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Tribological investigations on β-lactum cephalosporin antibiotics as efficient ashless antiwear additives with low SAPS and their theoretical studies

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Abstract

Antiwear behavior of β-lactum cephalosporin antibiotics such as cefixime, cefadroxil and cephalexin has been studied using Four Ball lubricant tester in paraffin oil. The results have been compared with high sulphated ash, phosphorous and sulfur (SAPS) containing conventional zinc dibutyldithiophosphate (ZDDP). The tests have been performed using optimized concentration of the additives(1% w/v) at various loads from 294, 392, 490, 588, 686 to 784 N for 30 min test duration and for various test durations from 15, 30, 45, 60, 75 and 90 min at 392 N load. Various tribological parameters such as mean wear scar diameter (MWD), friction coefficient (μ), mean wear volume (MWV), running-in, steady-state and overall wear rates show that all the studied antibiotics act as efficient antiwear additives. Among all the investigated antibiotics, cefixime shows excellent antiwear properties along with very high load bearing capacity. Surface topography of the worn surface has been studied by Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM). AFM and SEM micrographs of the wear scar in the presence of cefixime at 392 N applied load for 90 min test duration show drastic decrease in surface roughness. Energy-Dispersive X-ray (EDX) analysis of the worn surface under similar experimental conditions in presence of the cefixime exhibits presence of sulfur, nitrogen and oxygen on the steel surface indicating adsorption of the additive on the rubbing surface resulting into the formation of a strong tribofilm. Further, X-ray Photoelectron Spectroscopy (XPS) of tribofilm shows presence of $FeSO_4$ and Fe_2O_3/Fe_3O_4 and adsorbed nitrogen in the form of -N=C- and/or amide moiety. Quantum chemical calculations using density functional theory have been performed to investigate the structure-antiwear activity relationship of these antibiotics. The theoretical calculations explain very well the observed experimental results.

Keywords: Antiwear lubricant additives, β-lactum cephalosporin antibiotics, Surface analysis: AFM, SEM/EDX, XPS and Quantum chemical calculations.

1. Introduction

The organic molecules play an important role in the formation of chemical film on the interacting surfaces under lubricating conditions. The effective antiwear lubricant additives and friction modifiers are usually the organic compounds which consist of hetero-atoms like phosphorous [1-6], sulfur [7-9], halogen [10], nitrogen and oxygen [11-15]. Tribological applications of zinc, molybdenum and lanthanum complexes of dithiohydrazodicarbonamides [16,17], dialkyldithiophosphates [18-20], dithiocarbamates [21,22], tricresylphosphates [23] etc. are also well recognized. Zinc dialkydithiophosphates (ZDDP) have been used for several decades as the most important commercial multifunctional lubricant additives [23-26]. However, the excessive use of phosphorous, sulfur, halogen compounds alone and/or in combination with metals has been questioned lately due to the several negative impacts they have caused to the environment as well as to the engines [27]. The phosphorous and sulfur contents adversely affect the catalytic efficiency of exhaust emission catalytic converters [28]. The metallic contents remain unburnt to form ashes which contribute to particulate emissions. At present several norms are available which strictly limit the SAPS (Sulfated Ash, Phosphorous and Sulfur) contents of additives [29,30]. Therefore, new ashless and sulfur phosphorous-free additives are to be developed to partially or completely replace high SAPS additives like ZDDP without compromising the performance of the formulated base oil. Several substituted Schiff bases, thiosemicarbazones and their synergistic mixtures with borate esters have been recently reported as efficient low/zero SAPS antiwear additives in paraffinic base oil by our research group [31-33].

The present communication reports investigations on studies of non-toxic and eco-friendly heterocyclics β-lactum antibiotics like Cefixime, Cefadroxil and Cephalexin as new ashless low SAPS antiwear additives in neutral paraffinic base oil under boundary lubricating conditions. The chemical film formed on interacting metallic surfaces during sliding condition has been characterized by X-ray Photoelectron Spectroscopy (XPS) and its elemental composition has been determined by Energy Dispersive Spectroscopy (EDS). Surface morphology and roughness of worn surface have been examined using Scanning Electron Microscopy (SEM) and contact mode Atomic Force Microscopy (AFM) respectively. Quantum chemical calculations based on density functional theory (DFT) have been performed to correlate their antiwear properties with the structures. The obtained experimental results have been found to be in good agreement with the theoretical calculations using DFT.

2. Materials & methods

2.1. Chemicals.

All of the chemicals, base oil and solvents were obtained from commercial sources and used as supplied. The solvent *n*-hexane used for cleaning the specimen was obtained from Fisher Scientific Co. (Mumbai, India). Zinc dibutyldithiophosphate (ZDDP) was procured from Flexsys Chemicals (M) Sdn Bhd, U.S.A. and used as reference additive. The β-lactum antibiotics cefixime from Schwitz Biotech, Ahmedabad, India; cefadroxil and cephalexin from Orchid Chemicals & Pharmaceuticals Limited, Chennai, India were used in the investigation. Chemical structures and IUPAC names of the tested antibiotics are listed in Table 1. These were used without further purification.

The lubricating base oil, neutral liquid paraffin oil (Qualigens Fine Chemicals, Mumbai, India) having specific gravity 0.82 at 25℃, kinematic viscosity at 40℃ and 100℃ 30 and 5.5 c*S*t respectively, viscosity index 122, cloud point -2°C, pour point -8°C, flash point 180°C and fire point 200°C, was used without further purification.

2.2. Tribological Characterization.

2.2.1. Lubricant Sample Preparation.

Paraffin oil blends (uniform solution/suspension) with various concentrations of different β-lactum antibiotics as additives from 0.5, 1.0 and 1.5 % (w/v) were made by stirring for 1-2 h on magnetic stirrer. The entire antiwear and load carrying tests were carried out at an optimized concentration 1.0 % (w/v) of antiwear additives and compared with those of 1.0 % (w/v) ZDDP.

2.2.2. Specimen.

The balls of 12.7 mm diameter made up of AISI 52100 alloy steel having hardness 59-61 HRc were used for the tests. Before and after each test, balls were cleaned with n-hexane and thoroughly air-dried.

2.2.3. Antiwear Testing.

The friction and wear properties of these antibiotics as antiwear additives in base oil were evaluated using Four-Ball Lubricant Tester (Stanhope-Seta, London Street, Chertsey, UK) at 1475 rpm (equivalent to a sliding speed of 567 mm/sec) using different loads for different time durations according to ASTM D4172. The wear scar diameter on the lower three balls was measured after running for 15, 30, 45, 60, 75 and 90 min respectively at 392N load and at various loads 294, 392, 490, 588 and 686N for 30 min test duration. In order to get more reliable values, each tribological test was repeated thrice. An optical microscope was used to measure the wear scar diameter of three stationary balls, then a mean value was calculated and cited here as mean wear scar diameter (MWD). The details of experimentation and various tribological parameters have been mentioned in supplementary information [S1].

2.4. Surface Characterization.

ZEISS SUPRA 40 Scanning Electron Microscope (SEM) coupled with Energy Dispersive X-ray (EDX) was used to investigate surface morphology and composition of the entire tribofilm on the rubbed surface of steel balls. Contact mode Atomic Force Microscope (Model No. BT 02218, Nanosurf easyscan 2 Basic AFM, Switzerland) was used to investigate the surface roughness of worn surfaces with Si_3N_4 cantilever (Nanosensor, CONTR type) having spring constant of ~0.1Nm^{-1} and tip radii more than 10 nm. X-Ray Photoelectron Spectroscopy (AMICUS, Kratos Analytical, Shimadzu, U.K.) was used to detect the chemical composition of the formed tribofilm on worn surface of horizontal balls. The MgK$\propto$ line was used as X-ray source.

2.5 Theoretical studies.

To understand the antiwear properties of cefixime, cefadroxil and cephalexin β-lactum antibiotics, quantum chemical calculations have been performed using Gaussian 03, D.01 software. Among quantum chemical methods, the Density Functional Theory (DFT) is found to be a suitable method for such calculations. All the calculations were performed using B3LYP [34] that uses Becke's three-parameter functional (B3) and include a mixture of HF with DFT exchange terms associated with the gradient corrected exchange-correlation functional of Lee, Yang and Parr [35], and the full geometry optimizations of all additives were carried out with the standard B3LYP/6-31G++(d,p) basis set [36] using Gaussian 03, D.01 [37]. The energy of highest occupied molecular orbital (E_{HOMO}), lowest unoccupied molecular orbital (E_{LUMO}), Mulliken charge on hetero-atoms and energy gap (ΔE) between lowest unoccupied molecular orbital (LUMO) and Highest occupied molecular orbital (HOMO) were obtained by these calculations.

3. Results and discussion

3.1 Antiwear properties

The mean wear scar diameter (MWD) is an indication of extent of wear when sliding contacts occurs. The concentration of β-lactum antibiotics was optimized by varying it from 0.5 to 1.5 % w/v and measuring the corresponding MWD at 392N applied load for 60 min test duration. Fig. 1 exhibits the optimization results of β-lactum antibiotics showing variation of MWD with change in concentrations of the additives from 0.5, 1.0 and 1.5 % (w/v). It can be clearly seen that the value of MWD dramatically decreases for all the additives when their concentration is increased from 0.5 to 1.5 % (w/v). Thus the additives improve the antiwear properties of paraffin oil at all the tested concentrations. The observed MWD values for all the additives are found to be the lowest at 1.0 % w/v concentration. The cefixime shows maximum decrease in MWD at all the concentrations followed by cefadroxil and cephalexin. As distinct from the figure, beyond the optimum concentration of additives the MWD is almost constant. Therefore, entire antiwear tests were carried out at 1% w/v which is the optimized concentration of the additives.

