

CHEMISORPTION OF ENROFLOXACIN ON RUTILE-TiO₂ (110) SURFACE: A THEORETICAL INVESTIGATION

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Abstract. We investigated the adsorption of enrofloxacin (ENR) antibiotic on rutile-TiO₂ (r-TiO₂) (110) surface using DFT calculations. Stable configurations of the adsorption of ENR on r-TiO₂ (110) were observed. The origin and role of interactions in stabilizing the configurations are thoroughly analyzed using NBO and AIM analyses. Obtained results indicate that the adsorption process is characterized as a strong chemisorption with an associated energy of *ca.* -35 kcal.mol⁻¹ for the most stable configuration. Quantum chemical analysis shows that the stability of configurations is mainly determined by >C=O...Ti_{5f} electrostatic interaction along with supplement of H...O_b hydrogen bond. It can be suggested that the rutile-TiO₂ can be considered as a potential candidate for adsorption and removal of ENR from wastewater.

Keywords: adsorption, rutile TiO₂ (110), enrofloxacin, DFT calculations.

Classification numbers: 2.5.3; 2.4.2.

1. INTRODUCTION

Titanium dioxide (TiO₂) is one of the most widely studied materials in many fields such as photocatalysis in water and air treatment, solar fuel generation, sensor and photovoltaic devices [1, 2]. Of the three structurally stable phases of TiO₂, rutile is the most stable one, attracting thus much interest in surface science [3]. In particular, the dominant surface of rutile which is the (110) one, has thoroughly been studied both experimentally and theoretically [3, 4]. Results showed that elementary surface reactions on TiO₂ play important roles in many relevant applications, *e.g.* photocatalysis, and therefore have increasingly been investigated in recent years [5]. However, reported studies have just been focused on the reactions of small organic molecules [4-6]. More importantly, the origin and role of interactions formed on rutile-TiO₂ (r-TiO₂) surface upon adsorption process have not been thoroughly examined yet [2, 6, 7]. Therefore, study of interactions of large molecules on r-TiO₂ surface, specifically the (110) one, is an important step for a deeper understanding of the adhesion and/or decomposition process of biological molecules on this surface.

In recent years, the removal of toxic antibiotics from aquatic environments has become an extremely urgent activity due to the problem of antibiotic overuse and misuse particularly in

agriculture and related fields [8-10]. For example, fluoroquinolones are the antibacterial synthetic drugs, commonly used for humans and animals. Among fluoroquinolones bacterial antibiotics, enrofloxacin (ENR) is being used for treatment of infections in the respiratory, urinary and alimentary tract, septicemia. ENR is a pyridone carboxylic acid derivative (*cf.* Fig. 1), whose action inhibits bacterial DNA gyrase, thereby preventing DNA supercoiling and DNA synthesis [10]. Several previous investigations into adsorption and removal of ENR from aqueous solutions by using graphene, zeolite or clay mineral were conducted. However, the adsorption of this molecule on the surface of metal oxides has not yet been considered. Hence, in the present work, we investigate the adsorption process of ENR on r-TiO₂ (110) with the aim to understand the role and the origin of interactions in the formed stable configurations.

2. COMPUTATIONAL DETAILS

The r-TiO₂ (110) surface was simulated employing slab model from the bulk TiO₂ of rutile phase which is optimized by using VASP program [11]. The periodic slab is designed to be large enough to avoid artificial interactions between two consecutive surfaces within a supercell or between supercells. Four layers of TiO₂ unit in the [110] direction with two relaxed layers on top and two frozen layers at the bottom were used to describe interactions of molecule and surface. The simulated surface in this work is chosen with the lattice parameters as in the following: $a = 17.82 \text{ \AA}$; $b = 13.15 \text{ \AA}$; $c = 35.00 \text{ \AA}$ including vacuum space of 22 \AA . The Brillouin zone was sampled by a $2 \times 3 \times 1$ Gamma centered grid, and a value of 500 eV for plane wave cutoff energy was used to expand Kohn Sham states. The PBE functional of DFT-GGA was applied in our calculation [12]. Relaxations of the allowed ionic positions are performed using the conjugate gradient algorithm until forces on all atoms are smaller than 0.01 eV/\AA . Adsorption energy (E_{ads}) and interaction energy (E_{int}) are calculated as in the expressions:

$$E_{\text{ads}} = E_{\text{surf-mol}} - (E_{\text{surf}} + E_{\text{mol}}) \quad (1)$$

