CHEMISORPTION OF ENROFLOXACIN ON RUTILE-TiO\textsubscript{2} (110) SURFACE: A THEORETICAL INVESTIGATION

Nguyen Ngoc Tri, Ho Quoc Dai, Nguyen Tien Trung*

Department of Chemistry, and Laboratory of Computational Chemistry and Modelling, Quy Nhon University, 170 An Duong Vuong Str., Quy Nhon City, Binh Dinh Prov., Vietnam

*Email: Nguyientientrung@qnu.edu.vn

Received: 13 November 2018; Accepted for publication: 27 May 2019

Abstract. We investigated the adsorption of enrofloxacin (ENR) antibiotic on rutile-TiO\textsubscript{2} (r-TiO\textsubscript{2}) (110) surface using DFT calculations. Stable configurations of the adsorption of ENR on r-TiO\textsubscript{2} (110) were observed. The origin and role of interactions in stabilizing the configurations are thoroughly analyzed using NBO and AIM analayses. Obtained results indicate that the adsorption process is characterized as a strong chemisorption with an associated energy of ca. -35 kcal.mol\textsuperscript{-1} for the most stable configuration. Quantum chemical analysis shows that the stability of configurations is mainly determined by $>$C=O$\cdots$Ti\textsubscript{5f} electrostatic interaction along with supplement of H$\cdots$O\textsubscript{b} hydrogen bond. It can be suggested that the rutile-TiO\textsubscript{2} can be considered as a potential candidate for adsorption and removal of ENR from wastewater.

Keywords: adsorption, rutile TiO\textsubscript{2} (110), enrofloxacin, DFT calculations.

Classification numbers: 2.5.3; 2.4.2.

1. INTRODUCTION

Titanium dioxide (TiO\textsubscript{2}) 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 TiO\textsubscript{2}, 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 TiO\textsubscript{2} 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-TiO\textsubscript{2} (r-TiO\textsubscript{2}) surface upon adsorption process have not been thoroughly examined yet [2, 6, 7]. Therefore, study of interactions of large molecules on r-TiO\textsubscript{2} 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
Nguyen Ngoc Tri, Ho Quoc Dai, Nguyen Tien Trung

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-TiO$_2$ (110) with the aim to understand the role and the origin of interactions in the formed stable configurations.

2. COMPUTATIONAL DETAILS

The r-TiO$_2$ (110) surface was simulated employing slab model from the bulk TiO$_2$ 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 TiO$_2$ 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 Å; b = 13.15 Å; c = 35.00 Å including vacuum space of 22 Å. The Brillouin zone was sampled by a 2x3x1 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/Å. Adsorption energy ($E_{\text{ads}}$) and interaction energy ($E_{\text{int}}$) are calculated as in the expressions:

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

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

in (1) equation, the $E_{\text{surf-mol}}$, $E_{\text{surf}}$ and $E_{\text{mol}}$ are the energies of the optimized structures for complexes, surface and molecule, respectively. In (2) equation, the $E_{\text{surf}^+}$ and $E_{\text{mol}^+}$ 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 $E_{\text{mol}^+}$ and $E_{\text{mol}}$ and between $E_{\text{surf}^+}$ and $E_{\text{surf}}$, respectively. In order to have a deeper understanding on the role and nature of interactions formed between ENR and r-TiO$_2$, 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.

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···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···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$_{5f}$···O and O-H···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$_{5f}$···O distances in the investigated complexes are close to those of the Ti-O$_b$ bonds in the TiO$_2$ bulk (ranging from 1.86 to 2.01 Å). Therefore, the Ti$_{5f}$···O and O-H···O$_b$ contacts are predicted to be strong interactions during the adsorption process.

In addition, the values of 178.8° to 179.4°, 151.1° to 173.3°, and 175.2° are observed for the O-Ti-O$_{1(2)}$, C-O$_{1(2)}$-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 Ti₅f···O interactions, whereas the P1 is stabilized by both Ti···O and O-H···O₅ intermolecular interactions. The contribution of Ti₅f···O and H···O₅ 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 Ti₅f···O and O-H···O₅ 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···O₅ 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