Fig. 2 shows variation of MWD in the presence of all the tested antiwear additives, β-lactum antibiotics and zinc dibutyldithiophosphate (ZDDP) in paraffin oil at the applied load 392N for 60 min test duration. It is apparent from the figure that the largest MWD (0.681mm) was observed in case of pure paraffin oil while it was the smallest in presence of cefixime (0.524mm). Addition of additives to the base oil significantly reduces the value of wear scar diameter. All the β-lactum antibiotics reduce the MWD much more than the high SAPS containing conventional ZDDP. This is attributed to the fact that investigated additive are polar molecules with a number of active centers which facilitate the adsorption of additive molecules on steel surface. Among all β-lactum antibiotics, cefixime exhibits excellent antiwear properties.

In order to investigate the effect of sliding time on the mean wear scar diameter, the antiwear tests have been also carried out at 392N applied load for different time durations, 15, 30, 45, 60, 75 and 90 min for paraffin oil in presence and absence of antiwear additives. The variation of MWD with respect to time durations at 392N load is represented in Fig. 3 and the obtained results are collected in supplementary information (Table S1). It is evident from the Fig. 3 that the MWD in case of paraffin oil for all the test durations is found to be much larger than in the presence of additives. Initially, for 15 min of test duration, the MWD in the presence of β–lactum additives is nearly the same but it is much smaller in case of ZDDP. After that further increase in test duration up to 30 min, there is abrupt increase in MWD for ZDDP whereas its value increases quite smoothly for β-lactum additives. Although the activity of different β-lactum antibiotics could not be differentiated for 15 min test duration, these can be well differentiated at 30 min test run and thereafter. The blends with cefixime and cefadroxil additives show comparatively much smaller MWD than ZDDP indicating better adsorption of these additives on steel surface. On the other hand, in case of cephadroxil MWD observed is larger than that in presence of ZDDP. The value of MWD for cefixime was found to be the lowest for all test durations from 30-90 min.

It is apparent from the Fig. 3 that initially up to 30 min, the rate of increase in MWD is greater for paraffin oil in presence and absence of additives but later on up to 90 min, it slightly decreases and increases linearly with increase in time duration for all the additives. Further, there is sudden increase in the value of MWD at 90 min test run in case of paraffin oil alone, however, in presence of additives a gradual increase in MWD is observed.

This may be due to the fact that initially there is no tribofilm on the interacting surfaces. As the time increases the additive molecules get decomposed during sliding under operating conditions (high load and high temperature) and reacted with metal surface to form tribochemical film. The formation of tribofilm is time dependent; therefore, some time exposure is required to form a durable tribofilm on sliding surfaces [38]. The excellent antiwear behavior is shown by the cefixime since it contains greater number of active centers through which it may be adsorbed on the metal surface. It might be one of the reasons behind the observed trend of additives in the present investigation.

Fig. 4 illustrates the variation of friction coefficient with time in absence and presence of 1% w/v ZDDP/β-lactum antibiotics in paraffin oil for 392N applied load. It can be seen that the admixture of base oil with cefixime and cefadroxil gives the lower friction coefficient than that with ZDDP or cephalexin. For ZDDP and cephalexin the friction coefficient increases initially up to 45 min test run and then it slightly decreases or remains constant up to 75 min duration whereas cefixime and cefadroxil stabilize it earlier at 30 min test run. In every case, it has been observed that the value of friction coefficient starts shooting from 75-90 min duration. This may due to the wear assisted surface damage and generation of wear debris produced with time under operating conditions at the interface. The friction coefficient data support the order of efficiency for different additives as discussed above, accordingly the highest friction coefficient for every run is observed for plain paraffin oil and the lowest for cefixime.

On the basis of variation of mean wear scar diameter and friction coefficient with time the order of antiwear efficiency is given below:

Cefixime > Cefadroxil > ZDDP > Cephalexin > Paraffin oil

To estimate wear more realistically it is important to examine the variation of mean wear volume with time instead of variation of mean wear scar diameter with time. According to equation 3 (see supplementary information S1), MWV contains MWD to the fourth power. Therefore, little change in the dimension of MWD causes huge changes in the MWV. Mean wear volume in absence and presence of different additives at 392N load for paraffin oil were plotted with a function of time and a linear regression model was fitted on the points including origin to find overall wear rate, Fig. 5. Overall wear rate was found to be very high in absence of additives. Among various β-lactum additives, the following order emerged for overall wear rate:-

Cefixime < Cefadroxil < Cephalexin

This again is in conformity with the conclusion drawn earlier that cefixime gets most strongly adsorbed on metal surface to form most adherent tribofilm and thus reducing wear to the greatest extent.

Since running-in process refers to the adjustment of the surfaces moving under controlled conditions, the running-in wear rate is always higher than the steady-state wear rate. The values of overall, running-in and steady-state wear rate are listed in Table 2. Table 2 shows that the running-in wear rate is found to be much lower in case of cefixime and cefadroxil than ZDDP while the steady-state wear rates in their presence are comparable to ZDDP. The running-in and steady-state wear rate for paraffin oil in absence and presence of additives at 392N load have been mentioned in supplementary information (Fig.S1 and S2). The addition of antiwear lubricant additives to the paraffin base oil effectively reduces the overall, running-in and steady-state wear rates. Moreover, the steady-state wear rate is directly related to the machine life. Thus, for a better antiwear additive it is important to achieve steady-state as early as possible and it must be stable for longer duration. This behavior is evident with the additives cefixime, cefadroxil and ZDDP.

In order to investigate the effect of applied load on the mean wear scar diameter, the tests have been carried out at different loads 294, 392, 490, 588, 686 and 784N for 30 min test duration for paraffin oil in presence and absence of antiwear additives (1% w/v). Fig. 6 represents plots of MWD as a function of applied load at 30 min test duration and the obtained results are collected in supplementary information (Table S2). It can be clearly shown from the figure that paraffin oil, ZDDP could sustain the load up to only 490 and 588N respectively whereas β-lactum additives reflect appreciable load carrying ability up to 784N.

At initial load (294N), MWD is very large in the absence of additives but in presence of β-lactum additives it is fairly reduced. With increase in load, at 392N MWD increases appreciably in every case but this increase is maximum in absence of additives. This shows that the thin film of lubricant and additive adsorbed on the interacting surfaces resists much increase in MWD on increasing applied load. At 490N load the base oil shows abrupt increase in MWD; however, the increase is very small in presence of the additives. This can be attributed to the formation of tribofilm in presence of additives. Thus, the tribofilm formed is further capable of carrying higher load. Beyond 490N load the tribofilm fails to sustain the load in case of paraffin oil while the film fails at 588N load in case of blends with ZDDP. On further increase in the applied load cephalexin could sustain the load up to 686N, cefadroxil somehow bears load up to 784N with large MWD but cefixime could successfully bear the load up to 784N without surface destruction. A comparison of MWD shows that its value in presence of cefixime at 784N is much lower than ZDDP at 588N indicating higher load carrying capacity of cefixime. This is one of the most striking feature of the investigated β-lactum additives. Overall order of efficiency of β-lactum additives at every load was observed as:

Cefixime > Cefadroxil > Cephalexin > ZDDP > Paraffin oil

A plot of applied load and friction coefficient at 1% concentration of ZDDP and β-lactum additives for 30 min duration is presented in Fig. 7. However, the increase in friction coefficient with load is much higher in case of paraffin oil whereas in case of β-lactum additives it follows linearly at each test load. The efficiency of β-lactum additives towards their antifriction behavior lies in the same order as obtained in case of MWD-load correlation (Fig. 6).

3.2 Surface Characterization

3.2.1 Surface morphology

The topography of the wear scar surface has been studied by scanning electron microscopy (SEM) and Atomic Force Microscopy (AFM). The SEM micrographs of the wear scar in the presence and absence of 1% w/v ZDDP, β-lactum additives tested at 392N load for 90 min test run are shown in Fig. 8. A comparison of the SEM-images for paraffin oil alone and with additives, show that the surface is much more damaged in the former case (fig.8a) while it is much smoother in the latter case (fig.8b-e). Therefore, the new additives possess significant antiwear properties than ZDDP. The extent of smoothening of worn surfaces have been found to be maximum in case of cefixime as it is evident from Fig. 8c in which smaller grooves are seen. Besides this, the clear boundary of wear scar is also seen in inset. However, this extent of smoothening is found to be comparatively lesser in case of cefadroxil, cephalexin and ZDDP respectively. The observed smoothness of micrographs in presence of new additives follows the same order as inferred on the basis of their antiwear behavior discussed above. This smoothness of the surface may be correlated well with the observed order of running-in wear rate data:

Paraffin oil > Cephalexin > Cefadroxil > Cefixime

To investigate and compare the morphology of worn steel surfaces lubricated with cefixime and ZDDP at comparatively higher load, the SEM micrographs have been also taken at 588 N load for 30 min test duration. These micrographs are presented in supplementary information (Fig.S3). It can be seen that the there is much more destruction of surface in case of ZDDP (Fig.S3b), on the contrary, relatively much smoother surface has been obtained when cefixime (Fig.S3a) is used.

Surface topography of the wear scars on the steel balls observed after antiwear tests in paraffin oil were examined by contact mode Atomic Force Microscopy in the presence and absence of the β-lactum antibiotics and ZDDP at 392N load for 90 min test duration. The 3D-AFM images and corresponding line profile graphs of the wear scar are shown in supplementary information (Fig.S4). From the 3D-AFM images, it is evident that there are huge differences in the average peak-valley height in case of surface lubricated with paraffin alone. However, in the presence of additives this difference is extremely small. The value of area roughness has been found to be maximum, 409 nm (Sq) for the base oil. The maximum reduction of surface roughness has been observed in case of cefixime (Sq= 57 nm) which indeed is much better than that in case of ZDDP (Sq=75 nm) under similar conditions. The same is also confirmed through the roughness parameters summarized in supplementary information (Table S3). As apparent from the data (Table S3) and figures, the roughness has fairly reduced in the presence of additives. The addition of β-lactum antibiotics to the base oil drastically reduces the surface roughness. The reduction in surface roughness may be attributed to the tribofilm formed under test conditions by the adsorbed additive**.** The similar observations are also evident from their corresponding line profile graphs.

