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Unraveling the sorption mechanisms of ciprofloxacin on the surface of zeolite 4A (001) in aqueous medium by DFT and MC approaches

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ABSTRACT

The adsorption mechanism of ciprofloxacin (CIP) and its ionic form were investigated using density functional theory (DFT) and molecular dynamics (MD), with the goal of forecasting their adsorption behavior in terms of gap energy, global reactivity descriptors, Fukui functions, adsorption energies, and density of state on the surface of zeolite 4A (001). Quantum chemical parameters related to the adsorption process were calculated, as well as the overall reactivity. According to DFT calculations, the zwetterionic form $CIP^{\pm}$ are the most stable and reactive and have a greater power of electron transfer compared to the other species. Under aqueous conditions, zeolite can adsorb ciprofloxacin (CIP) and its ionic forms, as revealed by molecular dynamics simulation. Ciprofloxacin in the zwitterionic form ($CIP^{\pm}$) were more efficiently adsorbed to the surface of zeolite 4A (001) than the cationic (CIP^{+}), anionic (CIP^{-}), and neutral(CIP) forms; through the evaluation of adsorption energy, probability distribution, interaction, and density of state. The results also demonstrated that the compounds studied were adsorbed via the process of chemical bonding, which was confirmed by the negative values of the interaction energy. Furthermore, the negative adsorption energy values suggest a significant adsorption of all compounds, with electrostatic interactions (physisorption), diffusion into the pores, and n-π bonds (chemisorption) on the zeolite surface. The increase in adsorption energies and the proximity of the molecules studied to the zeolite surface indicate the predominance of chemisorption, and the adsorption of ciprofloxacin was found to be an exothermic and spontaneous process. Molecular dynamics (MD) modeling was in agreement with the DFT results.

Introduction

A significant turning point in the advancement of science and technology has been reached by medicine, which has increased life expectancy, cured millions of diseases that were life-threatening, and raised the standard of living [1]. Due to their widespread use and importance, they are now a rapidly growing set of environmental pollutants. Pharmaceutical contaminants have been found in almost every ecological matrix over the past three decades [1]. Pharmaceuticals, especially antibiotics, are commonly used in the treatment or prevention of disease [2]. Antibiotics are classified into several classes based on their physical and chemical characteristics. One can distinguish the classes of fluoroquinolones (FQ) that are used in the treatment of bacterial infections and respiratory infections [3]. Compared to other antibiotics, the concentrations of ciprofloxacin (CIP) prescribed in this class of FQ are higher in the aquatic environment [4,5]. In fact, pharmaceuticals are among the environmental pollutants of greatest concern. Due to their high hydrophilicity and low biodegradability, these compounds are difficult to remove from water sources using conventional wastewater treatment techniques [1]. For this reason, it is essential for the scientific community to work consistently to establish tried and tested methods for wastewater purification.

Various methods have been used to eliminate or reduce the level of antibiotic contamination present in aquatic environments, notably ectrocoagulation [6], adsorption [7], ozonation [8], electro-fenton [9], photodegradation [10]. Although each of the above techniques has

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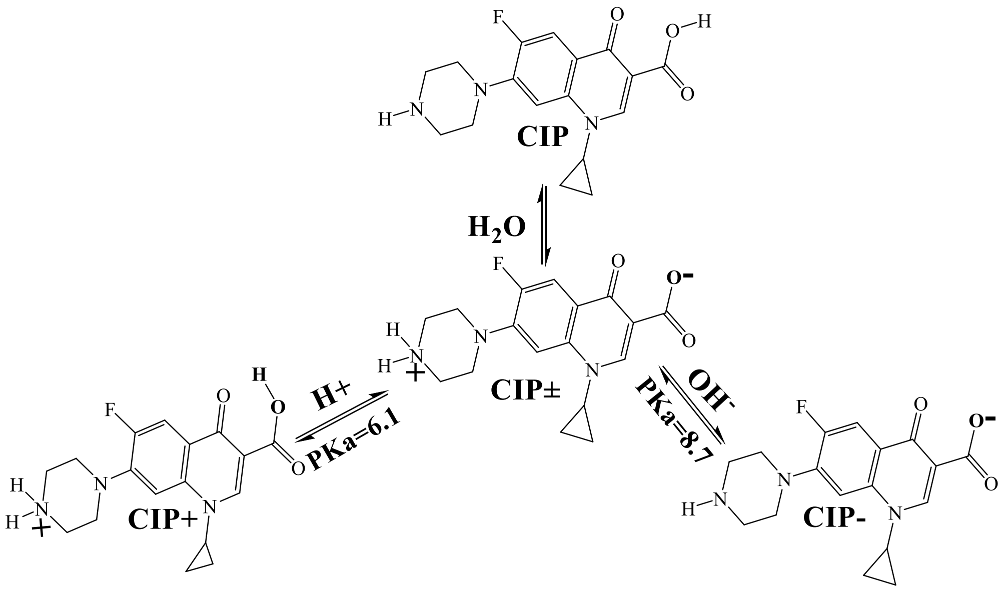


Fig. 1. Different form of CIP molecules mainly present in aqueous solution.

advantages and disadvantages, the adsorption technique is particularly effective, has a high regeneration capacity, is flexible and easy to use when it comes to removing pollutants using a wide range of adsorbents [11,12]. Therefore, for polar antibiotics, adsorption on a surface with a high ionic concentration is often effective and very quick [13]. The most well-known antibiotic is ciprofloxacin, among others. Ciproflocaxin inhibits bacterial replication and growth. It is a widely used broad-spectrum drug, with environmental concentrations of up to 20.321 ngL^{-1}, incomplete metabolism in humans and animals (15–20 %), and is frequently detected [3]. CIP is now one of the most important water contaminants in the environment that needs further study. Following its release into the environment, it was found in wastewater treatment plant effluent, surface water, and groundwater.

In recent years, several studies have been carried out on the different types of adsorbents, such as Zeolite [11,13,14], biochar [15], Υ-Al_2O_3 nanoparticles [16], CuO nanoparticles [17], multiparous carbon nanotubes [18] and oat hulls [4]. Nguena et al. [19], Wang et al. [11], and Neway et al. [13] removed water vapor, carbon dioxide and methylene blue, respectively using zeolite adsorbent derived from natural kaolin and commercially available alumino-silicate products. However, other materials such as durian rind and pectin-alginate-titania composite microparticles have been shown to be effective in adsorption of methylene blue comparable to zeolite [20,21]. The open structure of aluminosilicate zeolite continues to be a highly effective adsorbent. Zeolite has more pores of the same size in its network than other adsorbents, which can hold molecules that have been adsorbed, in addition to having a larger specific surface area [22]. Additionally, zeolite has a strong electrostatic field and a highly polarized inner surface[12].

Although the adsorption method is easy to use and accessible, it requires significant funding because it depends on the cost of preparing adsorbents, which are often very expensive [11,19]. Recently, scientists working on techniques for removing pollutants from water as well as in a number of other fields, such as energy, corrosion and the environment, have begun to use computer modelling, in particular DFT-based quantum chemical calculations, dynamic molecular simulations (MD) and Monte Carlo simulations (MC) [23–26], to effectively predict the existing form and adsorption mechanism of pollutants and help optimize the design of adsorbents. These calculation techniques are distinguished by the fact that, unlike experimental techniques, they do not require the use or release of hazardous chemicals into the environment. The orientation and adsorption behaviour of pollutants at sorbent interfaces are also usefully revealed by MD and MC simulations, enabling the design of the best performing sorbents to be pursued. In aqueous environmental phases, antibiotic concentrations are often in the nanogram range, which makes experimental work difficult (experimental antibiotics, for example, cannot be measured accurately at nanogram level) [26]. Therefore, laboratories always use high-dose antibiotics (usually measured in milligrams) for experiments to ensure accuracy. Consequently, the results of the experiment must be independently verified. In addition, while simulation microscopy studies are not yet very common, experimental studies and laboratory analyses are frequently used to produce results on antibiotic adsorption [26]. Currently, reports on antibiotics tend to focus more on environmental monitoring and laboratory experiments than on studies combining antibiotic removal experiments and DFT computer technology for simulation calculations.

The aim of this study was to better understand how and in what form ciprofloxacin adheres to the surface of zeolite 4A (001). To achieve this, electronic-scale information is needed to better understand the interaction mechanisms on the surface of an adsorbent, but experimental methods do not allow us to obtain this information. For this reason, modelling based on molecular dynamics and quantum chemistry calculations is intriguing. In reality, the interaction mechanism is closely linked to the phenomenon of molecules adhering to surfaces via strong or weak interactions. Usually, the ciprofloxacin molecule in aqueous solution has a high probability of protonation Fig. 1 [27]. Therefore, it is crucial to focus on the protonated forms and physicochemical properties of the chemical systems.

