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NGUYEN NGOC TRI

STUDY ON THE ADSORPTION ABILITY OF ORGANIC MOLECULES ON TiO$_2$ AND CLAY MINERAL SURFACES USING COMPUTATIONAL CHEMISTRY METHODS

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SUMMARY OF DOCTORAL THESIS IN CHEMISTRY

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Supervisors:
1. Assoc. Prof. Dr. Nguyen Tien Trung
2. Prof. Dr. Minh Tho Nguyen

Reviewer 1: **Assoc. Prof. Dr. Pham Tran Nguyen Nguyen**
Reviewer 2: **Assoc. Prof. Dr. Tran Van Tan**
Reviewer 3: **Assoc. Prof. Dr. Pham Vu Nhat**

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INTRODUCTION

1. Motivation

Over the past few decades, experimental and theoretical studies have been reported on advanced materials and nanomaterials with high applicability in the fields of science, technology, production, and life. Among nanomaterials, TiO_2 has been known as an important semiconductor and widely applied in the various fields of energy and health. Also, the solid TiO_2 is extensively used in the photocatalysis, adsorption, and decomposition of organic compounds due to its special surface properties. These processes are usually taking place on the surfaces of TiO_2, and depend on the nature and concentration of the substance, as well as on the different phases of materials. Systematic and detailed studies of the surfaces and phases of TiO_2 have provided clear insights into its structural and electronic properties. The adsorption of organic molecules onto surfaces of materials is a suitable way for reducing or removing amounts of pollutants in environments, including especially for antibiotics presented in wastewater. On the other hand, doped-TiO_2 materials and modified surfaces have been considered for photocatalysis and adsorption processes. Interaction of organic molecules, especially for biological compounds, on surfaces of doped-TiO_2 materials to support for catalysis, sensors, drug transmission processes, were observed. However, research on the fundamental nature and role of adsorptive interactions as well as the mechanism of processes that occurred on TiO_2 surfaces has not been investigated in detail yet.

Many materials have been examined to find out low-cost, environmentally friendly, and highly effective materials to remove

polluted compounds. Among various materials, scientists have paid a considerable amount of attention to clay minerals due to their high adsorption and ions exchange on surfaces, as well as their convenient fabrication, abundant availability in nature, and environmental friendliness. Notably, clay minerals promise to be a potential candidate for the treatment of persistent organic substances, as it eliminates antibiotic residues in aquatic environments. However, the role of intermolecular interactions and adsorption mechanism occurred on surfaces of minerals have not been fully understood. As a key to understanding the surface phenomena, investigations on adsorption of organic molecules, especially for antibiotics on material surfaces by using quantum chemical calculations, should be paid much attention.

Hence, we choose a theoretical investigation with the title: "*Study on the adsorption ability of organic molecules on TiO$_2$ and clay mineral materials using computational chemistry methods*". This is of high scientific and practical significance and can be oriented further in experimental observations in Vietnam.

2. Research purpose

i) Determination of the stable structures upon the adsorption of organic molecules on different surfaces of TiO$_2$ and clay minerals;

ii) Investigation and examinination of the adsorption ability of various organic molecules, antibiotics on TiO$_2$ and clay minerals surfaces;

iii) Obtention of insights into surface interactions, including their formation and role to stability of complexes and adsorption processes;

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iv) Evaluation of the use of TiO_2 and clay minerals in future experimental studies on the adsorption and removal of antibiotics and organic pollutants in wastewater.

3. Object and scope of this study

The scope of this study is theoretical investigations of the adsorption ability of organic molecules, especially antibiotics, on the surfaces of TiO_2 (anatase, rutile) and clay minerals (kaolinite, vermiculite) by using computational chemistry methods.

4. Research contents

Optimization of the structures of organic molecules containing different functional groups (-OH, -COOH, -NH_2, -CHO, -NO_2, -SO_3H), antibiotics, materials including TiO_2 (rutile-TiO_2 (110), anatase-TiO_2 (101) surfaces), clay minerals (kaolinite, vermiculite).