3.2.2 Chemical analysis of tribofilm

The EDX spectra of the worn surface lubricated with paraffin oil, admixtures with ZDDP and cefixime have been recorded to determine the elemental compositions of the tribofilm at 392N load for 90 min test duration are mentioned in supplementary information (Fig.S5). The EDX spectrum of the worn steel surface lubricated with paraffin oil alone showing absence of additional peaks due to hetero atoms except oxygen which may be due to the oxide formation (Fig.S5a). On the other hand, Fig.S5b shows prominent additional peaks for zinc, phosphorous, sulfur and nitrogen on the wear scar surface lubricated with additive ZDDP. Herein, the best antiwear behavior shown by cefixime is due to the presence of sulfur and nitrogen in the EDX spectra (Fig.S5c) of worn surface which reflects strong additive-metal interaction through which adsorption is facilitated. This brings about its tribochemical reaction with metal surface to form stable protective layers reducing friction and wear.

Besides this, to understand the tribochemical interaction of cefixime additive, the EDX spectrum (Fig.S6) was also taken at a higher load, 588N, for 30 min duration. Fig.S6 clearly depicts that the atomic concentration of hetero-atoms i.e. sulfur and nitrogen increases appreciably with increase in load which may be responsible for its high load-carrying capacity.

The detailed chemical analysis of these chemisorbed elements on worn surfaces has been studied using XPS. The tribofilms generated on steel surfaces in presence of admixtures at various temperatures show that the additives undergo decomposition at much lower temperature than their normal decomposition temperature [39]. Thus, in order to ascertain the tribochemistry, XPS analysis of the worn scar in presence of the blend with cefixime at 392N load for 90 min test duration was carried out. Fig. 9(a-e) show the XPS spectra of C 1s, N 1s, S 2p, O 1s and Fe 2p of the wear scar. The spectrum of C 1s on the worn surface exhibits peaks at 285.0 and 289.0

eV corresponding to -C(O)O-and C-C/C-H moieties respectively [40]. The binding energy of N 1s is about 399.9 eV which corresponds to the adsorbed nitrogen in the form of -N=C-and/or amide moiety [41]. These moieties are also present in the molecular structure of cefixime which shows that these are the favorable sites for chemisorption on metal surfaces during sliding process. The spectrum of S 2p on worn surface illustrates the existence of peak at 168.5 eV showing occurrence of tribochemical reaction. On combining the S 2p peak with binding energy 532.2 eV of O 1s spectra, it can be further ascertained that there must be *in-situ* formation of $FeSO_4$ during tribochemical reaction [42]. Further, in case of oxygen another peak of O 1s is also observed at binding energy of 530.2 eV corresponding to its chemical state in the tribochemical species Fe_3O_4 and/or Fe_2O_3. Combining the binding energies of O 1s at 530.2 eV with Fe 2p at 710.9 eV, it can be stated that iron has oxidized to Fe_2O_3 and Fe_3O_4 during rubbing process [43,44].

3.3 Theoretical studies

Since the tested additives contain several other functional groups in addition to β-lactum ring, theoretical calculations have been performed to find out the effect of these groups towards their antiwear lubrication behavior. The data obtained for all quantum chemical parameters such as E_{HOMO}, E_{LUMO}, ΔE, ΔE_1 and ΔE_2 are listed in Table 3. Frontier Molecular Orbital (FMO) theory is useful in predicting the adsorption behavior of the additive molecules which is responsible for interaction with metallic surface. Fig. 10 shows that β-lactum antibiotics have different HOMO and LUMO distributions. HOMO density distributions are mainly localized around the aromatic ring of all β-lactum antibiotics except cephalexin, which might be due to the presence of hetero atom like N, O and S with π-electron in the additive molecules. High values of E_{HOMO} are likely to indicate a tendency of the molecule to donate electron to appropriate accepter molecules with low energy and empty molecular orbital. On the other hand, E_{LUMO} refers to the suitability of the molecule to accept electron, thus lower the value of E_{LUMO}, there is higher possibility that the electrons are accepted. As for the value of ΔE is concerned, it describes the minimum energy required to excite an electron from the HOMO. Therefore, lower the value of ΔE, higher will be the tendency of the additive to get adsorbed. Thus ΔE is important quantum chemical parameter to correlate the experimental results with the theoretical ones. The obtained results (Table 3) indicate that the cefixime has the highest E_{HOMO}, lowest E_{LUMO} and also lowest value of ΔE as compared to cefadroxil and cephalexin. On the basis of density functional theory parameters the order of β-lactum antibiotics as antiwear additives is as follows:-

Cefixime > Cefadroxil > Cephalexin

Interaction with metallic surface

A literature survey reveals that the adsorption of heterocyclic compounds on the metal surface can occur on the basis of donor-accepter interaction between the active centers of the heterocyclic compound and the vacant d-orbitals of metal atom [45,46]. The investigated β-lactum lubricant additives are the polar molecules which get adsorbed onto the metal surface through their active sites. Therefore, for the investigation of antiwear behavior it is important to correlate molecular orbital energies of the additive molecules to those with the energy of metal [47,48]. Huang *et al.* [49] have calculated the energy of frontier molecular orbitals of iron by considering the iron as five-atom clusters. The interaction between additives and iron can be discussed on the basis of ΔE_1 (ΔE_1= E_{LUMO} of additive - E_{HOMO}) and ΔE_2 (ΔE_2= E_{LUMO} of iron – E_{HOMO} of additive) as mentioned in Table 3. From these values it is evident that the additive molecules are electron donors while iron acts as an electron acceptor and this can be regarded as a nucleophilic reaction [50]. The results show that the difference between E_{HOMO} of cefixime and E_{LUMO} of iron is smallest among all the three β-lactum additives, suggesting that the maximum interaction will take place between cefixime and iron. To be a good antiwear additive it is not only to donate the electron from HOMO of the additive molecules to the LUMO of the vacant d-orbitals of the iron atom but also there must be a significant interaction between the HOMO of the iron and LUMO of the additive molecules (Reterodonation/Backbonding). Since the antiwear additives are the polar molecules, the extent of interaction between $HOMO_{Additives}$ to $LUMO_{Iron}$ may always be higher than the $HOMO_{Iron}$ to $LUMO_{Additives}$. A greater transfer of electron density from additive molecules to the vacant d-orbital of iron atom accumulates the electron density on the iron. Consequently, it develops more tendencies to donate back electron to the vacant orbital of the additives. This favors the extent of backdonation (Synergistic bonding). It is evident from Table 8 that the values of interaction parameters ΔE_1 (E_{LUMO} of iron - E_{HOMO} of additive) are always lower than ΔE_2 (E_{LUMO} of additives - E_{HOMO} of iron) for all the β-lactum additives. The order of antiwear efficiency of β-lactum additives emerged on the basis of values of ΔE, ΔE_1 and ΔE_2, is found to be exactly the same as that of their antiwear lubrication behavior evaluated experimentally with four ball tester.

4. CONCLUSIONS

- The addition of β-lactum antibiotics as an antiwear additive into neutral paraffin oil significantly improves its antiwear properties. The order of their efficiency towards antiwear behavior is as follows:

  Cefixime > Cefadroxil > Cephalexin

- The load carrying ability of the β-lactum antibiotics has been found to be much higher than paraffin oil alone and its admixture with ZDDP.
- Among three β-lactum antibiotics, the overall, running-in and steady-state wear rates are found to be lowest in case of cefixime followed by cefadroxil, ZDDP and then cephalexin.
- Surface studies by SEM and AFM support the order of their antiwear properties.
- XPS analysis of the worn surface provides evidence in favor of formation of protective tribofilm containing N, S, O, Fe and C elements. It appears that there is strong adsorption of the additives and tribochemical reactions might have resulted in formation of a complex boundary lubrication film containing –O-C(O)-, C-C/C-H moieties, adsorbed organic-nitrogen and amide moiety, $FeSO_4$, Fe_2O_3 and/or Fe_3O_4 on the metallic surface.
- The density distributions of the frontier molecular orbitals (HOMO & LUMO) of the additive molecules obtained from quantum chemical calculations have been found to be in accordance with the experimental observations.
- The experimentally observed order of the antiwear properties of the additives can be fully explained in terms of theoretically calculated values of E_{HOMO} and E_{LUMO} values of the additives.