Computational details

Programs

All theoretical calculations were performed on the electronic molecular structures of CIP^{-}, CIP^{+}, $CIP^{\pm}$ and CIP respectively, with the following module tools: $DMol^3$, Reflex, CASTEP, Forcite and adsorption locators included in Materials Studio Software (BIOVIA Materials Studio Academic Reseach (Product N°.5CB-LUR)).

Quantum chemical calculations

In this case, the $DMol^3$ module tool was used to optimize the molecular structure in the aqueous phase and determine the chemical

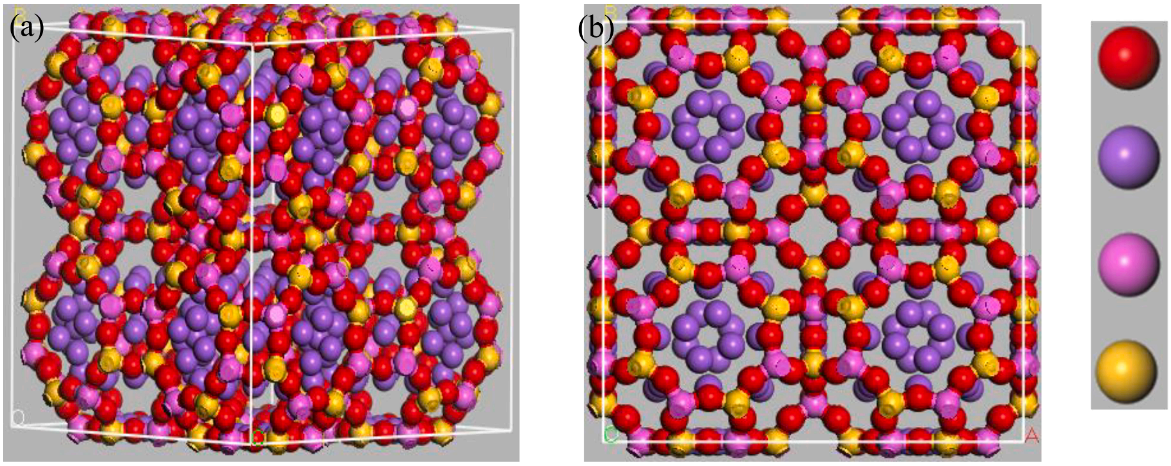


Fig. 2. Spatial representation of the zeolite molecule in 3D dimension, side view (a) and top view (b).

reactivity parameters possessed by the molecules. The simulation parameters used include generalized gradient approximation (GGA) related exchange functions, spin-free Perrdew-Burrke-Errnzerhof (PBE) [28], 3.5 double numerical plus "d" functions basis (DND) basis set, the use of COSMO control and solvation effect (aqueous phase) incorporated during stimulation [29]. The optimized molecular research structure was analyzed, and important quantum chemical parameters were analyzed, such as high occupied molecular orbital (HOMO), energy (E_{HOMO}), low molecular orbital (LUMO), energy (E_{LUMO}), energy gap energy (ΔEgap), Hardness (η), softness (σ), chemical potential (μ), electronegativity (χ), electrophile (ω), nucleophile (ε), electron donor force (ω-), electron acceptor force (ω+), backdonation (ΔE-backdonation), transport electron (ΔN) and Fukui function indices which show the positions of electrophilic, nucleophilic and radical sites in $CIP^{\pm}$, CIP^{-}, CIPand CIP^{+}molecules were also calculated [24]. These useful and reliable quantum chemical parameters were calculated using equations based on E_{HOMO} and E_{LUMO} of molecular atoms and ions. The equations used are given as follows [25,26,30]:

$$\Delta Egap = E_{LUMO} - E_{HOMO} \tag{1}$$

$$\mu = -\chi = -\frac{(-E_{LUMO} + E_{HOMO})}{2} \tag{2}$$

$$\eta = -\frac{(-E_{HOMO} + E_{LUMO})}{2} \tag{3}$$

$$\sigma = \frac{1}{\eta} \tag{4}$$

$$\omega = \frac{\chi^2}{2\eta} = \frac{\mu^2}{2\eta} \tag{5}$$

$$\varepsilon = \frac{1}{\omega} \tag{6}$$

The electron donor (ω^{-}) and electro-acceptor (ω^{+}) powers used to predict and compare the electron donation capacities in a chemical system are calculated using the following equations:

$$\omega^{+} = \frac{(I + 3A)^2}{16\,(I - A)} \tag{7}$$

$$\omega^{-} = \frac{(3I + A)^2}{16\,(I - A)} \tag{8}$$

The retrocession energy ($\Delta E_{back\text{–}donation}$) is a descriptor that depends on the chemical hardness. It also makes it possible to study the adsorption of molecular species on the surface of the material. It is given by the relationship:

$$\Delta E_{back-donation} = -(\eta / 4) \tag{9}$$

It should be noted that ΔN makes it possible to measure the electronic charge that can be accepted by the electrophilic entity. If the value of ΔN of a molecule is high and greater than zero, the molecule would be a good electrophile. The value of ΔN is given by the following relation:

$$\Delta N = \chi / 2\eta \tag{10}$$

The Fukui Functions make it possible to identify accessible sites for electrophilic, nucleophilic and radical attacks of chemical compounds [31]. Each index is studied by the equations below:

$$f_i(\overrightarrow{r})^{+} = q_i(N+1) - q_i(N) \tag{11}$$

$$f_i(\overrightarrow{r})^{-} = q_i(N) - q_i(N-1) \tag{12}$$

Where $q_i(N+1)$, $q_i(N)$, $q_i(N-1)$ are the electron densities at point r for the molecules with $N+1$, N, N-1 electrons respectively.

Molecular dynamic simulation

The crystal structure of the zeolite (Fig. 2) was imported into the material studio software. Simulation is used to calculate the interaction between the molecules of CIP^{-}, CIP^{+}, $CIP^{\pm}$ and CIP and the surface of zeolite (001) in an aqueous medium with an adsorption localization module. It is a tool for determining the orientation and position of molecules above immobilized substrates and determining binding energies using Monte Carlo methods. The simulation of the interaction of single molecules with the surface of the zeolite (001) was carried out in the simulation box (35 Å) ^{3} . A 35 Å thick vacuum plate was introduced on the surface of the zeolite (001) and then expanded into a super cell (5 × 5). The COMPASS force field [28] was employed throughout the simulation to optimize the structure of all system parts (surfaces, molecules, and solvent molecules). To mimic the impact of the solvent, 350 H_2O molecules were added as a liquid phase. This interesting study set out to identify low-energy adsorption sites and investigate the preferential adsorption of various substances on zeolite 4A's surface. The predetermination of the potential interaction energies of the adsorbate-matrix system forms the basis of the study of the adsorption of molecules or molecular groups. Three contributions are added together to calculate this energy:

- E_{Tot} (surface + molecule) denotes the total interaction energy between the molecule and equilibrium surface.