$$E_{\text{int}} = E_{\text{surf-mol}} - (E_{\text{surf}^*} + E_{\text{mol}^*}) \quad (2)$$

in (1) equation, the $E_{\text{surf-mol}}$, E_{surf} and E_{mol} are the energies of the optimized structures for complexes, surface and molecule, respectively. In (2) equation, the E_{surf^*} and E_{mol^*} are single point energies of the surface and molecule geometries (without re-optimization) which are separated from the optimized configurations. The deformation energies for the adsorbate molecule ($E_{\text{def-mol}}$) and for rutile surface ($E_{\text{def-surf}}$) in adsorbate-adsorbent systems are computed as the differences between E_{mol^*} and E_{mol} and between E_{surf^*} and E_{surf} , respectively. In order to have a deeper understanding on the role and nature of interactions formed between ENR and r-TiO₂, the topological analysis based on the Atoms-In-Molecules theory was carried out by using B3LYP functional in conjunction with the 6-31+G(d,p) basis set. Moreover, the total electron density (EDT) in complexes was calculated using NBO method at the same level. The molecular electrostatic potential (MEP) for ENR is carried out at B3LYP/6-31++G(d,p) level with charge regions ranging from -5.10^{-5} e to 0.15 e and electron density is considered at 0.02 au . All these quantum chemical calculations are performed by Gaussian 09, AIM2000 and NBO 5.G programs [13, 14].

3. RESULTS AND DISCUSSION

3.1. Stable structures

Structures of ENR molecule and r-TiO₂ (110) surface are optimized using PBE functional and shown in Figure 1. The corresponding MEP of ENR is calculated at the B3LYP/6-31++G(d,p) level and also illustrated in Figure 1. The adsorption of ENR on r-TiO₂ (110) gives rise to two stable configurations corresponding to assigned symbols **P1**, **P2** (cf. Figure 1). The horizontal arrangement of ENR onto r-TiO₂ surface was considered to obtain stable configuration. However, these designed configurations are not found in optimization. This can be understood to be due to space effects of -CH groups of ENR in adhesion molecule onto material surface. Some selected geometric parameters are given in Table 1.