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Fig. 8. SEM micrographs at different magnifications of the worn steel surface lubricated with β–lactum additives (1% w/v) in paraffin oil for 90 min test duration at 392 N applied load: (a) Paraffin oil, (b) ZDDP, (c) Cefixime, (d) Cefadroxil and (e) Cephalexin

Fig. 9. XPS spectra of tribochemical film formed on worn steel surface lubricated with cefixime additive (1% w/v) at 392 N applied load for 90 min test duration in liquid paraffin. **(a).** C 1s **(b).** N 1s **(c).** S 2p **(d).** O 1s and **(e).** Fe 2p

Fig. 10. HOMO and LUMO density distributions of β-lactum additives respectively for (a,b). Cefixime, (c,d). Cefadroxil and (e,f). Cephalexin

Table 1. Molecular structure and commercial name of investigated β–lactum antiwear lubricant additives

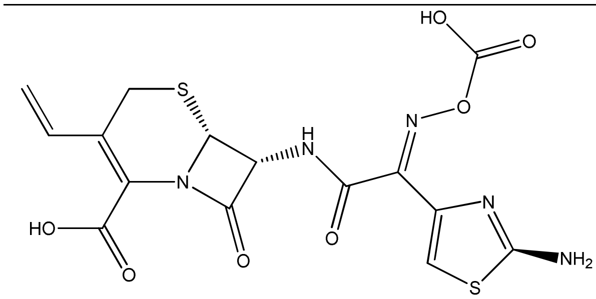
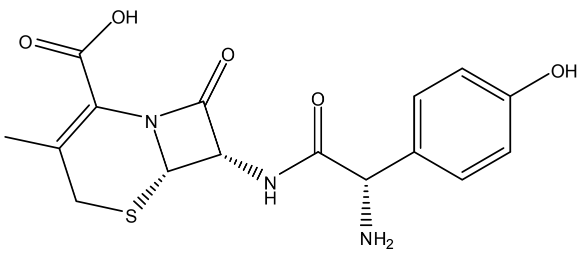
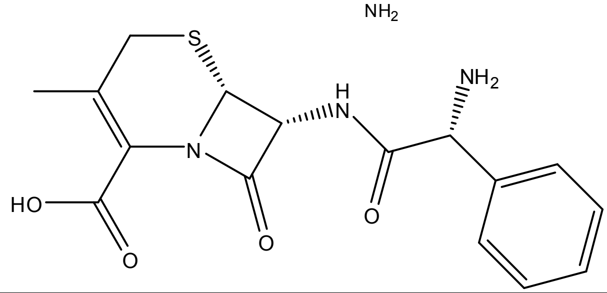
Structure	IUPAC Name	Commercial Name
	(6R,7R)-7-((E)-2-((R)-2-amino-2,3-dihydrothiazole-4yl)-2-(corboxyimino)acetamido)-8-oxo-3-vinyl-5-thia-1-azabicyclo [4,2,0]oct-2-ene-corboxylic acid	Cefixime
	(6S,7S)-7-((S)-2-amino-2-(4-hydroxyphenyl)acetamido)-3-methyl-8-oxo-5-thia-1-azabicyclo [4,2,0]oct-2-ene-corboxylic acid	Cefadroxil
	(6R,7R)-7-((R)-2-amino-2-phenylacetamido)-3-methyl-8-oxo-5-thia-1-azabicyclo[4,2,0] oct-2-ene-corboxylic acid	Cephalexin

Table 2. Wear rates of paraffin oil in absence and presence of *β*-lactum antiwear additives at 392N applied load for 90 min test duration

S.N.	Additives	Wear Rate(10^{-4}x mm^3/h)		
		Running-in	Steady-state	Overall
1.	Paraffin oil	69.99	38.70	63.06
2.	ZDDP	24.92	18.52	22.45
3.	Cefixime	16.66	13.49	16.60
4.	Cefadroxil	20.16	18.39	19.09
5.	Cephalexin	32.70	29.36	29.09

Table 3. Quantum chemical parameters for *β*-lactum antiwear additives calculated with B3LYP/6-31G++(dp) basis set

Additive	**Total Energy (a.u.)**	**E_{HOMO} (Hartree-fock)**	**E_{LUMO} (Hartree-fock)**	**ΔE (Hartree-fock)**	**ΔE_1 (Hartree-fock)**	**ΔE_2 (Hartree-fock)**	**wear rate (10^{-4} x mm^3/h)**
Fe_5[49]		-0.18651	-0.06420	0.12231			
Cefixime	-2177.3221	-0.20657	-0.10184	0.10473	0.08467	0.14237	16.60
Cefadroxil	-1558.5791	-0.23250	-0.06807	0.16443	0.11844	0.16830	19.09
Cephalexin	-1483.3504	-0.24599	-0.06509	0.18090	0.13560	0.18179	29.09

ΔE_1= E_{LUMO} of additive - E_{HOMO} of iron

ΔE_2= E_{LUMO} of iron - E_{HOMO} of additive

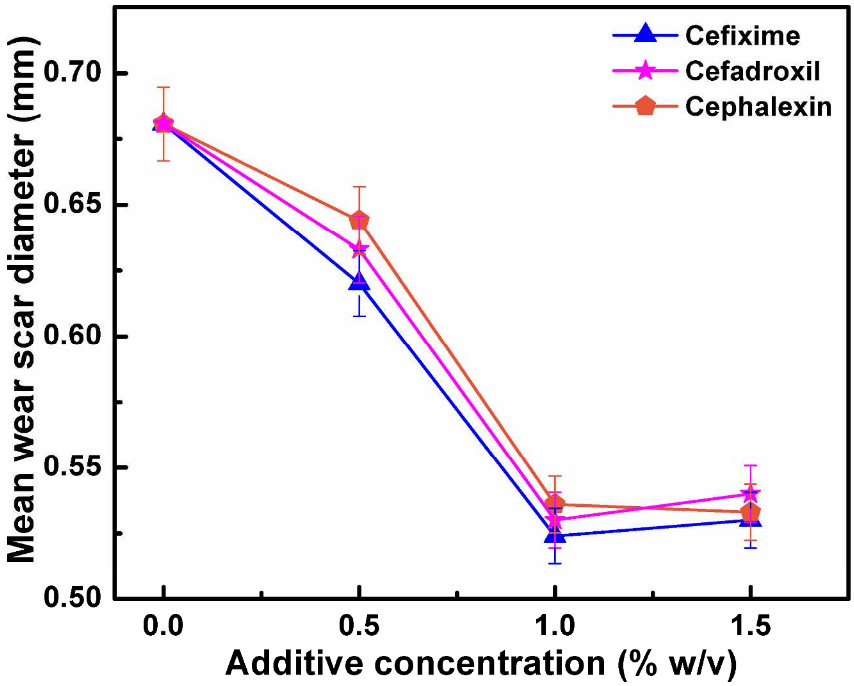


Fig. 1. Variation of mean wear scar diameter in absence and presence of different concentrations of β–lactum additives in paraffin oil at 392N applied load and 60 min duration

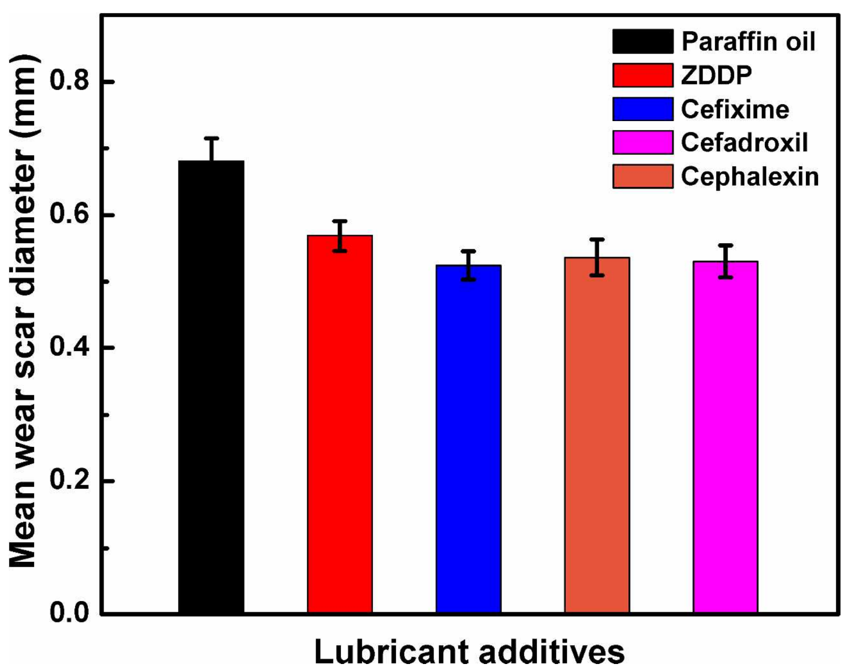


Fig. 2. Variation of mean wear scar diameter in paraffin oil with and without different antiwear additives (1% w/v) at 392N applied load for 60 min test duration

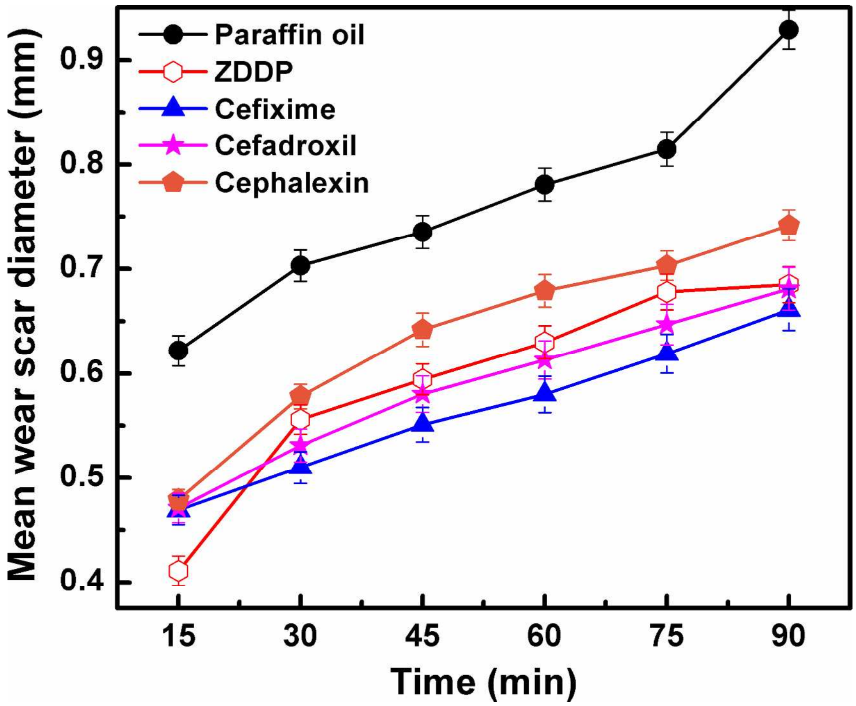


Fig. 3. Variation of mean wear scar diameter with time in paraffin oil containing (1% w/v) zinc dibutyldithiophosphate and β–lactum additives at 392N applied load

