load (686N), Figure 4.14 have also been taken. All the additives show almost similar roughness values as displayed in Figure 4.15.

4.2.4.2. Tribochemistry

The EDX analysis of the worn steel surface supplemented with paraffin oil alone and in presence ofloxacin for 60 min. test duration at 392N applied load has been examined and obtained results are mentioned in Figure 4.16. There is no active element in case of surface lubricated with base oil alone whereas additionally N and F triboactive elements appeared in the EDX spectra of the surface lubricated with ofloxacin. The presence of N and F on the worn surface confirms the protective tribochemical film/s made up with the help of these triboactive elements of the studied additives.

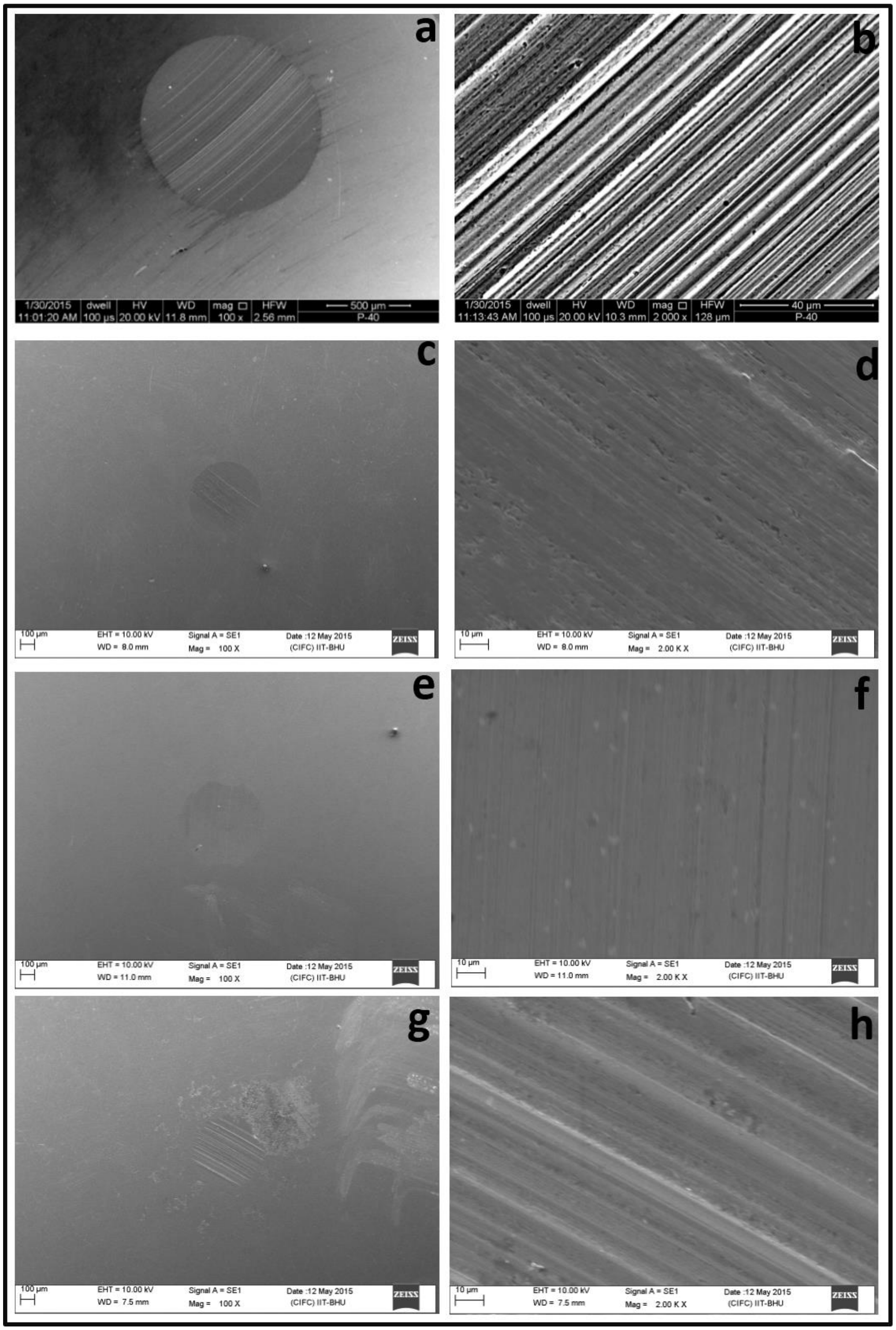


Figure 4.10. SEM micrographs of the worn steel surface lubricated with different additives in paraffin oil for 60 min. test duration at 392N applied load: **(a,b)**. Paraffin oil, **(c,d)**. Ofloxacin **(e,f)**. Ciprofloxacin and **(g,h)**. Norfloxacin