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 (ρ(r)), Laplacian of electron density values (∇²(ρ(r))) in Table 3 proves the existence of stable intermolecular interactions between O···Ti, H···O as shown in Figure 1.
The ρ(r) value of O···H(O) BCP is 0.0933 au and slightly larger than that of Ti_{5f}···O BCP in P1. As a result, the O···H(O) hydrogen bond is highly stable and play an important role to the stability of P1 as compared to Ti_{5f}···O interaction. Remarkably, the ρ(r) values of O···H(O) 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) 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) 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, O and Ti_{5f} atoms directly involved in the O···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 investigations [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-TiO$_2$ were optimized by using the VASP program and employing DFT method. The adhesion of ENR molecule onto the r-TiO$_2$ (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) hydrogen bond found in P1 plays an important role in stabilizing this adsorbate-adsorbent system. The adsorption of ENR on r-TiO$_2$ 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-TiO$_2$ is expected to be a potential material for adsorption and removal of ENR from aquatic environment.
Acknowledgements. This work is supported by Flemish VLIR-UOS program under a TEAM project with grant number ZEIN2016PR431 for Quy Nhon University. We are grateful to prof. Minh Tho Nguyen at KU. Leuven. NNT thanks KU. Leuven and Quy Nhon University (LCCM) for computing facilities.

REFERENCES

1. Carp O., Huisman C. L., Reller A. - Photoinduced Reactivity of Titanium Oxide, Prog. Solid State Chem. 32 (2004) 33–177.
2. Fujishima A., Zhang X., Tryk D. A. - TiO2 Photocatalysis and Related Surface Phenomena, Surf. Sci. Rep. 63 (2008) 515–582.
3. Diebold U. - The surface science of titanium dioxide, Surf. Sci. Rep. 48 (2003) 53-229.
4. Pang C. L., Lindsay R., Thornton G. - Chemical Reactions on Rutile TiO2 (110), Chem. Soc. Rev. 37 (2008) 2328-2353.
5. Qing G., Chuanzyao Z., Zhibo M., Zefeng R., Hongjun F., and Xueming Y. - Elementary Chemical Reactions in Surface Photocatalysis, Annu. Rev. Phys. Chem. 69 (2018) 451-472.
6. Tillotson M. J., Brett P. M., Bennett R. A., Crespo R. G. - Adsorption of Organic Molecules at the TiO2 (110) Surface: The Effect of van der Waals Interactions, Surf. Scie. 632 (2015) 142-153.
7. Henderson M. A., Lyubinetsky I. - Molecular-level Insights into Photocatalysis from Scanning Probe Microscopy Studies on TiO2 (110), Chem. Rev. 113 (2013) 4428–4455.
8. Yadav S., Goel N., Kumar V., Tikoo K., and Singhal S. - Removal of Fluoroquinolone from Aqueous Solution using Graphene Oxide: Experimental And Computational Elucidation, Environ. Sci. Pollut. Res. 25 (2018) 2942–2957.
9. Otker H. M. and Balcioglu I. A. - Adsorption and Degradation of Enrofloxacin, a Veterinary Antibiotic on natural Zeolite, J. Hazar. Mater. 122 (2005) 251-258.
10. Chamani M., Panahi H. A., Tayebi P., Aminafshar M. and Sadeghi A. A. - Kinetic and Adsorption Study of Enrofloxacin from Aqueous Solutions by Modified Magnetic (Fe3O4) Nano-particles, European Journal of Experimental Biology 3 (4) (2013) 35-42.
11. Jurgen Hafner - Ab-Initio Simulations of Materials Using VASP: Density-Functional Theory and Beyond, J. Comput. Chem. 29 (2008) 2044–2078.
12. Perdew J. P., Burke K., Ernzerhof M. - Generalized Gradient Approximation Made Simple, Phys. Rev. Lett. 77 (1996) 3865-3868.
13. Frisch M. J., Trucks G. W., Schlegel H. B., Seuseria G. E., Robb M. A., Cheeseman J. R., Pople J. A. - Gaussian 09 (Revision B.01), Wallingford, CT: Gaussian (2010).
14. Bader R. F. W. - Atoms in molecules: A quantum theory, Oxford: Oxford University Press (1990).
15. Zhang Y., Zhang C. R., Wang W., Gong J. J., Liu Z. J., Chen H. S. - Density Functional Theory Study Of A-Cyanoacrylic Acid Adsorbed on Rutile TiO2 (110) Surface, Comput. Theor. Chem. 1095 (2016) 125-133.
16. Manzhos S., Giorgi G. and Yamashita K. - A Density Functional Tight Binding Study of Acetic Acid Adsorption on Crystalline and Amorphous Surfaces of Titania, Molecules 20 (2) (2015) 3371-3388.
17. Carvalho A. J. P., Dordio A. V., Ramalho J. P. P. - A DFT study on the adsorption of benzodiazepines to vermiculite surfaces, J. Mol. Model 20 (2014) 2336 (1-8).

18. Nguyen Ngoc Tri, Carvalho A. J. P., Dordio A. V., Minh Tho Nguyen, and Nguyen Tien Trung - Insight into the Adsorption of Chloramphenicol on a Vermiculite Surface, Chem. Phys. Lett. 699 (2018) 107-114.