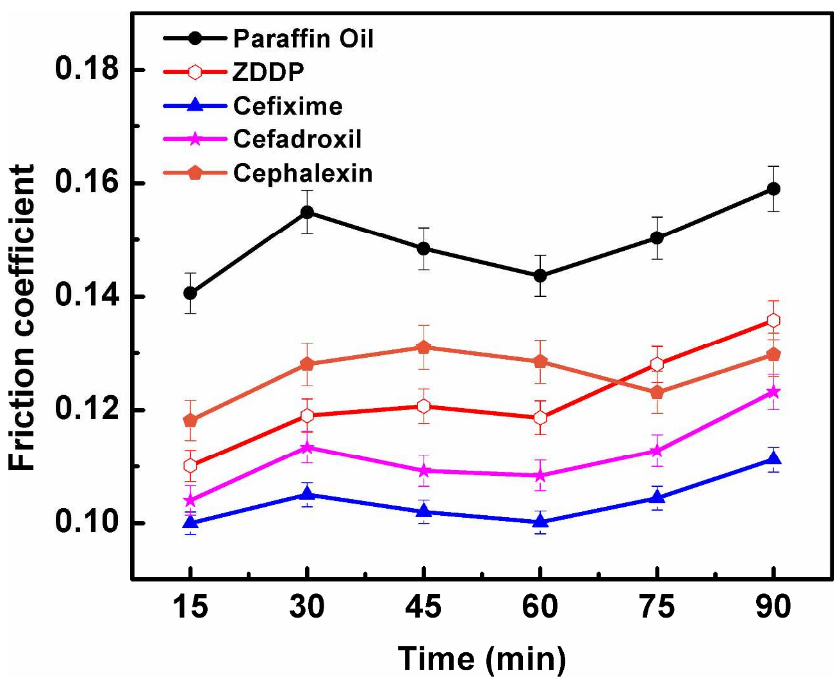


Fig. 4. Variation of friction coefficient with time in paraffin oil containing (1% w/v) zinc dibutyldithiophosphate and β–lactum additives at 392N applied load

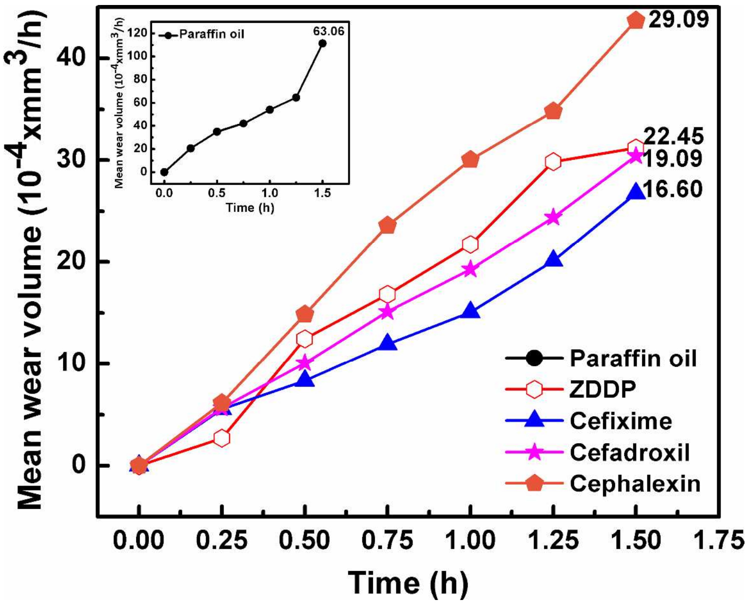


Fig. 5. Determination of overall wear rate by varying mean wear volume with time (h) in paraffin oil containing (1% w/v) zinc dibutyldithiophosphate and β–lactum additives at 392N applied load

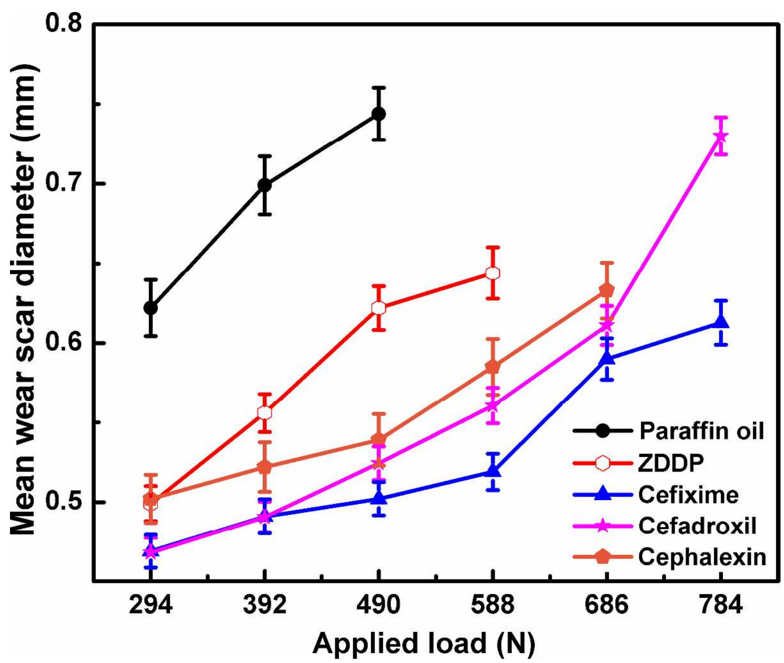


Fig. 6. Variation of mean wear scar diameter with applied load in paraffin oil containing (1% w/v) zinc dibutyldithiophosphate and β–lactum additives for 30 min test duration

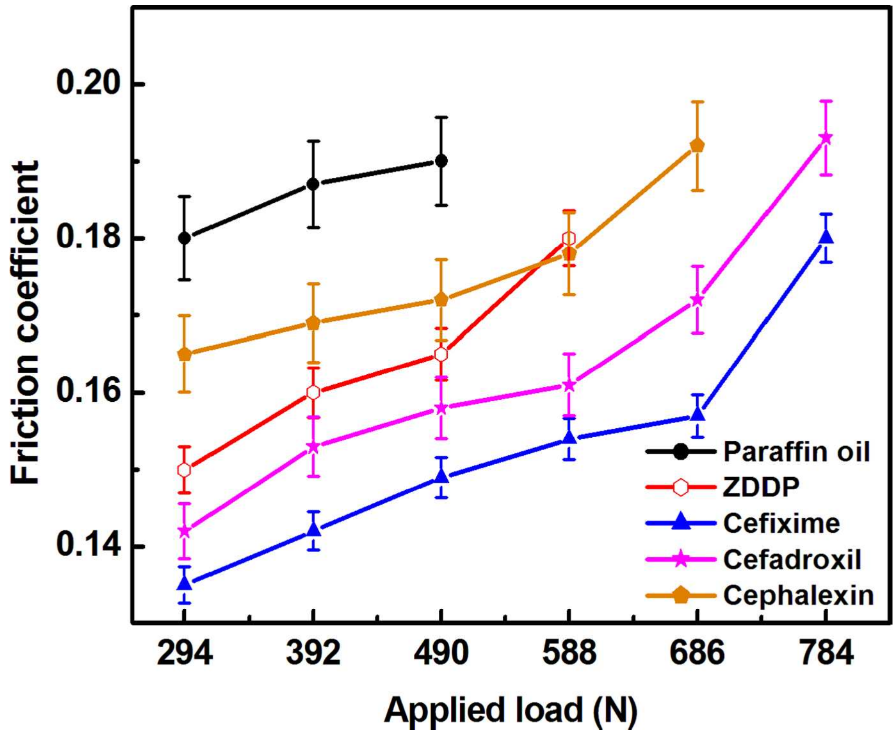
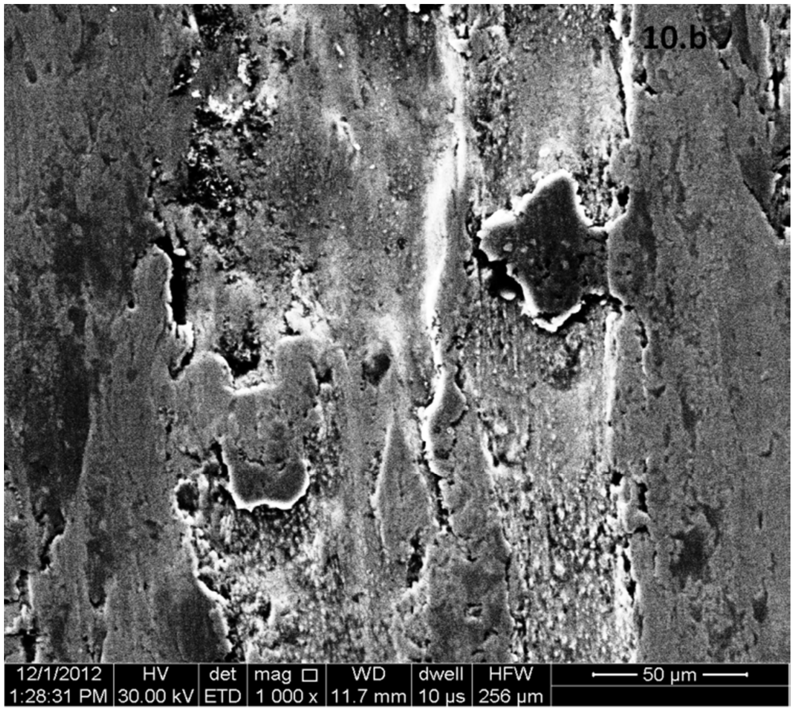