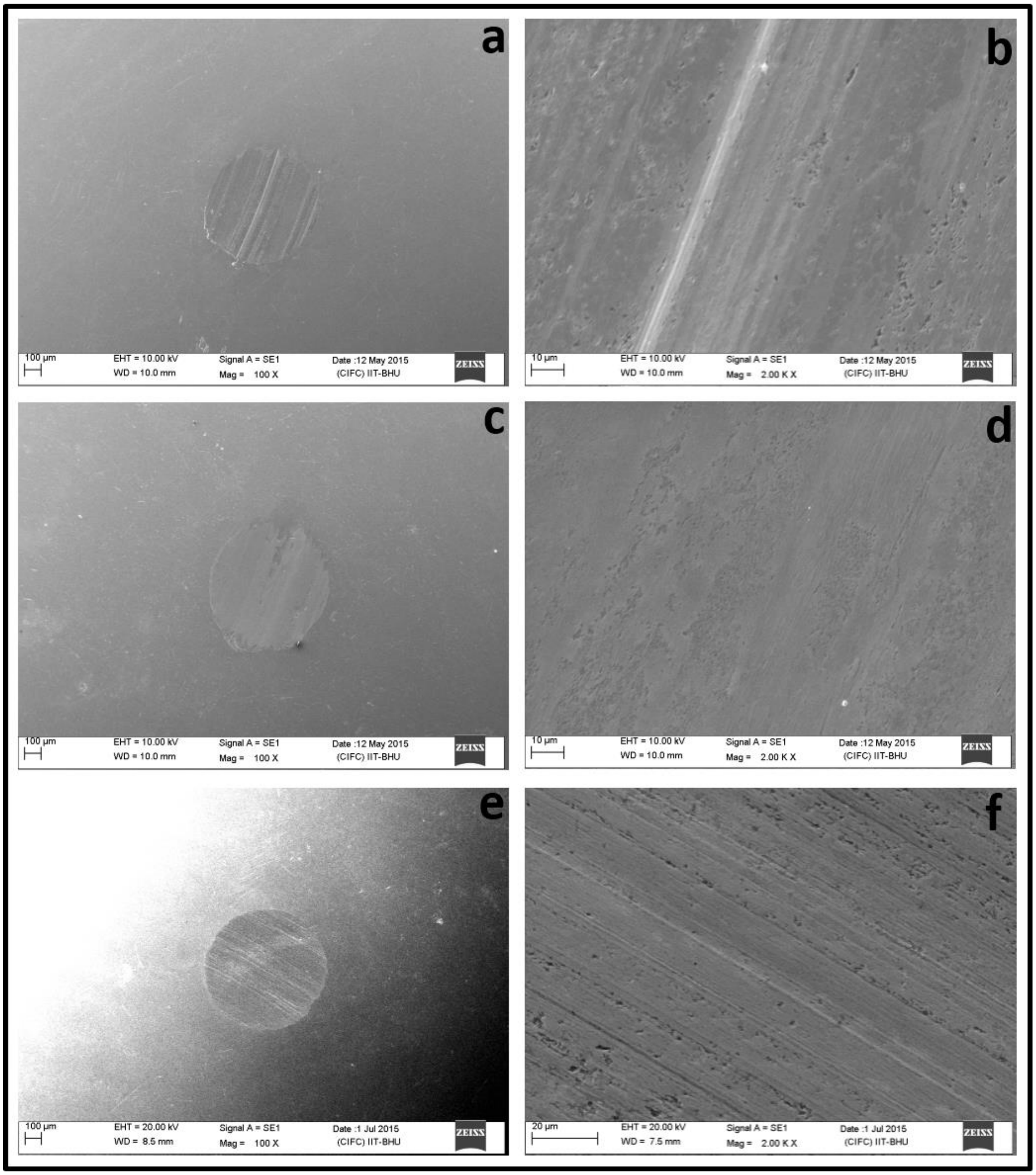


Figure 4.11. SEM micrographs of the worn steel surface lubricated with different additives in paraffin oil for 30 min. test duration at 686 N applied load: **(a,b)**. Ofloxcin, **(c,d)**. Ciprofloxacin and **(e,f)**. Norfloxacin