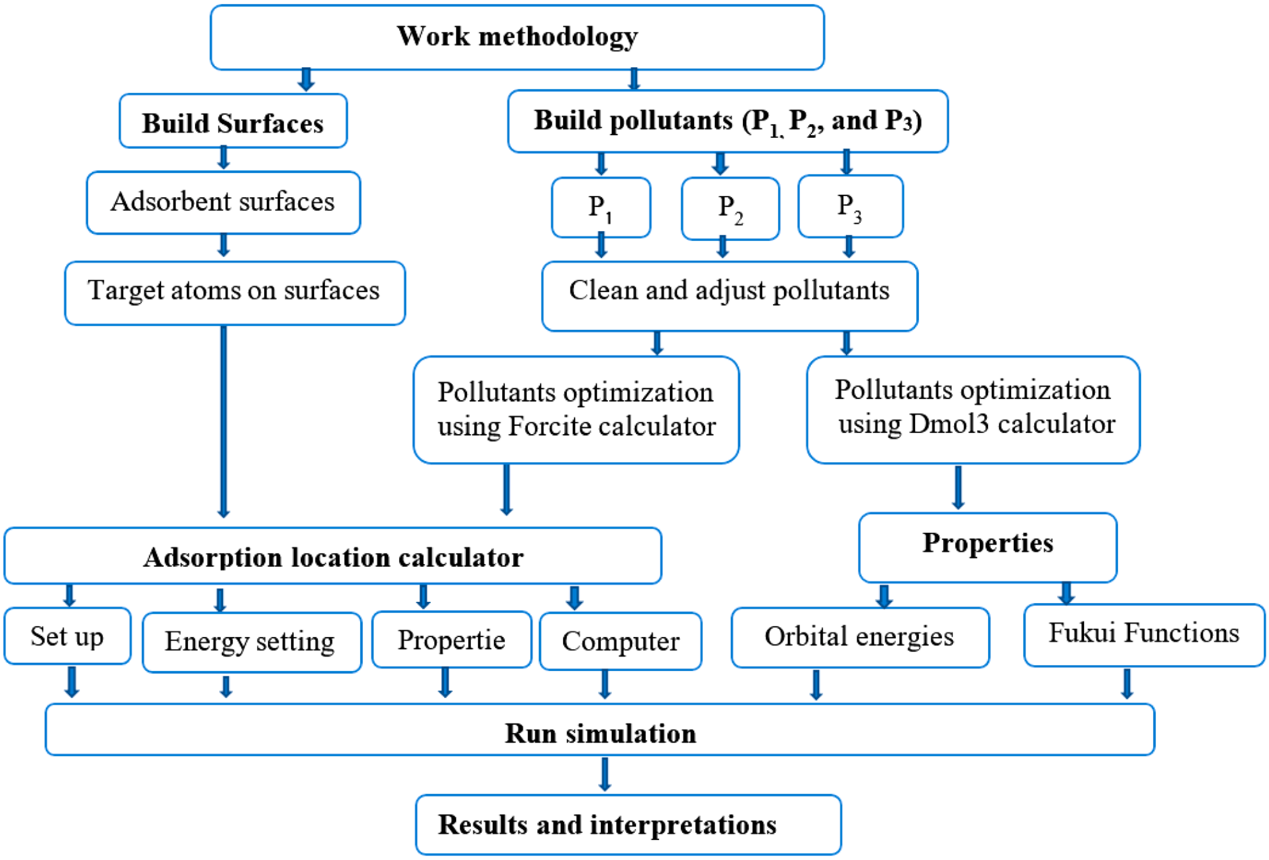


Fig. 3. Summary of the flow methodology for the study.

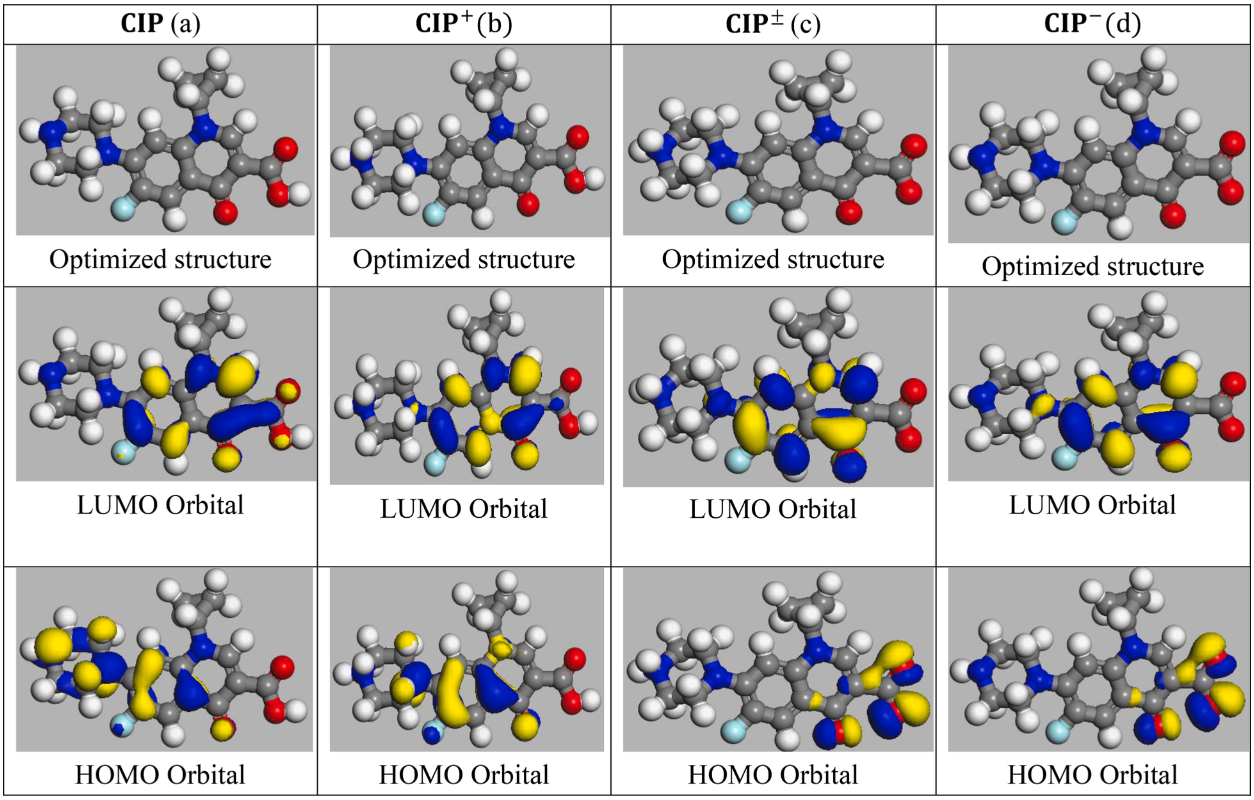


Fig. 4. Quantum descriptors of CIP^- (a), CIP^+ (b), $\text{CIP}^\pm$ (c) and CIP (d) compounds. Legend of atoms: Gray=C, Red=*O*, White=*H*. yellow and blue isosurface represent electron density: yellow regions represent electron loss and regions represent electron buildup.

Table 1
Results of quantum chemical parameters for HC and VH molecule in an aqueous medium.

Parameter	CIP	CIP^{+}	$CIP^{\pm}$	CIP^{-}
E_{HOMO}	−5.298	−5.655	−4.362	−4.575
E_{LUMO}	−2.455	−2.564	−3.405	−2.065
ΔE_{gap} (eV)	2.843	3.091	0.957	2.51
χ (eV)	3.877	4.110	3.884	3.32
μ (eV)	−3.877	−4.110	−3.884	−3.32
η (eV)	1.421	1.546	0.479	1.255
σ (eV^{-1})	0.703	0.647	2.090	0.797
(ω)	5.286	5.467	15.759	4.391
(ε)	0.189	0.183	0.063	0.228
(ω^{+})	3.525	3.602	13.877	2.888
(ω^{-})	7.402	7.712	17.761	6.208
ΔN	1.364	1330	4.058	1.323
$\Delta E_{Back-donation}$	−0.355	−0.386	−0.120	−0.314
Dipolar moment (Debye)	8000	12.570	46.958	14,243
Total energy	−1147.524	−1147.981	−1147.511	−1148.014

- –The total internal energy of the surface, denoted as E_{Tot} (surface). after any potential relaxation in the absence of molecules.
- E_{Tot}(molecule) represents the total relaxation energy of molecules in the absence of the surface. The absorption energy of a surface molecular system is therefore of the form: interaction energy between the surface of the zeolite and the molecules was estimated by calculating the single point energy as follows [29].

$$E_{Interaction} = E_{Tot} - \left(E_{Surface} + E_{Polluant}\right) \tag{13}$$

Among them, E_{Tot} represents the total adsorption energy of the studied species on the zeolite surface, and $E_{surface}$ and $E_{pollutant}$ are respectively the total energy of clean zeolite plate and isolated molecules. The binding energy is the absolute value of the interaction energy.

$$E_{Liaison} = -E_{Iinteraction} \tag{14}$$

Optimised structures, HOMO and LUMO energies of CIP molecules, universal force field, electrostatic summations, adsorption distance, target atoms, energy configuration distribution, density field and energy field were defined to better elucidate and simulate the adsorption behavior of different forms of CIP molecules at the surface and within the open pores of the zeolite. Fig. 3 summarises the sequence of steps performed to unravel the adsorption process of CIP on the surface of zeolite (001).