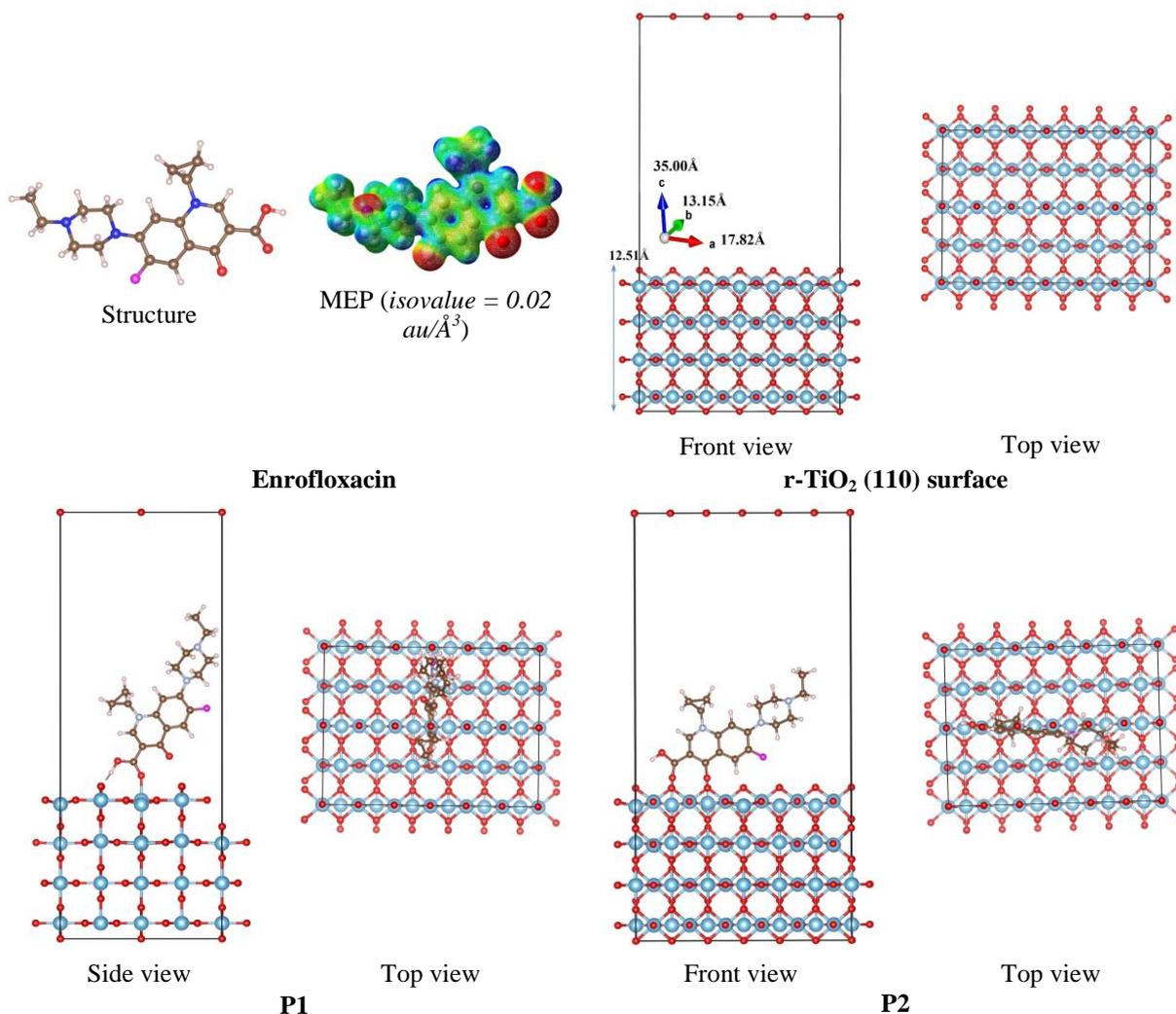


Figure 1. Optimized structures of enrofloxacin, r-TiO₂ 110 surface and two stable configurations of the adsorption process (C, H, O, N, F and Ti atoms are signed by dark, white, red, green, violet and cyan green colors, respectively).

As shown in the MEP of ENR, the high negative charge regions are found at O atoms, whereas the high positive charge regions are located at H atoms. Therefore, O and H atoms are favorable interacting sites when ENR molecules are adsorbed on r-TiO₂ (110). Figure 1 shows that **P1** stable structure is formed by adhesion of -COOH group of ENR on the surface. **P2** structure is obtained by arrangement of ENR molecules along rows containing Ti five-fold

coordination (Ti_{5f}) sites due to the interaction between two $>C=O$ groups of ENR and those of Ti_{5f} sites. Accordingly, the $Ti\cdots O$ interactions are formed by Ti_{5f} sites of surface and O atoms in $>C=O$, $-OH$ groups of the adsorbed molecule. Besides, an $O-H\cdots O$ hydrogen bond emerges between bridging O (O_b) site of $r-TiO_2$ (110) and H atom in O-H bond of ENR. The distances of intermolecular interactions presented in Table 1 are in the range of 2.00-2.20 Å and 1.41 Å for $Ti_{5f}\cdots O$ and $O-H\cdots O_b$, respectively. All these values are significantly smaller than the total van der Waals radii of Ti and O (3.82 Å), O and H (2.72 Å) atoms involving in the interactions. It is noteworthy that the $Ti_{5f}\cdots O$ distances in the investigated complexes are close to those of the Ti-O bonds in the TiO_2 bulk (ranging from 1.86 to 2.01 Å). Therefore, the $Ti_{5f}\cdots O$ and $O-H\cdots O_b$ contacts are predicted to be strong interactions during the adsorption process.

Table 1. Some selected parameters for two stable complexes using PBE functional.

Complex	P1	P2
$d(O\cdots Ti_{5f})$	2.00	2.20/2.05
$d(O-H\cdots O_b)$	1.41 (O)	
$\angle OHO_b$	175.2 (O)	
$\angle O_bTiO_{1(2)}$	179.4 ¹	179.0 ¹ /178.8 ²
$\angle CO_{1(2)}Ti_{5f}$	151.1 ¹	173.3 ¹ /172.9 ²
$\Delta r(C=O_1)$		0.0296
$\Delta r(C=O_2)$	-0.1171	-0.1606
$\Delta r(O-H)$	0.4347	
$\Delta r(Ti-O_a)$	0.2995	0.1766
$\Delta r(Ti-O_b)$	0.0517	0.0667