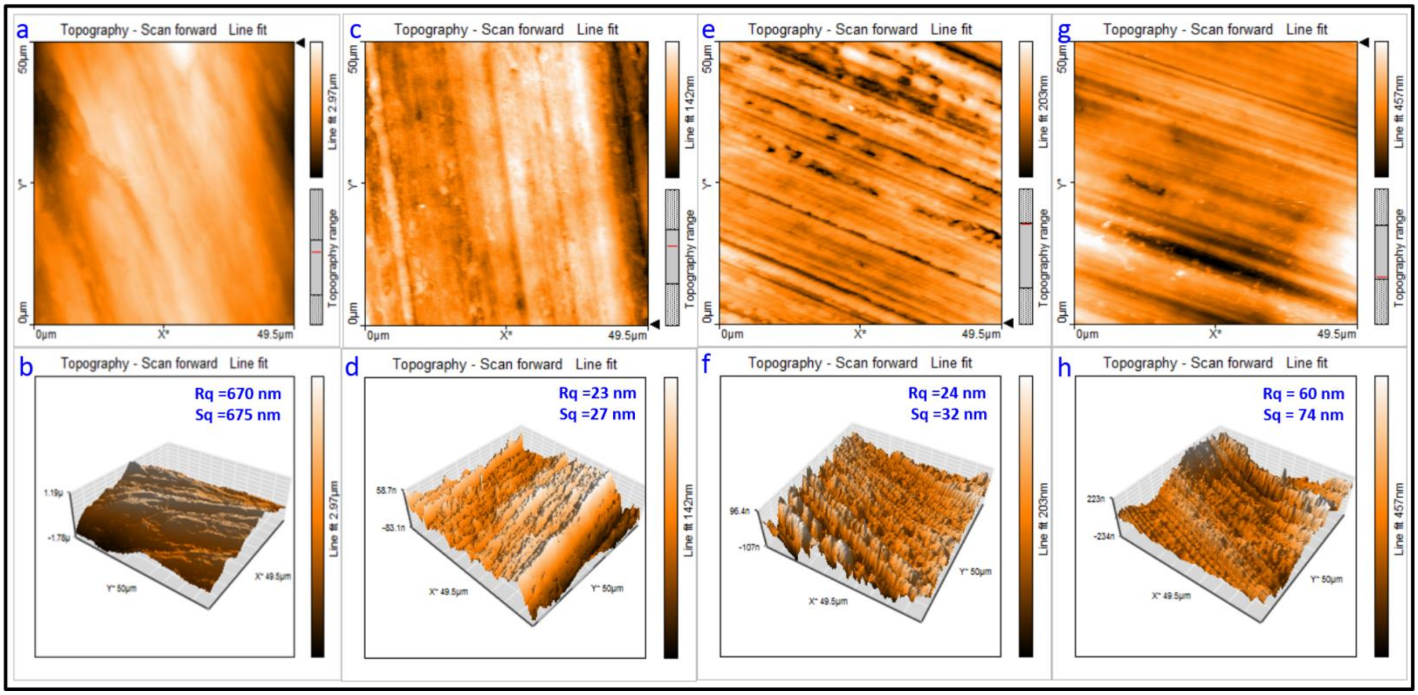


Figure 4.12. 2*D* and3*D*-AFM images of the worn steel surface lubricated with different additives in paraffin oil for 60 min. test duration at 392N applied load: **(a,b)**. Paraffin oil, **(c,d)**. Ofloxacin, **(e,f)**. Ciprofloxacin