Results and discussions

Studies of the theory of functional density

Electronic distribution

The optimized structures and boundary orbitals (HOMO and LUMO) of the molecules studied, obtained by the GGA/PPE method, were used to identify the reactivity of the molecules, to determine the electrophilic and nucleophilic sites of the reagents, and to investigate the impact of the adsorption of CIP molecules on the surface of the adsorbent [25]. It is observed in Fig. 4 that in the HOMO orbitals of the molecules CIP and CIP^{+}, the electrons are delocalized on the six-membered heterocycle bearing two nitrogen atoms and on the ring bearing fluorine. On the other hand, in the structures of CIP^{-} and $CIP^{\pm}$, the electrons of HOMO orbitals are strongly concentrated around the carboxylate and ketone groups. This indicates a strong ability to donate electrons to electrophilic centers. These centers are active sites for nucleophilic reactions and promote dative bonds with empty orbitals on the adsorbent surface. In the structure of the LUMO orbitals of the four molecules studied, the electrons are mainly uniformly concentrated in the six-membered heterocyclic bearing the ketone, and in the six-membered ring bearing the fluorine. This indicates that these molecules can mainly receive electrons through these regions and can be easily attacked by nucleophilic reagents. In general, it can be observed that the molecules CIP^{-} and $CIP^{\pm}$have a high donor power. This can be attributed to the deportation of the carboxylic group thus making this group electron-rich. While the acceptor power is mainly linked to the presence of unsaturated rings.

Quantum chemical parameters

The energy difference between HOMO (E_{HOMO}) and LUMO (E_{LUMO}) is known as deviation energy (**Δ**Egap) and is a crucial quantum descriptor [30,31]. Their ability to provide electrons was indicated by a high HOMO energy value, while their capacity to receive electrons was shown by a low LUMO energy value. High values of ΔEgap result in weaker adsorption of molecules on the adsorbent surface, while lower values indicate more effective adsorption of the molecule on the absorbing surface [11,26]. The compounds under study are described quantum chemically in Table 1.

The results show that the energies of HOMO believe in the following order: $CIP^{\pm} > CIP^{-} > CIP > CIP^{+}$. It can be seen that the $CIP^{\pm}$ molecule has the highest HOMO (−4.362 eV), which indicates that it has the greatest capacity to donate electrons to other electron-deficient centers. The observation of the values of the energies of LUMO makes it possible to note that the value of the energy of LUMO of $CIP^{\pm}$ is weaker than that of those others. This indicates the $CIP^{\pm}$ molecule has a higher electron acceptance capacity compared to other species. On the other hand, the greater ability to accept electrons is associated with the greater ability to interact with molecules leading to their adsorption [32] . The E_{LUMO} values of the studied molecules increase in the following order: $CIP^{-} > CIP > CIP^{+} > CIP^{\pm}$. Thus, the electron donation capacity is in the order: $CIP^{\pm} > CIP^{+} > CIP > CIP^{-}$. Now, on the basis of these observations, it can be said that despite the fact that the ability of interaction varies, all these molecules can be adsorbed on the surface of the zeolite. Moreover, the molecule has $CIP^{\pm}$ the smallest energy gap value (ΔE_{gap} =0.957 eV) suggesting a higher chemical reactivity and adsorption efficiency on the surface of the zeolite compared to the others [33]. Electronegativity (χ) is a quantum chemical parameter used to indicate a molecule's ability to attract electrons. Its low value implies a greater potential for the molecule to release electrons [32] . The values of electronegativity increase in the following order: $CIP^{+} > CIP^{\pm} > CIP > CIP^{-}$. This result suggests that CIP^{+}has a great ability to retain electrons than others. The existence of a dipole moment in a molecule is linked to the difference in electronegativity of the atoms, the electronegative leads to an asymmetry in the distribution of electrons within the molecule, hence an increase in the dipole moment and therefore a low capacity of the molecule gaving up the electrons. Generally, high dipole moment molecules have a tendency to form strong dipole-dipole interactions with the surface of the adsorba, resulting in strong surface adsorption [34].

Chemical hardness is a parameter reflecting the stability of a chemical system and has the resistance to the polarization of electronic clouds of atoms, ions or molecules [32] . Hard molecules exhibit high stability (low value of η) compared to soft molecules. The values of the chemical hardness are in the following order: $CIP^{+} > CIP > CIP^{-} > CIP^{\pm}$.We therefore deduce from these results that the molecule $CIP^{\pm}$ (η= 0.479 eV) is the most stable molecule compared to the other molecules.

The stability and responsiveness of a system or molecule can also be described with respect to softness (σ). The higher the sweetness value, the sweeter the molecule or compound [35] . The soft molecule is more reactive than the hard molecule because it can easily interact with the chemically soft atoms of the zeolite and this can give rise to a favorable soft-soft interaction. The values of softness evolve in the order: $CIP^{\pm} > CIP^{-} > CIP > CIP^{+}$, consequently, the molecule $CIP^{\pm}$ (σ =

Table 2
Distribution of the Fukui index in an aqueous solution.

Atoms	CIP		CIP$^+$		CIP$^\pm$		CIP$^-$	
	f_k^-	f_k^+	f_k^-	f_k^+	f_k^-	f_k^+	f_k^-	f_k^+
F_1	0.023	0.025	0.04	0.026	0.008	0.026	0.008	0.026
O_2	0.041	0.076	0.084	0.089	0.097	0.098	0.101	0.099
O_3	0.004	0.022	0.006	0.014	0.329	0.02	0.326	0.021
O_4	0.011	0.046	0.019	0.034	0.161	0.019	0.162	0.02
C_5	−0.001	0.012	0.006	0.013	0.003	0.01	0.004	0.012
C_6	0.094	0.013	0.106	0.012	0.005	0.011	0.006	0.015
C_7	0.093	0.001	−0.002	−0.001	0	−0.002	0	0.001
C_8	−0.008	−0.018	−0.011	−0.018	−0.007	−0.016	−0.007	−0.017
C_{11}	0.022	0.022	0.037	0.025	0.013	0.029	0.013	0.029
C_{12}	0.015	0.168	0.023	0.139	0.031	0.095	0.031	0.099
C_{13}	0.043	0.011	0.063	0.007	0.009	0.009	0.009	0.008
C_{14}	0.048	0.06	0.047	0.071	0.01	0.072	0.01	0.067
C_{15}	0.017	0.025	0.031	0.038	0.012	0.054	0.012	0.051
C_{16}	−0.023	−0.007	−0.018	−0.008	−0.002	−0.009	−0.003	−0.01
C_{17}	−0.028	−0.011	−0.022	−0.011	−0.002	−0.007	−0.003	−0.01
C_{18}	0.011	0.024	0.024	0.02	0.008	0.018	0.007	0.017
C_{19}	0.018	0.067	0.029	0.082	0.036	0.091	0.035	0.093
C_{22}	0.026	0.06	0.036	0.079	0.008	0.102	0.008	0.097
C_{23}	0.042	0.049	0.065	0.042	0.013	0.042	0.013	0.043
C_{24}	0.009	0.045	0.015	0.032	0.128	0.023	0.125	0.023

2.090 eV) has the highest softness value and is therefore more reactive. Thus, a greater interaction CIP$^\pm$is expected on the surface of the zeolite than that of the others. Values of $\Delta E_{\text{back-donation}}$ below zero ($\Delta E_{\text{back-donation}} < 0$) indicate that electron transfer is energetically favorable to all system studies [24]. Therefore, the zeolite becomes enriched with electrons and positive charges accumulate on the substrate molecules. Chemical descriptors consider nucleophilicity and electrophilicity as parameters that quantitatively determine the nature of attack on a molecule. They are directly linked to the electro-donor and electro-acceptor powers of a system or a molecule. A molecule with a high ω^+value is a good electron acceptor, while a molecule with a low $\omega-$ value is a good electron density donor [36] . It has also been reported that the ΔN value is used to measure the ability of a chemical system to transfer electrons to the surface of the adsorbent. A molecule with positive values of ΔN ($\Delta N > 0$) has a better electron transfer potential while a molecule with an opposite tendency is characterized by a negative value of ΔN ($\Delta N < 0$) [33,37,38]. The ΔN values for all systems are positive indicating that these molecules have a strong tendency to transfer electrons into the empty orbitals of the adsorbent through a process of chemical bonding [25]. So all the molecules studied have a strong tendency to transfer electrons. Moreover, the ΔN value of +4.058 indicates CIP$^\pm$ a strong electron donor. From the above results, we can conclude that the studied compounds can be considered Lewis bases and can therefore form coordination bonds with the empty orbitals of the adsorbent surface.