Fig. 7. Variation of friction coefficient with load in paraffin oil containing (1% w/v) zinc dibutyldithiophosphate and β–lactum additives for 30 min test duration

Fig. 8a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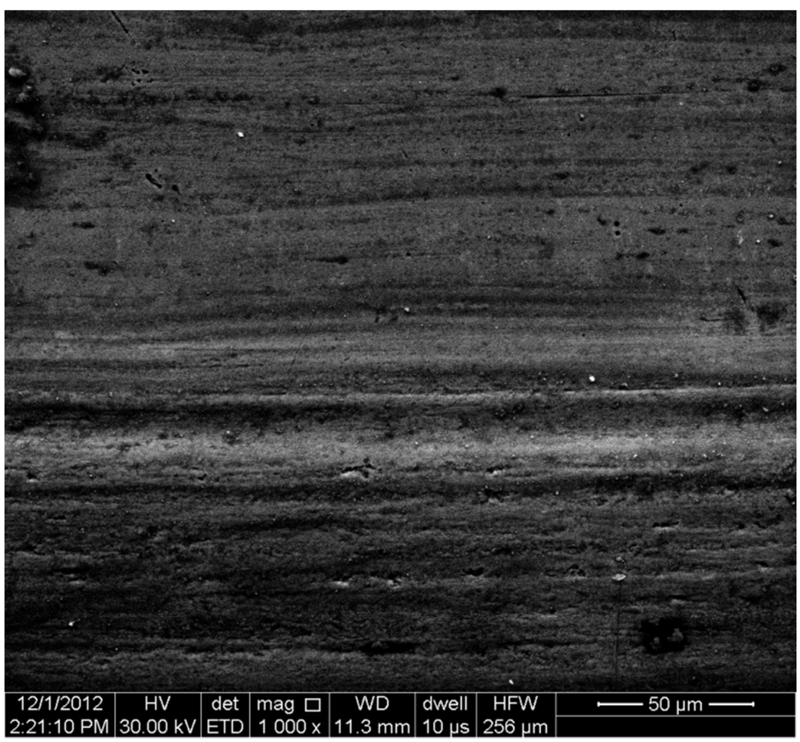
dwell 10 µs
HFW 256 µm
50 µm

Fig. 8b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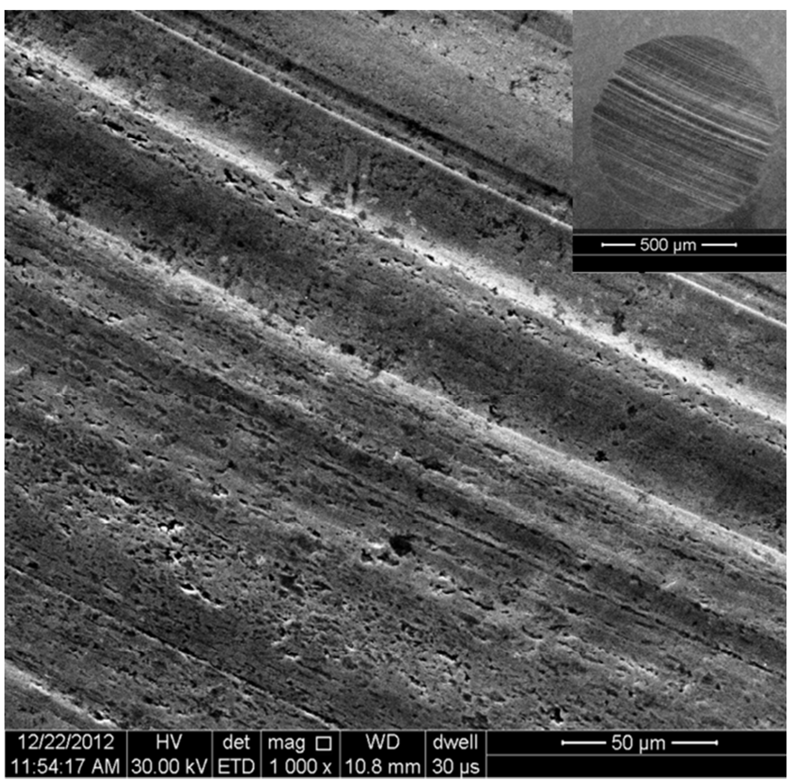
HV 30.00 kV
det ETD
mag 1 000 x
WD 11.3 mm
dwell 10 µs
HFW 256 µm
50 µm

Fig. 8c


500 µm
12/22/2012
12:04:21 PM
HV
30.00 kV
det
ETD
mag
1 000 x
WD
10.5 mm
dwell
30 µs
50 µm

Fig. 8d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12/22/2012
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det
ETD
mag
1 000 x
WD
10.8 mm
dwell
30 µs
50 µm

Fig 8e

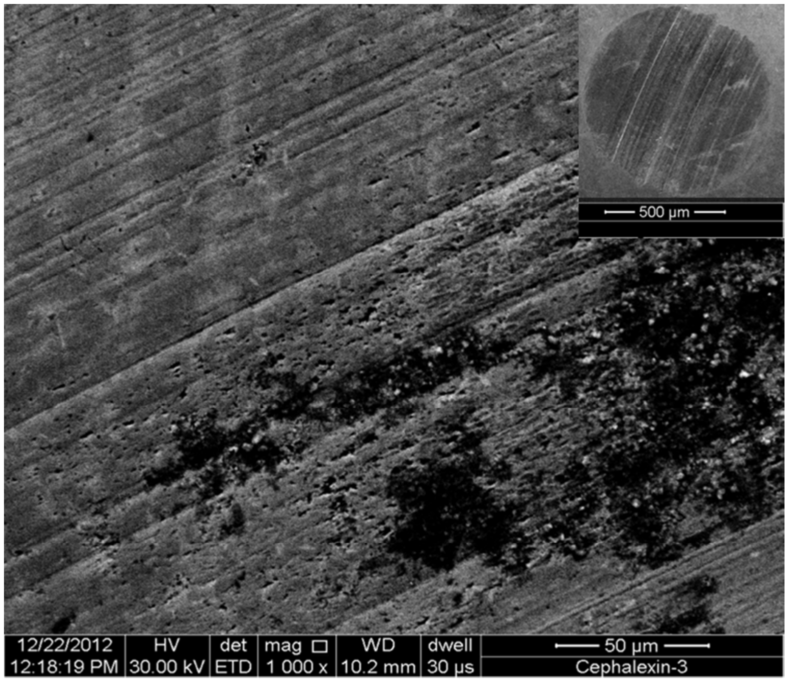
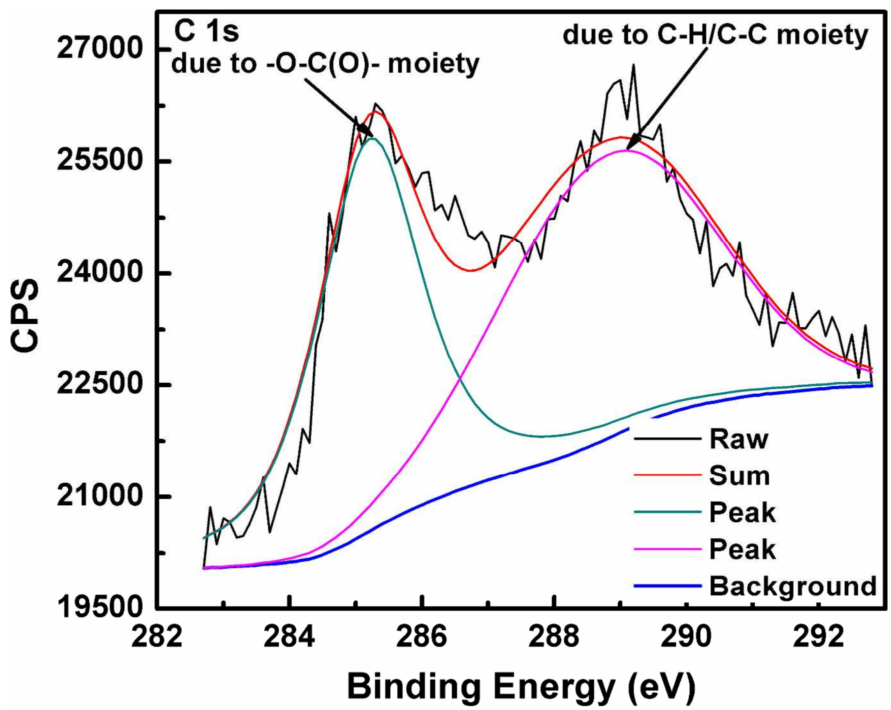


Fig. 8. SEM micrographs at different magnifications of the worn steel surface lubricated with β–lactum additives (1% w/v) in paraffin oil for 90 min test duration at 392 N applied load: (a) Paraffin oil, (b) ZDDP, (c) Cefixime, (d) Cefadroxil and (e) Cephalexin