and **(g,h)**. Norfloxacin

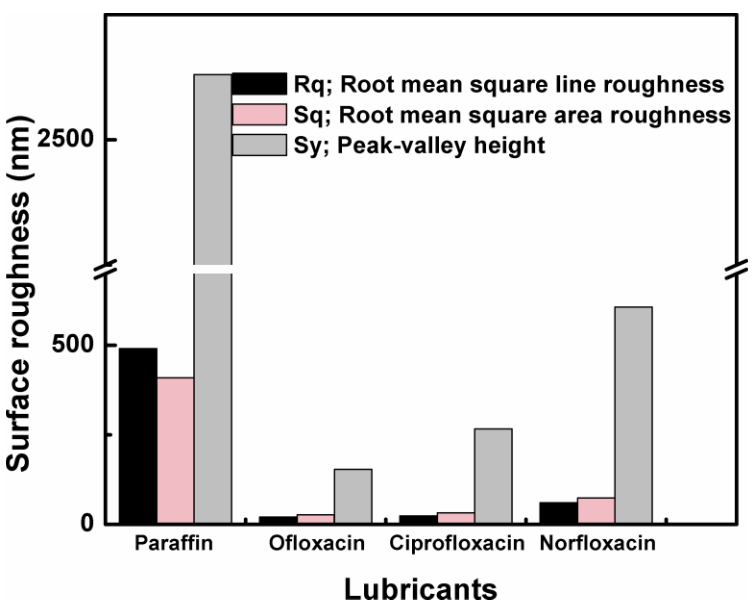


Figure 4.13. Surface Roughness parameters obtained from digital processing software of Nanosurf basic Scan 2 for different additives at 392N load for 60 min. test duration