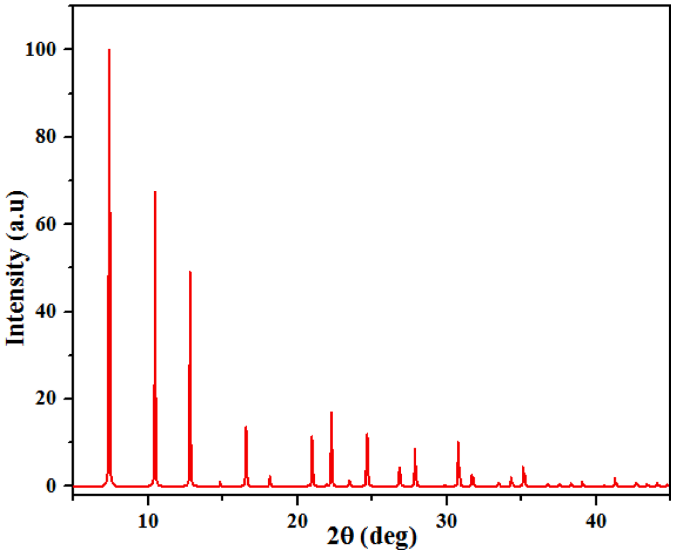
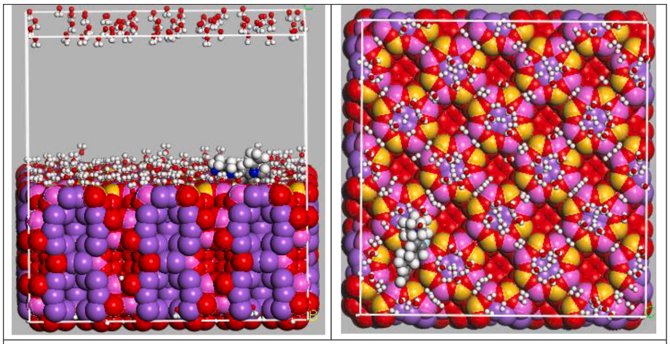


Fig. 5. X-ray difractogram of zeolite.

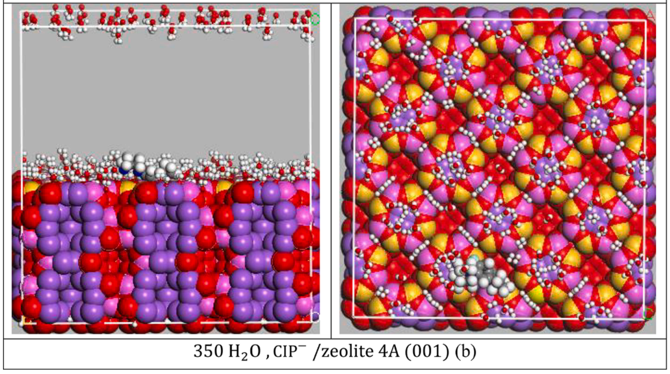
Fukui function indices-based local responsiveness

Mulliiken population analysis is used to determine the compression index of the Fukuii function. The results are shown in Table 2. The maximum values of f_k^- and f_k^+, respectively, regulate nucleophilic and electrophilic attacks [39]. High values of the Fukuii function indicate a chemical system with highly reactive centers. When a molecule loses electrons, its reactivity to electrophilic attack is indicated by the value of f_k^-,whereas its reactivity to nucleophilic attack is indicated by the value of f_k^+ [31].

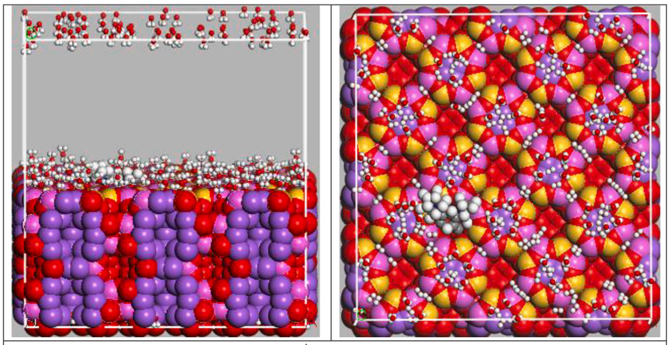
From the Fukui function indices presented in Table 2, it is clear that the attack sites preferred by nucleophiles in the CIP molecule are on the atoms $O_2, O_3, O_4, N_5, C_{12}, C_{14}, C_{22}$ et C_{24}. As said, the preferred sites for electrophiles are onN_6, N_7 et C_{13}. Additionally, the most reactive sites for nucleophilic attack in the molecule CIP$^+$are on $O_4, C_{12}, C_{14}, C_{17}, C_{19}$, C_{22} et C_{22}. While the preferred sites for electrophilic attacks are on the atoms F_1, $N_6.C_{11}, C_{17}$ et C_{23}. For the molecule of CIP$^\pm$the attack sites preferred by the nucleophiles are located on the atoms of F_1,C_{11},C_{12},C_{14}, $C_{19}, C_{22}, C_{23}, C_{24}$. Similarly, the preferred sites for the electrophilic attacks are on the atoms of O_3, O_4 et C_{24}.With regard to the molecule of CIP$^-$the attack sites preferred by the nucleophilic entities are F_1,C_{11},C_{14}, C_{15},C_{19},C_{12} et C_{22}. Similarly, the preferred sites for electrophilic attacks are on the atoms O_3, O_4 et C_{24}. The most active centers for electron donation and acceptance reside in the molecular systems of nitrogen, carbon and oxygen atoms. As can be observed in Table 2, the studied molecules have different attack centers of electrophiles and nucleophiles, which could facilitate their interactions with the zeolite. By observing the most significant values of $f_k^-$the molecules studied, it can be deduced that the electron donation effect evolves in the following order: CIP$^\pm$ > CIP$^-$ > CIP > CIP$^+$. These electron-rich centers are mainly located on the oxygen and nitrogen atoms. These atoms and constitute nucleophilic centers donating electrons to the empty molecular orbital of the zeolite to form coordination bonds while the carbon atoms constitute the electrophilic sites through which the system accepts the electron to form retrodonation bonds towards the surface of the zeolite [38]. The results of the Fukui function indices agree with the



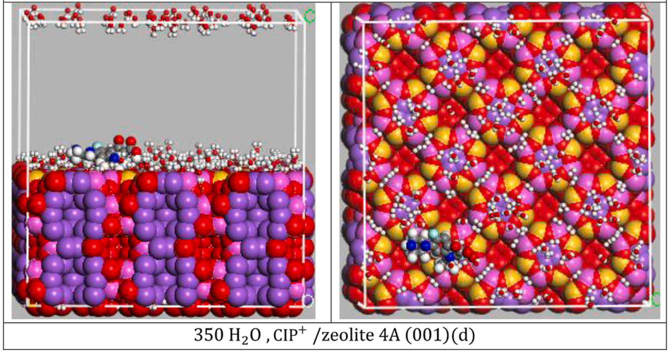
350 H_2O , CIP /zeolite 4A (001) (a)



350 H_2O , CIP^- /zeolite 4A (001) (b)



350 H_2O , $CIP^{\pm}$ /zeolite 4A (001)(c)



350 H_2O , CIP^+ /zeolite 4A (001)(d)

Fig. 6. Side view (left) and top view (right) of the most stable low-energy configuration for adsorption of CIP (a), CIP^-(b), $CIP^{\pm}$(c)and CIP^+ (d) molecules on the surface of zeolite 4A (001) in aqueous medium at 308 K.

quantum descriptors.

Theoretical analysis of X-ray diffraction

It is known that each material has a specific crystal field strength characteristic. XRD characterization is used to confirm and, identify the phases, purity, and crystallinity of materials, and to ensure that the material used corresponds to that described in the literature. The XRD analysis of the imported zeolite in the material studio software was carried out using the Reflex Tools software, and the results are illustrated in Fig. 5.

From the Fig. 5, the diffraction peaks occurring at $2\Theta = 7.3°$; 10.4°; 12.8°; 16.3°; 21.9; 24.2°;27.8°;34.3° which corresponds to the reference values of monophase zeolite 4A [12] . This result can also be confirmed from the experimental results that the zeolite 4A synthesized by peng Wang et al. [11]. So we can conclude that the zeolite studied corresponds to zeolite 4A.

Molecular dynamics results

The interaction between the studied molecules ($CIP^{\pm}$, CIP^-, CIP, CIP^+) and the surface of zeolite 4A (001) in an aqueous medium at 308 K was evaluated using the molecular dynamics simulation technique via Forcite tools and localization modules. Adsorption respectively. This approach uses computer calculations to provide quantitative and qualitative information on the interactions involved in the molecular adsorption process as well as on the adsorption mechanism between adsorbent/adsorbate. Furthermore, molecular modeling is a computational method that uses Newton’s second law to detect the motion of atoms in a chemical system and then predict its physicochemical properties. All simulation processes reach equilibrium only when the temperature and energy of the system reach equilibrium [25] . The results obtained are shown in Fig. 6.