Fig. 9a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due to C-H/C-C moiety
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Sum
Peak
Peak
Background
CPS
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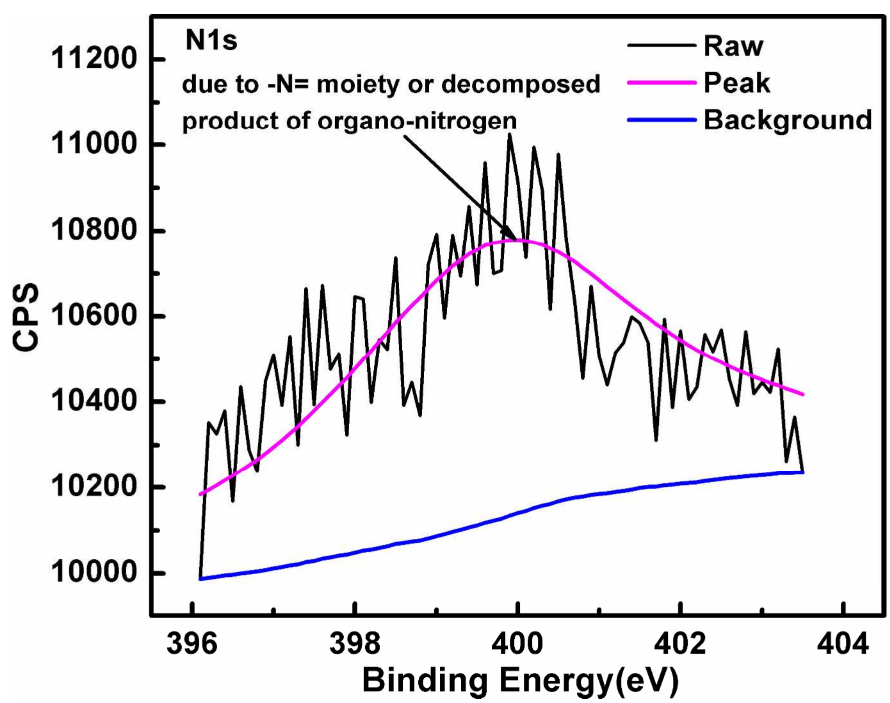
22500
21000
19500
282
284
286
288
290
292
Binding Energy (eV)

Fig. 9b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due to -N= moiety or decomposed
product of organo-nitrogen
Raw
Peak
Background
CPS
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11000
10800
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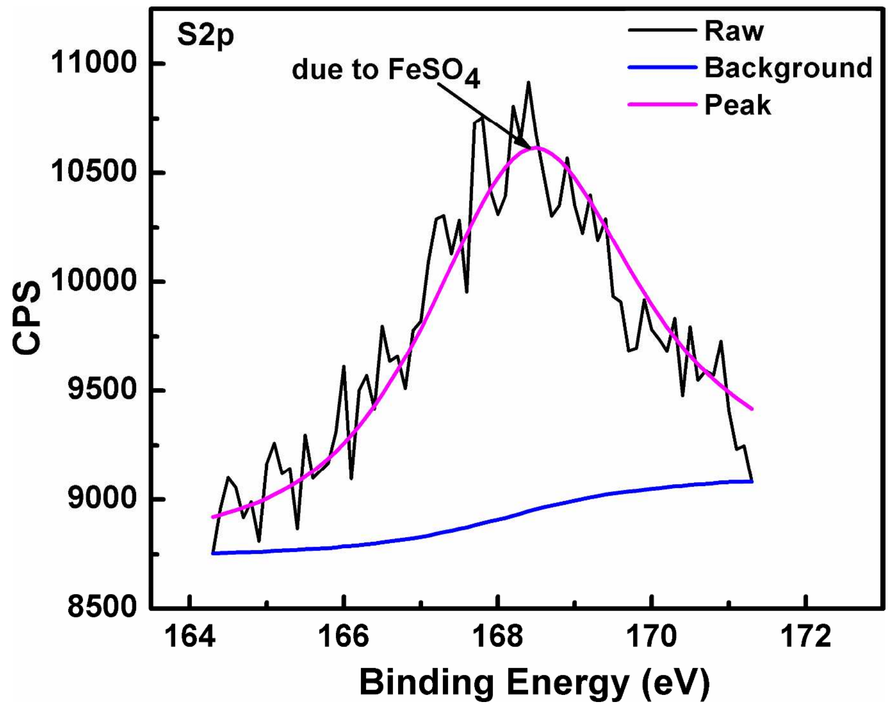
10400
10200
10000
396
398
400
402
404
Binding Energy(eV)

Fig. 9c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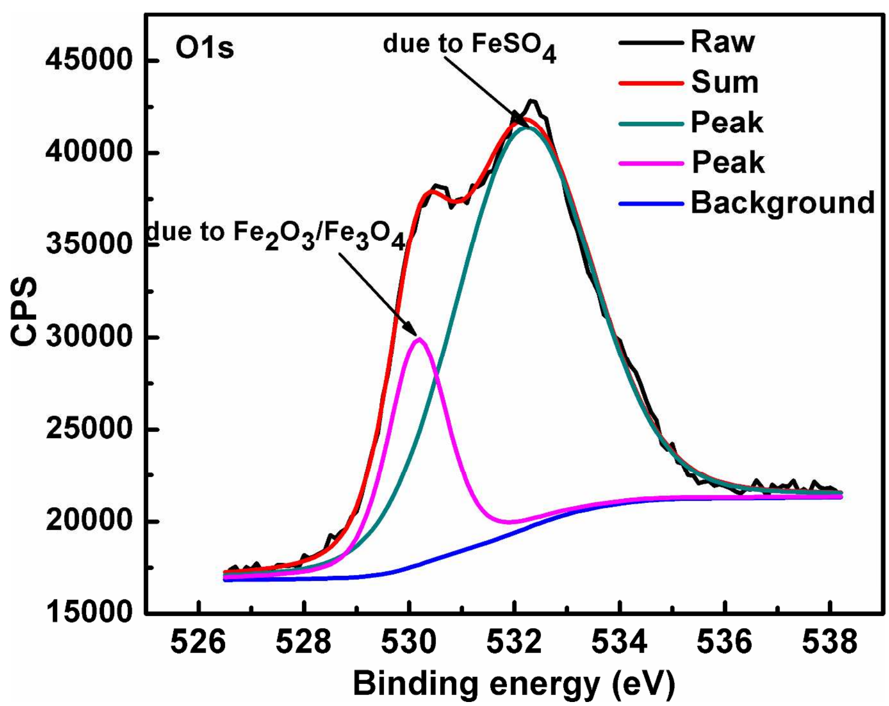
168
170
172

Fig. 9d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due to Fe2O3/Fe3O4
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536
538

Fig. 9e

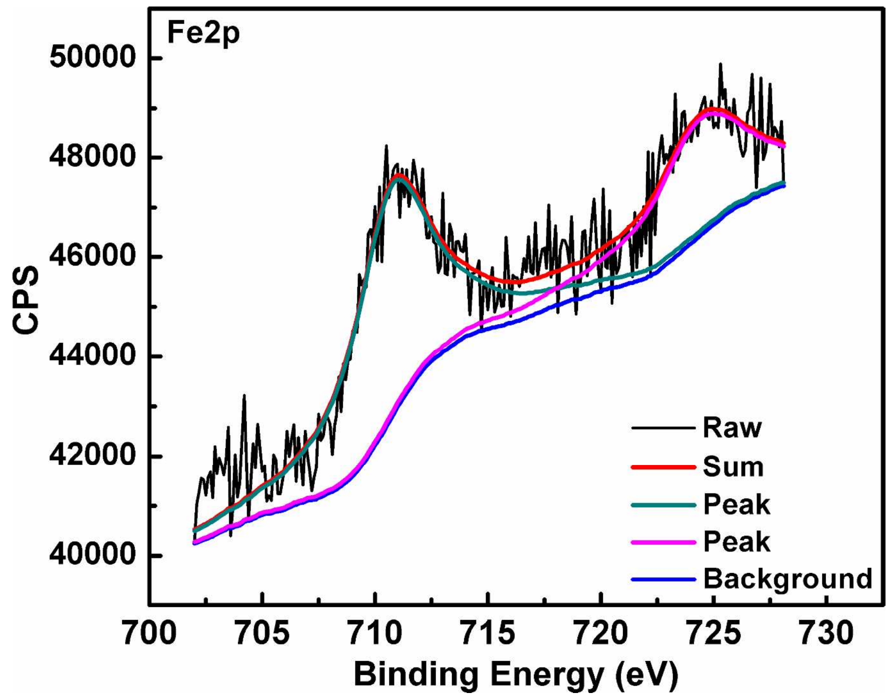


Fig. 9. XPS spectra of tribochemical film formed on worn steel surface lubricated with cefixime additive (1% w/v) at 392 N applied load for 90 min test duration in liquid paraffin. **(a).** C 1s **(b).** N 1s **(c).** S 2p **(d).** O 1s and **(e).** Fe 2p