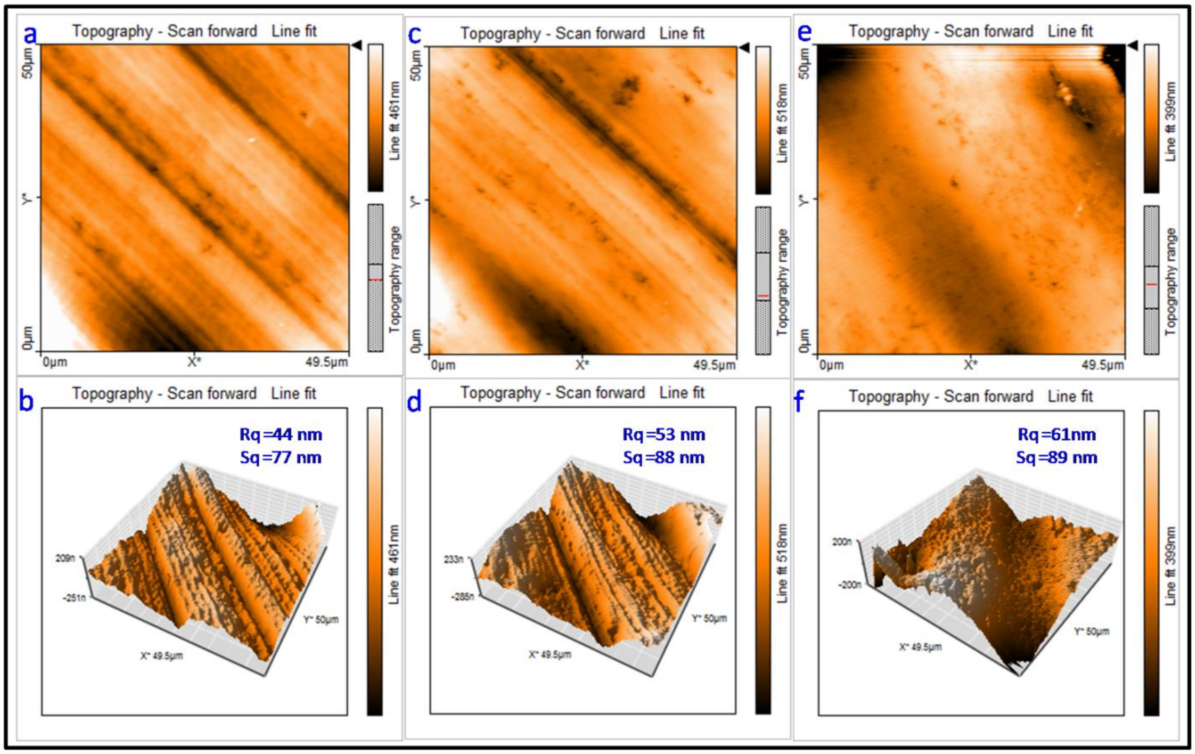


Figure 4.14. 2*D* and 3*D*-AFM images of the worn steel surface lubricated with different additives in paraffin oil for 30 min. test duration at 686N applied load: **(a,b)**. Ofloxacin, **(c,d)**. Ciprofloxacin and **(e,f)**. Norfloxacin

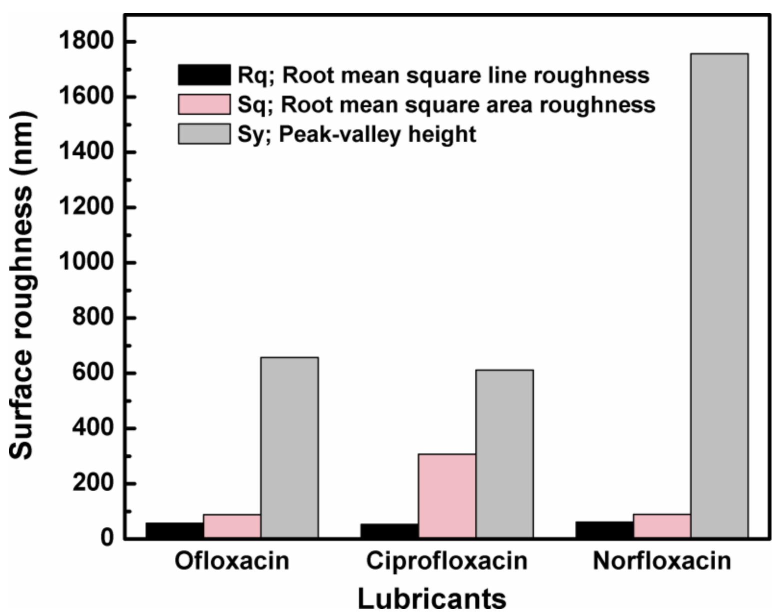


Figure 4.15. Surface Roughness parameters obtained from digital processing software of Nanosurf basic Scan 2 for different additives at 686N load for 30 min. test duration