The top and side views show the configuration of the equilibrium of the studied compounds on the surface of the zeolite for a clear visualization. The entire molecular structure of the molecules studied is visibly adsorbed on the surface of the zeolite mainly by the oxygen and nitrogen atoms and the aromatic ring. As can be seen in Fig. 6, in all systems, the studied molecules are oriented parallel on the surface of the zeolite 4A (001). Additionally, the molecules are nearly planarly adsorbed in the water solvent molecules with maximum contact on the surface of the zeolite, resulting in a strong interaction between the adsorbent and the adsorbate. The system’s robust planar adsorption suggests that chemisorption controls the adsorption process [25,26]. The interaction energies of molecules with the surface of zeolite 4A (001) were also calculated using MD simulation. The outcomes are displayed in Table 3.

It can be observed in Table 3 that the adsorption energies are all negative, indicating a spontaneous process and a strong adsorption behavior of all the compounds studied on the surface of the zeolite [25, 40]. Although the adsorption energy values of all the complexes are close, the large negative value of the adsorption energy for $CIP^{\pm}$ indicates its complex is more stable and strongly adsorbed on the surface of zeolite (001) compared to others [42]. Moreover, the value of the adsorption energy of the zeolite/molecule complex follows the order of the quantum descriptors. This highlights the importance of the pore structure of the zeolite which makes a significant contribution to the

Table 3

Dynamic simulation descriptors for the adsorption of $CIP^{\pm}$, CIP^-, CIP, CIP^+ molecules onto the surface of zeolite 4A (001) in the aqueous phase (all values in Kcal /mol).

Compounds	E_{Tot}	E_{Ads}	RAE	$E_{Deformation}$	H_2O dEad/dNi	Ead/dNi
CIP	−126.931	−127.294	−165.467	38.173	−0.719	−13.661
CIP^-	−129.082	−129.500	−167.943	38.442	−0.181	−27.764
$CIP^{\pm}$	−128.990	−129.443	−167.896	38.452	−0.244	−28.871
CIP^+	−126.907	−127.305	−165.632	38.327	−0.18	−12.221

Table 4
Energy of interaction between the molecular systems component and the zeolite (in Kcal/mol).

Compounds	$E_{Interaction}$	$E_{Binding}$	$E_{Electrostatic}$
CIP	−126.962	126.962	−73.834
CIP^{-}	−129.058	129.059	−75.272
$CIP^{\pm}$	−128.931	128.931	−76.261
CIP^{+}	−126.903	126.903	−74.399

adsorption of these molecules. Indeed, heteroatoms such as nitrogen and oxygen as well as the "pi" electrons of the aromatic ring act as an adsorption center during the zeolite-contaminant interaction. Negative values of total energies indicate favorable adsorption processes. This result is in agreement with the experimental results and the calculations obtained by DFT.

The use of MD simulation has also been used to study the mode of action of molecular systems on the surface of zeolite (001) in aqueous solution. The values obtained for the bond, interaction and electrostatic energies are illustrated in Table 4.

Table 4 also shows the magnitude of the interaction for each molecule as a function of the different forms of CIP molecules in aqueous solution. According to these results, all the negative values of the interaction energies and electrostatic energies suggest that the adsorption of CIP onto the surface of zeolite (001) can occur by two different methods: physisorption via electrostatic interactions between the charged surface of the CIP molecules and the zeolite and/or chemisorption via ion exchange between the compensating sodium ion atoms and the active Lewis sites generated by the oxygen atoms [43–45]. For all complexes, the results of the bond energies are positive and very high, indicating an exothermic reaction [31]. These binding energy values also provide a qualitative estimate of the adsorption mechanisms of the chemical system on the surface of the zeolite. It is important to emphasize that high values of binding energies lead to stable interaction with the highest chemical system. Therefore, the energy values obtained in the $CIP^{\pm}$/zeolite 4A complex are superior to those of the other complexes. In conclusion, the high negative value of the interaction energies 350 H_2O, $CIP^{\pm}$/zeolite 4A (001) complex (−129.059 Kcal/mol) indicates a strong interaction between the adsorbed and adsorbent components [24]. While the positive value of the binding energy (129.059 Kcal/mol) reflects a large adsorption of $CIP^{\pm}$ on the surface of the zeolite by chemisorption [46].

This positive energy indicates that the heteroatoms of the aromatic rings have formed chemical bonds through the lone electron pairs [37]. Molecular systems can be adsorbed tightly on zeolite 4A by forming coordination bonds. Work in the literature has shown that the adsorption reaction of Ciprofloxacin is spontaneous and follows a process of chemisorption [41]. Therefore, it should be noted that dynamic descriptors calculations support experimental results.

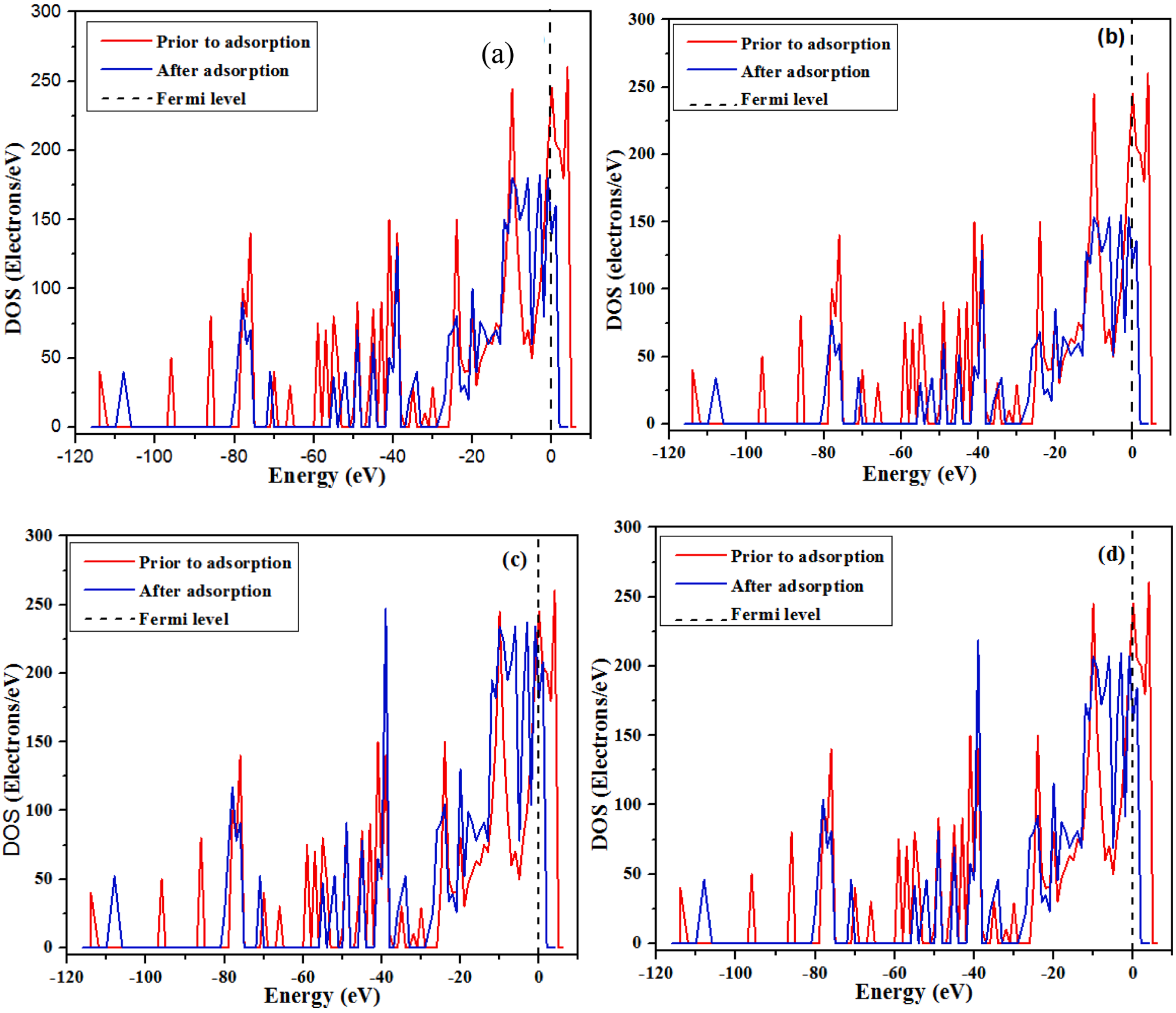


Fig. 7. Density of states before and after adsorption of CIP (a), CIP^{+} (b), $CIP^{\pm}$ (c), CIP^{-} (d) on the surface of zeolite 4A (001) in aqueous medium at 308 K.