^(1,2,a,b) for O atoms in $>C=O$, $-COOH$ groups of molecule, O sites in plane, and at bridge of surface, respectively; d and Δr are in Å, \angle in °)

In addition, the values of 178.8° to 179.4°, 151.1° to 173.3°, and 175.2° are observed for the O-Ti-O₁₍₂₎, C-O₁₍₂₎-Ti and the O-H-O_b angles, respectively. Besides, the changes of bond length for C=O, O-H and Ti-O in ENR and $r-TiO_2$ (110) are determined. The lengths of C=O bonds of carbonyl group are elongated by *ca.* 0.03 Å whereas that of carboxyl groups are shortened with an amount within the range of 0.12-0.16 Å. The largest value of 0.43 Å is found for the O-H bond in ENR upon interaction. Also, the Ti-O bonds of surface are elongated in the range of 0.05 to 0.30 Å. This indicates that the bond lengths and angles at atoms involving in interactions change considerably due to complexation.

3.2. Energetic aspects of adsorption process

To evaluate the adhesion capacity of $r-TiO_2$ (110) for ENR and the stability of configurations, adsorption (E_{ads}), interaction (E_{int}) and deformation ($E_{def-surf}$, $E_{def-mol}$) energies are given in Table 2, which are calculated employing the PBE functional.

As presented in Table 1, the adsorption energies of ENR on $r-TiO_2$ (110) are highly negative and of -26.4 and -35.1 kcal.mol⁻¹ corresponding to **P1** and **P2**; therefore, **P2** is more

stable than **P1**. Due to large negative adsorption energies and the form of strong interactions on surface, the process of adhesion ENR on r-TiO₂ is characterized as strong chemisorption. The stability of **P2** illustrated in Figure 1 is mainly contributed by two Ti_{5f}···O interactions, whereas the **P1** is stabilized by both Ti···O and O-H···O_b intermolecular interactions. The contribution of Ti_{5f}···O and H···O_b interactions on rutile-TiO₂ surfaces following adsorption of some organic molecules was also found in the previous studies [6, 15, 16].

Table 2. Energies for adsorption of ENR on r-TiO₂ (110) surface (in kcal.mol⁻¹).

Complex	E _{ads}	E _{int}	E _{def-surf}	E _{def-mol}
P1	-26.4	-55.6	19.3	9.9
P2	-35.1	-54.9	16.7	3.1

Further, it is clear that a good understanding on interactions between absorbed molecules and the materials' surface can provide better insights into the various aspects of the adhesion process of molecules on surfaces. The interaction energies of **P1** and **P2** configurations are -55.6 and -54.9 kcal.mol⁻¹, respectively (cf. Table 2). Therefore, the Ti_{5f}···O and O-H···O_b contacts formed in these complexes can be regarded as strong interactions. The highly negative values of E_{int} for **P1** as compared to those of **P2** counterpart implies a significant contribution of O-H···O_b hydrogen bond to the overall stability of the complexes.

The deformation energy is a characteristic parameter for evaluating the ability of separating the substrate and the surface from its stable configuration [17]. As tabulated in Table 2, these energy values for TiO₂ surface are larger than that for ENR molecule. For this reason, the ability of separation and then to form stable structures is less convenient for r-TiO₂ than for ENR. These obtained results are consistent with the remarkable changes of the surface structure as compared to the molecule in the aforementioned stable configurations. This is similar to our previous results on separating surface-molecule systems [18].

3.3. Characteristics of interactions on the surface

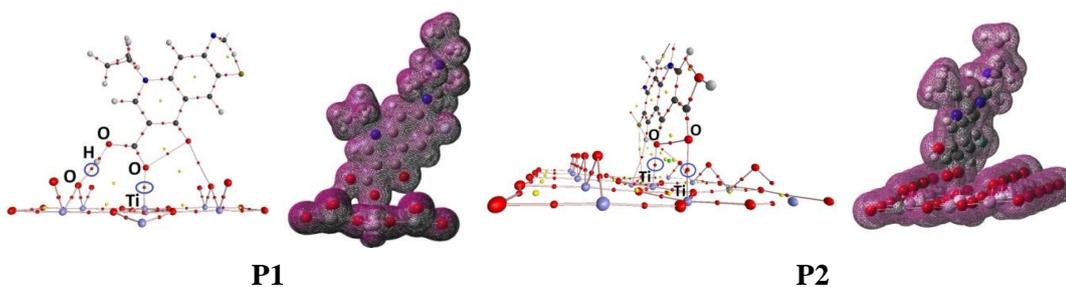


Figure 2. The topology and total electron density map for the first-layered structures of **P1** and **P2** at the B3LYP/6-31G(d,p) level.