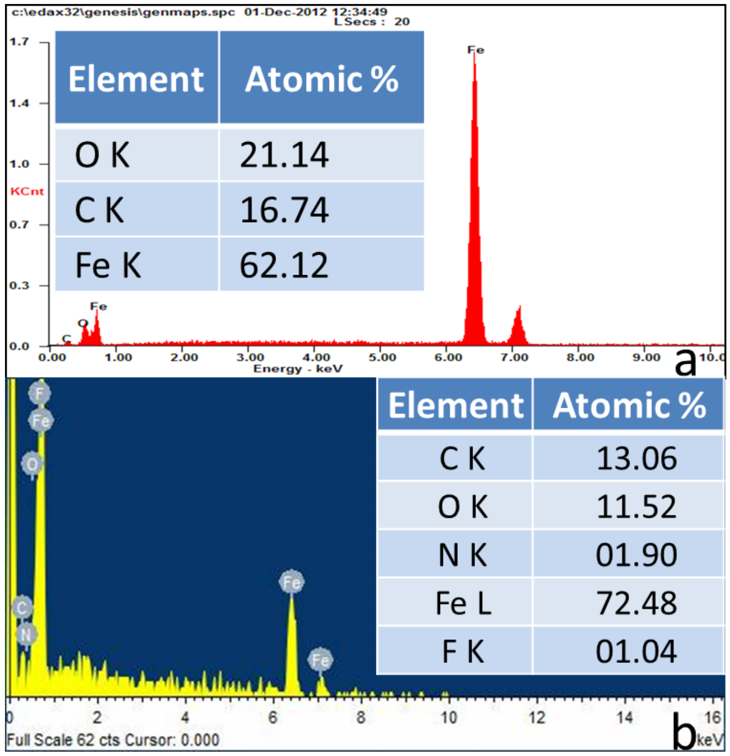


Figure 4.16. EDX analysis data of the worn steel surface lubricated with (a). Paraffin oil and (b).Ofloxacin for 60 min. test duration at 392N applied load

4.2.5. Theoretical study

The density distributions of fluoroquinolone antibiotic additives in terms of frontier molecular orbitals; highest occupied molecular orbital (E_{HOMO}), lowest unoccupied molecular orbital (E_{LUMO}), energy gap (ΔE) between LUMO and HOMO have been shown in Figure 4.17. The figure shows that the electron density is evenly distributed on the entire molecule in case of E_{HOMO} but in case of E_{LUMO} only quinoline moiety is responsible for the interaction. The observed data have been tabulated in Table 4.3. The higher value of E_{HOMO} of additives is responsible for their electron donation tendencies while lower value of E_{LUMO} is accorded to their acceptable behavior [Jaiswal *et. al*(2014) and Heckerman *et al.*(1966)]. The stability of an additive is correlated with energy gap ΔE. A higher value of

ΔE denotes high stability of the additive and therefore, its least affinity towards adsorption on metal surface. On the other hand, lower value of ΔE favors its strong adsorption. The tested additives donate electron from their E_{HOMO} to empty d-orbital of metal which in turn, donates back electron density to the vacant antibonding orbital of the additives, thus showing synergic effect. From Table 4.3, it can be seen that the values of ΔE and $\Delta E_{Fe\text{-}A}$ are found to be the lowest in case of ofloxacin, followed by ciprofloxacin and norfloxacin. It can be inferred that maximum adsorption of ofloxacin would have occurred on the metal surface. Thus the highest values of E_{HOMO}, and lowest values of E_{LUMO}, ΔE and $\Delta E_{Fe\text{-}A}$ are in accordance with the best tribological results of the antibiotic ofloxacin. Quantum chemical calculations therefore, support very well the experimentally observed behavior of antiwear additives.