Fig. 10a

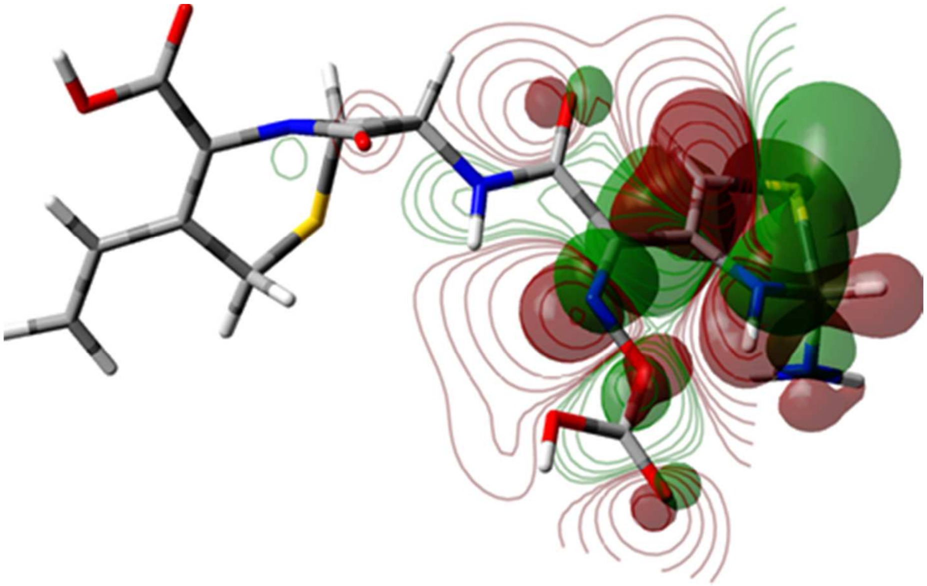
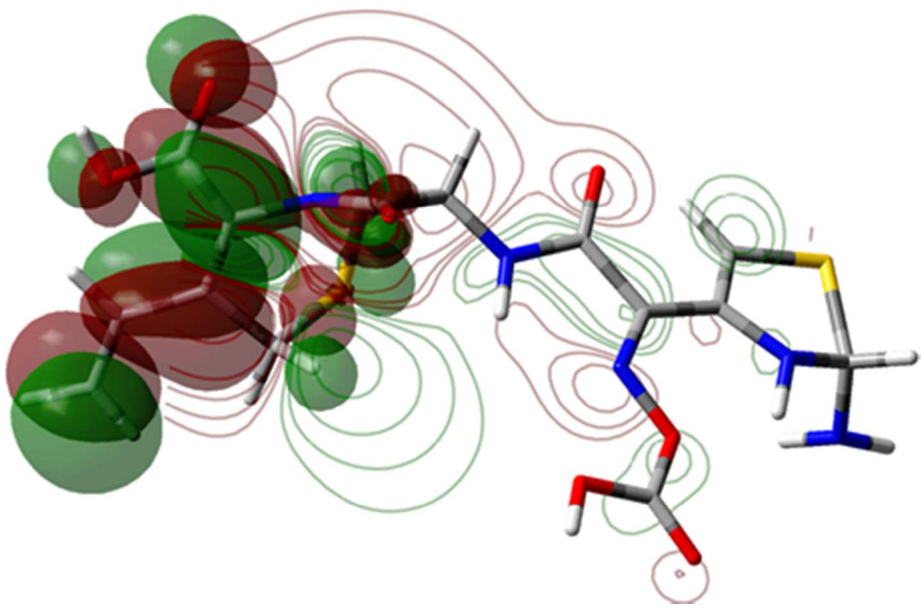


Fig. 10b



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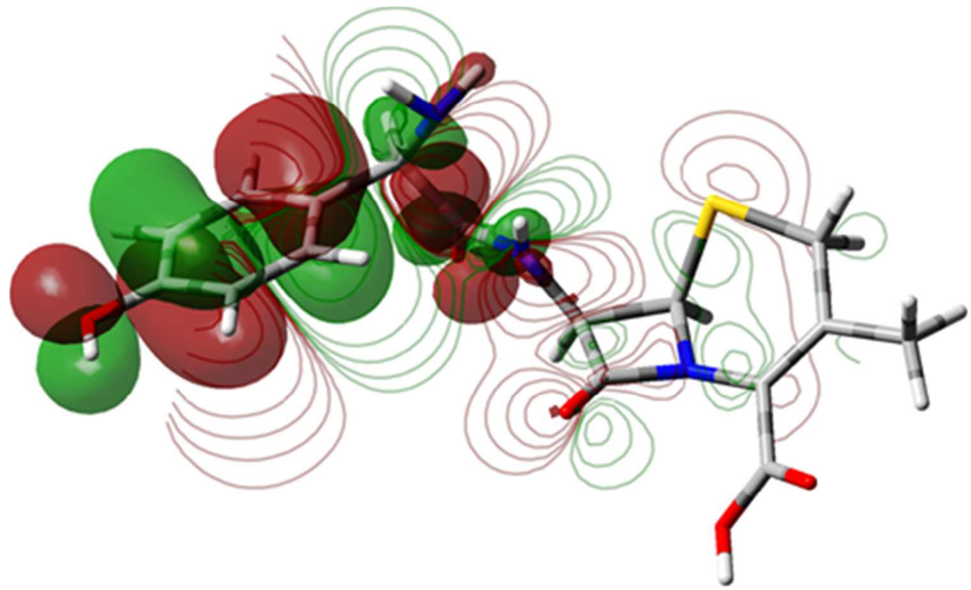

Fig. 10d

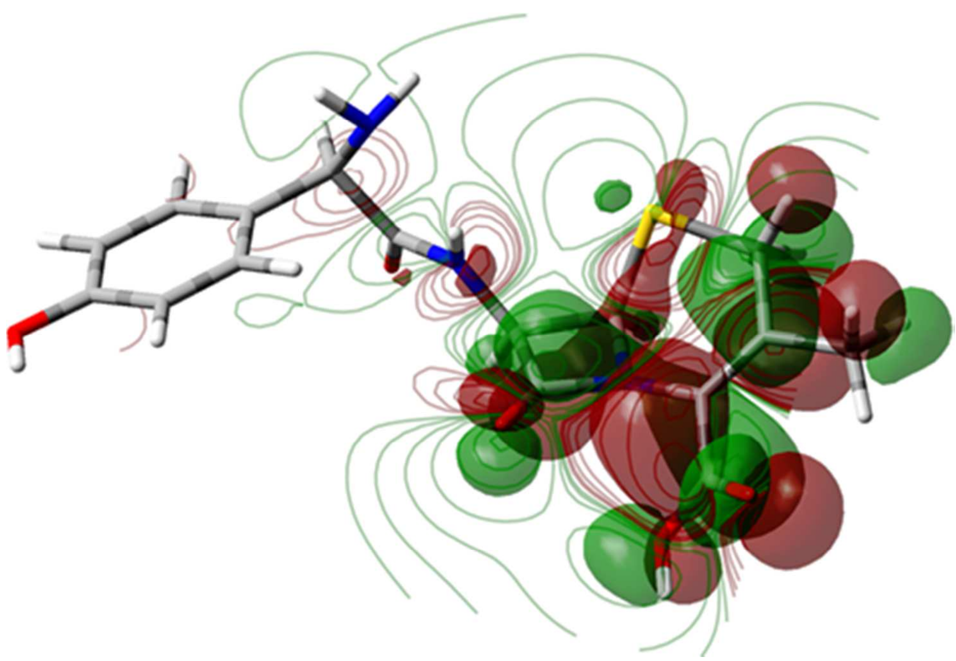

Fig. 10e

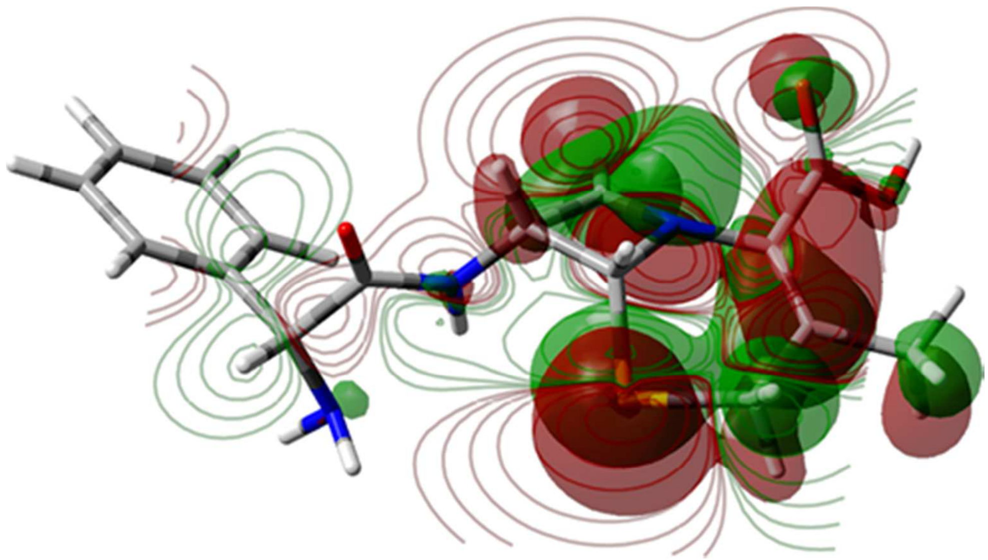

Fig. 10f

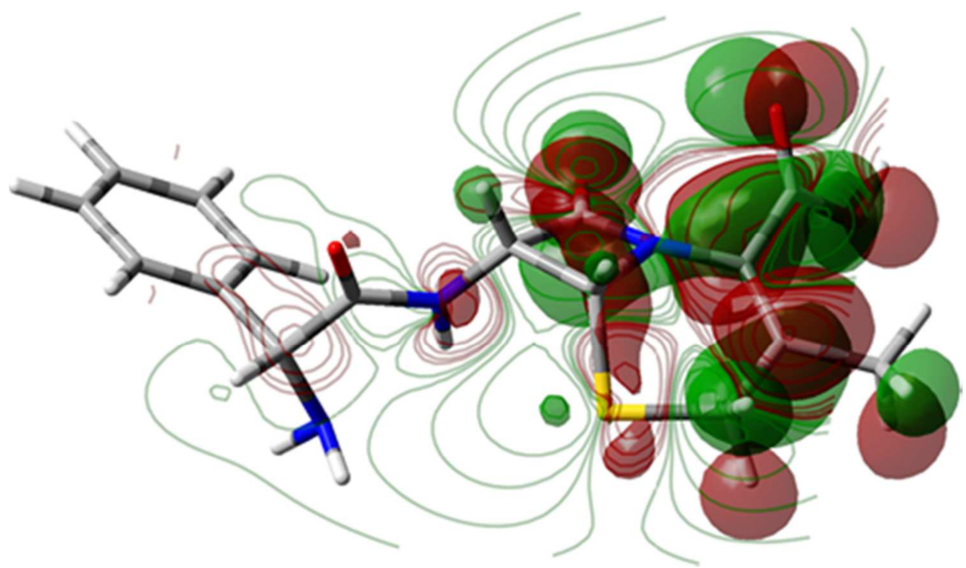

Fig. 10. HOMO and LUMO density distributions of β–lactum additives respectively for (a,b). Cefixime, (c,d). Cefadroxil and (e,f). Cephalexin