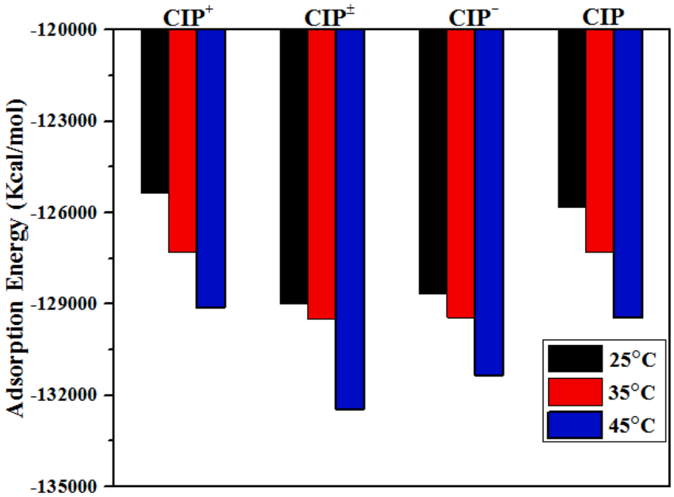


Fig. 8. Adsorption energies of the most stable configurations of different complexes.

Analysis of the total state density

To better understand the electronic interactions between the studied compounds and the zeolite 4A (001) surface, the total density of states (DOS) of the surface atoms of the most stable complex structures was assessed. By comparing the differences in DOS curves before and after the adsorption phenomenon, the nature of electron transfer during the adsorption process can be estimated. The overall density of states (DOS) of zeolite and complex unit cells is shown in Fig. 7. However, the adsorption and binding energy results confirm that electron transport occurs during the adsorption process.

The density of each of the most stable low-energy configurations varies considerably before and after the adsorption stage, as shown in Fig. 7. Additionally, the study's molecule is strongly adsorbed on the surface of zeolite 4A (001), according to the positive DOS value [28]. The adsorption of various molecules on the zeolite surface is what makes this modification significant. Fig. 7 demonstrates that the separated zeolite's DOS peak is primarily made up of 3S and 3P orbitals. Adsorption lowers the energy level by causing the S and P orbitals of Des to shift to the left. Furthermore, it is a sign that the affected orbitals are involved in the interaction mechanism if the peak intensity of the adsorbed complex is found to be higher than that of the isolated zeolite surface. Total energy has decreased, indicating that it has been consolidated into the final composite [26,42,43]. Above the Fermi energy, all structures change dramatically after adsorption. It can be said that the surface of

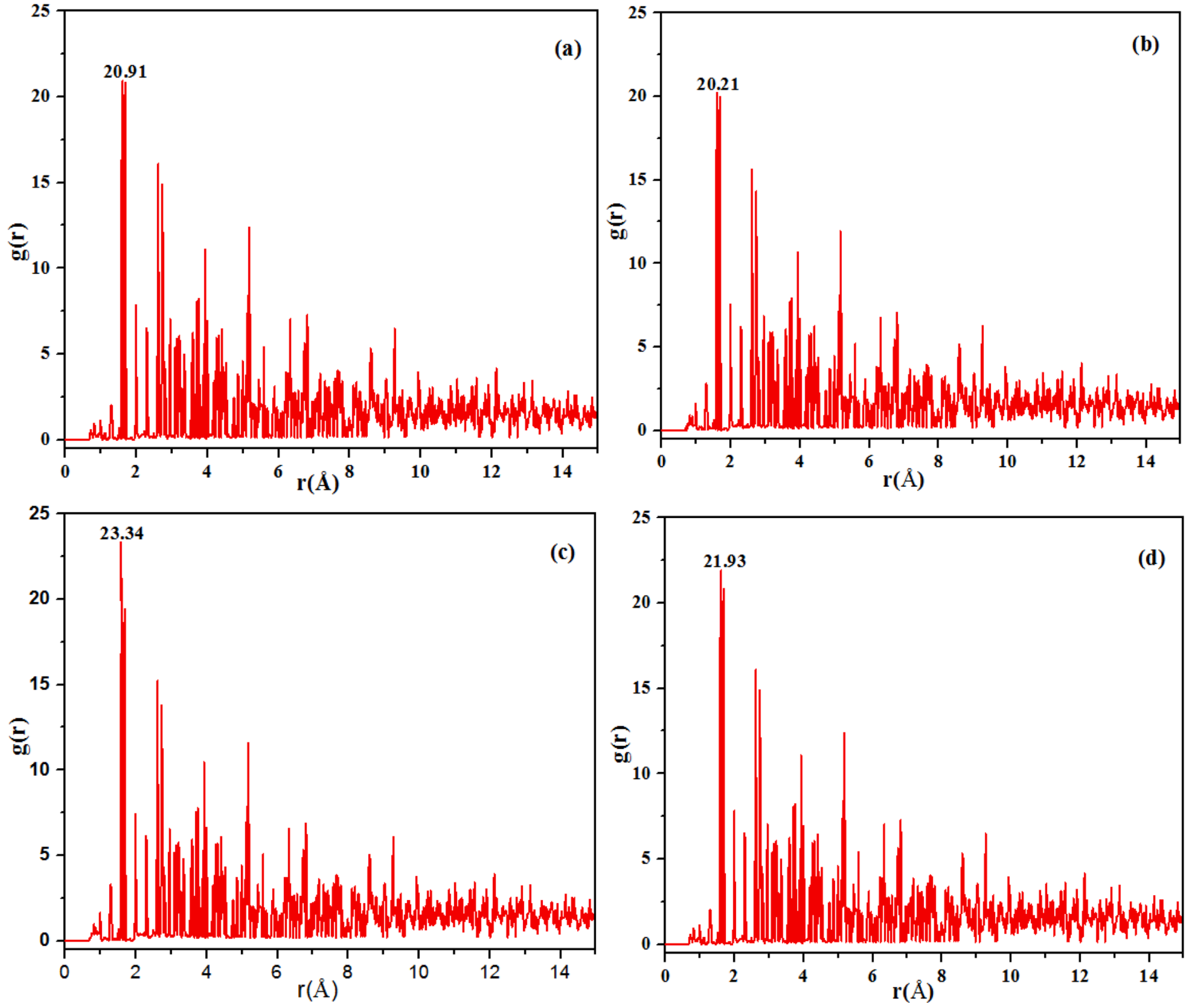


Fig. 9. Radial distribution function for interactions between CIP (a), CIP$^+$ (b), CIP$^\pm$ (c), CIP$^-$ (d) on the surface of zeolite 4A (001) in aqueous medium at 308 K.

the zeolite transports the low energy electrons to the molecules. It is also worth noting that the change in DOS of the four complexes is mainly due to the contribution of the surfactant sites of the zeolite (001) and of the molecules studied. Given the intensities of the peaks, it can be deduced that the interactions are effective at the surface of the zeolite in the following order: $\mathrm{CIP}^{\pm} > \mathrm{CIP}^{-} > \mathrm{CIP} > \mathrm{CIP}^{+}$. This result agrees with the experimental study and the DFT calculations.

Effects of temperature on the investigated molecular zeolite systems' adsorption energies

The energy released when one mole of a compound is adsorbed on the surface of an adsorbent is known as adsorption energy [26]. Adsorption energy serves as a nuanced description of the adsorption mechanism. As a result, adsorption energy can give us a simple way to categorize the adsorption capabilities of molecular systems [44]. Fig. 8, shows the adsorption energies of the molecules studied on surfaces of zeolite 4A (001) at different temperatures in an aqueous solution.

Negative values of the adsorption energy indicate the endothermic and spontaneous character of the adsorption process at all temperatures [45] . This means that the molecules are attracted to the surface of the zeolite causing physical and/or chemisorption [46]. The larger the magnitude of the released energy (the larger the negative value), the stronger the adsorption force, and therefore the greater the adsorption capacity, which shows that the adsorption of this compound is relatively more favorable than that of $\mathrm{CIP}^{\pm}$the other compounds whatever the temperature. Moreover, it can be observed from Fig. 8 that the energy of asorption for all the complexes increases with temperature. If indicated, an increase in temperature causes an activation of the surface of the adsorbent or the activation of certain active sites, hence an increase in adsorption [47] . Likewise, the dynamic descriptors corroborated the results obtained experimentally in the literature. Therefore, theoretical and experimental results indicate zeolite is a better adsorbent for the removal of Ciprofloxacin.