To get more insight into origin and role of interactions formed between ENR molecule and r-TiO₂, the quantum chemical analyses are carried out at the B3LYP/6-31G(d,p) level of theory. Some characteristic parameters are given in Table 3 and presented in Figure 2. The presence of Bond Critical Points (BCPs) topology in Figure 2 and their large electron density ($\rho(r)$), Laplacian of electron density values ($\nabla^2(\rho(r))$) in Table 3 proves the existence of stable intermolecular interactions between O···Ti, H···O as shown in Figure 1.

Table 3. The topological analysis and EDT of investigated structures at B3LYP/6-31G(d,p) level.

	BCPs	$\rho(r)$	$\nabla^2(\rho(r))$	$H(r)$	EDT
P1	O ₁ ···Ti	0.0796	0.4518	-0.0047	0.2194
	O-H···O	0.0933	0.1115	-0.0458	
	O···O	0.0110	0.0375	0.0016	
P2	O ₁ ···Ti	0.0415	0.2536	0.0069	0.3578
	O ₂ ···Ti	0.0684	0.4036	0.0008	

^{1,2}- for O atoms in >C=O and -COOH groups

The $\rho(r)$ value of O-H···O_b BCP is 0.0933 au and slightly larger than that of Ti_{5f}···O BCP in **P1**. As a result, the O-H···O_b hydrogen bond is highly stable and play an important role to the stability of **P1** as compared to Ti_{5f}···O interaction. Remarkably, the $\rho(r)$ values of O-H···O_b and Ti_{5f}···O interactions in **P1** are larger than those of Ti_{5f}···O interactions in **P2**. This result leads to the strength of interactions formed in **P1** being more significant than that in **P2**. As a consequence, the interaction energy for **P1** is larger than that for **P2** and in a good agreement with the values shown in Table 2. The existence of O···O chalcogen-chalcogen interaction in **P1** with an electron density of 0.0110 au indicates a slight contribution to the stability of **P1**.

In addition, the $\nabla^2(\rho(r))$ values for Ti_{5f}···O BCPs are large and in the range of 0.25 to 0.45 au, therefore, they are regarded as highly stable interactions. The $\nabla^2(\rho(r))$ values for O-H···O_b and O···O interactions are 0.0375 and 0.1115 au, respectively, falling within the range for weak interactions [14]. It should be noted that the negative values of $H(r)$ for O-H···O_b and Ti_{5f}···O BCPs in **P1** (cf. Table 3) imply that these interactions are stabilized by covalent component. In contrast, the $H(r)$ values for O···O (**P1**) and Ti_{5f}···O (**P2**) BCPs are all positive, suggesting that they are non-covalent interactions [14].

Moreover, the total electron density map shown in Figure 2 and the values given in Table 3 corroborate the formation of aforementioned interactions. This can be understood due to the high electron density overlaps between H and O_b, O and Ti_{5f} atoms directly involved in the O_b···H hydrogen bond and Ti_{5f}···O interaction, respectively. The larger overlap in **P2** leads to its stronger stability as compared to **P1** and in a good agreement with adsorption energies in Table 2. These characteristics for interactions on surface are clearly analyzed in previous investigation [18]. Hence, the Ti···O and O-H···O contacts formed in investigated complexes are regarded as strong interactions.

4. CONCLUSIONS

Two stable configurations formed by interaction between ENR and r-TiO₂ were optimized by using the VASP program and employing DFT method. The adhesion of ENR molecule onto the r-TiO₂ (110) surface is a strong chemical adsorption with associated energies of -26 and -35 kcal.mol⁻¹ for **P1** and **P2** complexes, respectively. The stability of the complexes formed significantly depends on the strong O···Ti_{5f} electrostatic interactions. The O-H···O_b hydrogen bond found in **P1** plays an important role in stabilizing this adsorbate-adsorbent system. The adsorption of ENR on r-TiO₂ preferably forms >C=O···Ti_{5f} interactions. Also, the O···O chalcogen interaction examined in **P1** slightly contributes to the complex's strength. Our calculated results suggest that r-TiO₂ is expected to be a potential material for adsorption and removal of ENR from aquatic environment.

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