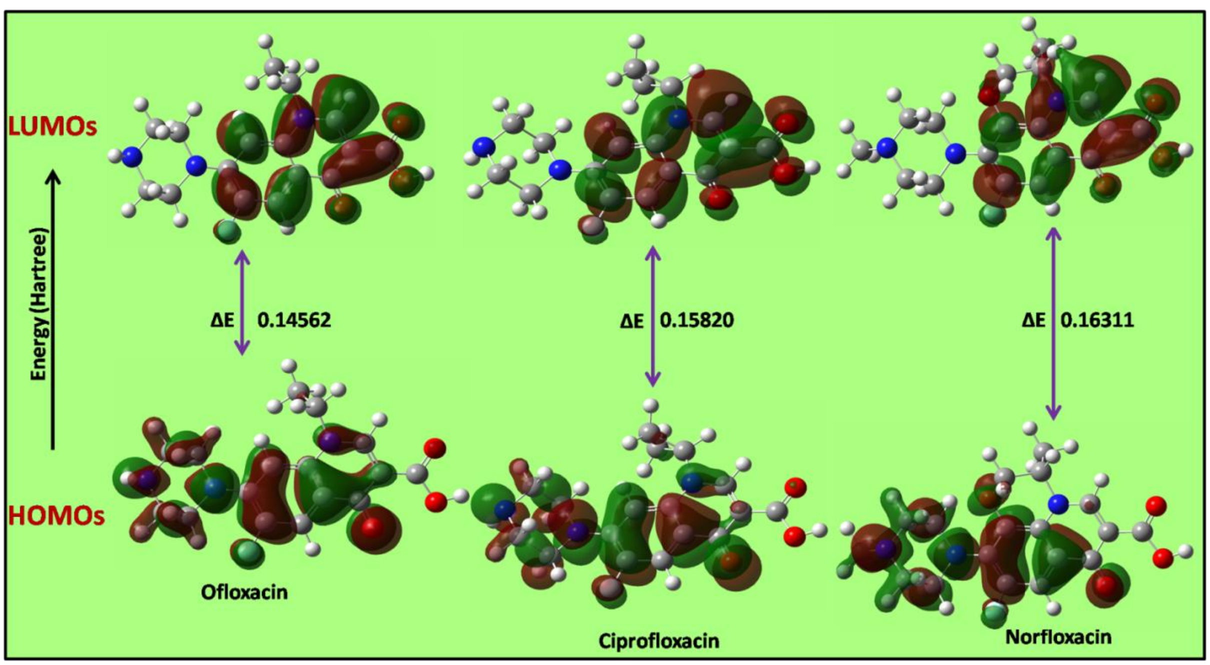


Figure 4.17. HOMO and LUMO density distributions of fluoroquinolone antibiotics additive

Table 4.3. Quantum chemical parameters for quinolinium derivatives as antiwear additives calculated with B3LYP/6-31G++(d,p) basis set

Additives	**E_{HOMO} (Hartree)**	**E_{LUMO} (Hartree)**	**ΔE (Hartree)**	**$ΔE_{Fe-A}$ (Hartree)**
Fe_5 [Huang *et al.*(2003)]	-0.18651	-0.06420	0.12231	
Ofloxacin	-0.20728	-0.06166	0.14562	0.14308
Ciprofloxacin	-0.22243	-0.06423	0.15820	0.15823
Norfloxacin	-0.22470	-0.06150	0.16311	0.16050

ΔE= E_{LUMO} of additive - E_{HOMO} of additive

$ΔE_{Fe-A}$= E_{LUMO} of iron - E_{HOMO} of additive

4.3. Conclusions

The fluoroquinolones antibiotics incorporated into paraffin oil appreciably enhance the antiwear and friction reducing properties of the base oil. These tested additives effectively reduced the MWD, friction coefficient and wear rates of the paraffin oil. The order of efficiency of these additives towards antiwear behaviour is as follows:

Ofloxacin > Ciprofloxacin > Norfloxacin

In case of additives, the steady-state wear rate is much smaller than that of running-in wear rate. Along with desirable antiwear properties, these fluoroquinolones also enhance the load bearing capacity of paraffin oil up to 686N. The surface morphology has been examined by SEM and AFM which confirms the surface smoothening for the surface lubricated with the additives in the same order as that observed from the tribological behaviour. The presence of N and F elements in addition to C, O and Fe in the EDX spectra of the surface lubricated with additive confirms the role of tested additives to form *in situ* protective tribochemical film. The theoretical studies using density functional theory also strengthen the observed order of studied additives towards their tribological properties.