Radial distribution function (RDF)

The radial distribution function (RDF) or pair correlation function g (r) was used to examine the results of simulation studies by averaging the interaction duration between different molecules [48,49]. To better understand the nature of the bond formed between the $\mathrm{CIP}^{\pm}$, CIP^{-}, CIP, CIP^{+} molecules and the surface of zeolite 4A (001), the interactions were estimated using Eq. (15). The probability that the studied species occur at a distance r from the surface of the Zeolite is calculated by RDF [50].

$$\mathrm{g}(\mathrm{r}) = \left(\frac{\mathrm{n}(\mathrm{r})}{4\pi \mathrm{r}^2 \mathrm{dr}}\right) \Big/ \left(\frac{N_B}{V}\right) \tag{15}$$

Where, n (r) is the average number of molecules in the area of $r \pm \mathrm{dr}$, N is the total number of molecules B, V is the volume of the system and r is the distance between the studied molecules and the atoms on the surface of the Zeolite (001). Peaks at a distance greater than 3.5 Å, on the other hand, are associated with electrostatic interaction, while peaks at a distance less than 3.5 Å are directly associated with chemisorption [48,50,51,52]. The RDF plots of each compound studied with the Zeolite surface are shown in Fig. 9.

Fig. 9, shows that for all the compounds studied, the most intense peaks are visible at a distance less than 3.5 Å. which suggests that all of these species studied can bind strongly to the surface of Zeolite 4A through a chemisorption process. Low intensity peaks are visible for all species at a distance greater than 3.5 Å, suggesting a weak electrostatic interaction (physisorption) [53]. In addition, we can observe that the value of the intensity of the peaks varies depending on the complex formed, it is 23.34 for $\mathrm{CIP}^{\pm}$, 21.93 CIP^{-}, 20.91 CIP and 20.21 CIP^{+} which shows a strong interaction of these species and the surface of the zeolite. According to these values, it can be concluded that the binding order according to the peak intensity values is as follows $\mathrm{CIP}^{\pm}>\mathrm{CIP}^{-}>\mathrm{CIP}>\mathrm{CIP}^{+}$. These results are also in agreement with the DFT descriptors.

Prediction of the adsorption mechanism

According to previous studies and literature, the mechanism of interaction of components adsorbed on the surface of zeolite 4A (001) has been attributed to physical and chemical interactions. Due to the presence of active sites in the ciprofloxacin molecule. Fluorine atoms and delocalized carboxyl groups can lead to electron deprivation in adjacent aromatic rings, thereby inducing π acceptor properties, while amine groups can lead to π donor properties in aromatic rings adjacent. However, ciprofloxacin molecules are very active and stable in aqueous media as zwitterions $\mathrm{CIP}^{\pm}$(Table 3), and they can act as electron donors and acceptors to facilitate interaction with the zeolite surface. Since the highest adsorption was found in our environment and zwitterions have the highest hydrophobicity among other ciprofloxacin species, the contribution of hydrophobic forces to the enhancement of adsorption is significant. Additionally, the polar groups (silanol Si-OH groups) on the surface of zeolite can act as active sites for electrostatic interaction with the amine protone group ($\mathrm{H_2N}^{+}$) in weak van der waals forces and hydrogen bonds. The nitrogen atom in the heterocycle and the -COO- group of the molecule $\mathrm{CIP}^{\pm}$ can interact with one another to form Lewis acid-base interactions (chemisorption). Bronsted acid sites generally make up the zeolite structure, which includes ≡Si-OH-Al≡ groups that can simply be hydrolyzed to give rise to the ≡Si-OH group [54]. The silanol group is a proton $\equiv \mathrm{Si}-\mathrm{OH}_2^{+}$ under acidic conditions, and the number of groups$\equiv \mathrm{Si}-\mathrm{O}^{-}$ and CIP zwitterions ($\mathrm{CIP}^{\pm}$increases in aqueous media, which increases the electrostatic attraction and results in the formation of hydrogen bonds between the polar functional groups of the zeolites and the $\mathrm{CIP}^{\pm}$adjacent molecules [55,56]. The diffusion of the pores in the zeolite channels also contributes to better adsorption by accessing more active sites. Zeolite micropores are large enough (0.3–1.3 nm) for molecules to $\mathrm{CIP}^{\pm}$escape into the crystal structure [57]. Cation exchange interactions are occasionally possible between monovalent and divalent cations found in the crystal structure and the $\mathrm{CIP}^{\pm}$ [57]. Can $\mathrm{CIP}^{\pm}$also bind to the surfaces of zeolites via electrostatic interactions with protonated silanol groups ($\equiv \mathrm{Si}-\mathrm{OH}_2^{+}$).

Conclusion

MD simulations were carried out to identify the low-energy and most stable configuration of ciprofloxacin molecules adsorbed on the surface of 4A (001) zeolite in aqueous media. This was done in order to study the centers and the mechanism of potential contact between the ciprofloxacin molecules and the zeolite 4A (001). We also used DFT to examine the ciprofloxacin molecules structural and electronic characteristics. Based on the foregoing discussion, calculated quantum chemical descriptors show that ciprofloxacin molecules has a high degree of chemical and electrostatic reactivity and predict a strong adsorption to 4A zeolite. Ciprofloxacin was more strongly adsorbed in the zwitterionic form on the surface of zeolite 4A (001) in an aqueous medium than in the cationic, anionic, and neutral forms. This result was derived from the MD method by evaluating the adsorption energy, probability distribution energy, interaction energy, and density of states (DOS). The results showed that the studied compounds were adsorbed via chemical bonds. Negative values of adsorption energies indicate more favorable adsorption of all compounds in aqueous media, and the adsorption of these molecules increases with increasing temperature. The process of adsorption of the molecules studied is spontaneous and exothermic in nature. Compared to studies in the literature, zeolite 4A showed a very high adsorption energy for Ciprofloxacin molecules. Based on these results and the correlations reported in this work, we can say that the

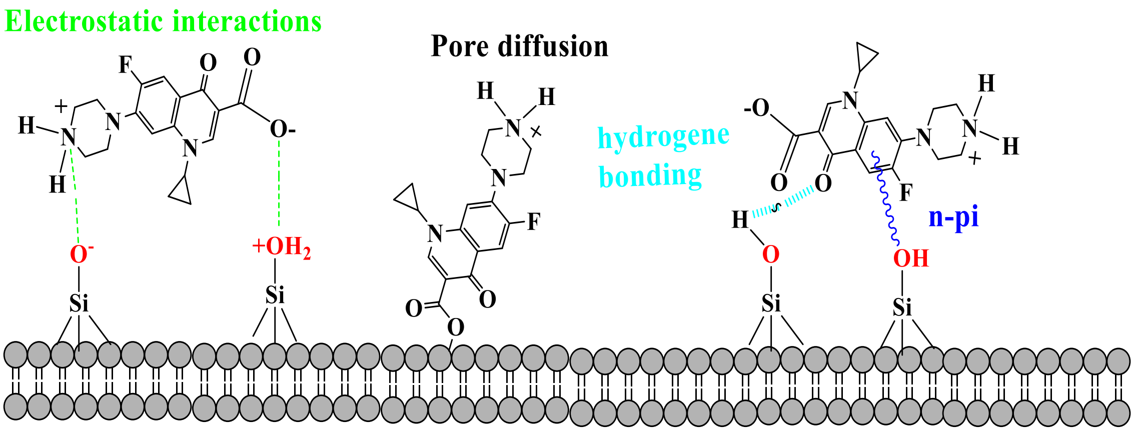


Fig. 10. Schematic representation of the molecule on the surface of the zeolite showing the dominant interactions.

removal efficiency of zeolite can be directly and qualitatively estimated by quantum chemical calculations. The descriptors of DFT and MD provide a better explanation of the adsorption mechanisms of ciprofloxacin on the surface of zeolite 4A (001). Fig. 10

CRediT authorship contribution statement

Fredy Harcel Kamgang Djioko: Conceptualization, Data curation, Investigation, Methodology, Software, Validation, Writing – original draft, Writing – review & editing, Formal analysis, Resources. **Cyrille Ghislain Fotsop:** Conceptualization, Investigation, Writing – review & editing. **Georges Kamgang Youbi:** Conceptualization, Methodology, Supervision, Writing – review & editing. **Simeon Chukwudozie Nwanonenyi:** Conceptualization, Investigation, Methodology, Supervision, Validation, Writing – review & editing. **Chinyere Ada Madu:** Conceptualization, Investigation, Methodology, Supervision, Validation, Writing – review & editing. **Emeka Emmanuel Oguzie:** Project administration, Resources, Software, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper

Data availability

Data will be made available on request.

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