Design and optimization of structures for the adsorption of selected molecules on the surfaces of TiO_2 and clay minerals.

Calculation of interested parameters, energetic aspects following the adsorption of molecules onto TiO_2 and clay minerals surfaces.

Analysis and evaluation of the adsorption ability of organic molecules, antibiotics on different surfaces of TiO_2, clay minerals, and the role of intermolecular interactions formed on the material surfaces in the investigated systems.

5. Methodology

The density functional theory (DFT) methods with suitable and highly correlated functionals, such as the PBE, optPBE-vdW, vdW-DF-C09, are considered for the optimization and calculations of characteristic parameters. The VASP, GPAW packages are used to simulate the structures of TiO_2, clay minerals materials, and the configurations formed by the adsorption of molecules onto surfaces.

Besides, calculations on DPE, PA, MEP, topological geometries, EDT are performed by using Gaussian, AIM2000, and NBO 5.G programs to consider the formation and role of intermolecular interactions upon adsorption.

6. Novelty, scientific and practical significance

The results of the thesis provide us an insight into the adsorption of organic molecules, antibiotics containing different functional groups such as -OH, -COOH, -CHO, >C=O, NO_2, $-NH_2$, $-SO_3H$ on the material surfaces including TiO_2 and clay minerals.

The achieved results in this work give a good assessment of the adsorption processes that take place on the surfaces of TiO_2 and clay minerals. This is an important investigation for guiding subsequent experimental studies to remove or decompose pollutants in wastewaters.

The role and origin of intermolecular interactions contributing to the stability of configurations as well as the adsorption ability of molecules on the TiO_2 and clay mineral surfaces are clarified by using quantum chemical methods.

PART 1. DISSERTATION OVERVIEW

1. Organic pollutants and antibiotics residues in wastewaters

In recent decades, as environmental pollution has emerged as a global and persistent issue, scientists and policymakers have been paying a considerable attention to its consequences. Because compounds containing benzene rings, phenol derivatives were accumulated for a long time in large amounts as part of the human living conditions, it was more and more difficult to remove them completely from environments. Besides, antibiotics have been using extensively not only for the treatment of human and animal diseases but also for industry-scale production of aquatic organisms. The uncontrolled use and release of antibiotics-containing waste are continuously causing many environmental and health problems. For the well-being of society, it is imperative to remove pollutants, especially antibiotics in wastewaters.

2. TiO₂ nanomaterial and its applications

Of the nanomaterials, TiO_2 emerges as one of the most important materials in reaction processes, and it is widely used in the fields of energy, health, and food technology. Specifically, TiO_2 materials are commonly used in photocatalysis, adsorption, and decomposition of compounds based on their special surface properties. In fact, adsorption is an important stage in photocatalytic reactions. Recently, the adsorption of simple molecules on different surfaces of TiO_2 has been examined on rutile and anatase phases. Interactions between organic molecules such as carboxylic acids, benzene, alcohol, ether, amines, or metal ions on TiO_2 surfaces were also been evaluated. According to these reports, functional organic compounds including

>C=O, -COOH, -OH, -NH$_2$, -CHO, -CONH- are favorably adsorbed on TiO$_2$ surfaces. However, in most of previous studies, the formation and role of surface interactions to stability of complexes as well as adsorption processes are still not analyzed thoroughly.

3. Clay minerals and their applications in the treatment of pollutants

Clay minerals have layered structures that may consist of various combinations of tetrahedral and octahedral sheets. Among clay minerals, kaolinite is one of the potential materials used by the water purification industry to reduce soil pollution due to its high surface area, low cost, and environmental friendliness. The adsorption capacity of organic compounds including some dyes on kaolinite and amorphous aluminum oxide has been conducted recently. The results showed that the hydrogen-rich surface of kaolinite (H-slab) is capable of adsorbing organic compounds efficiently, better than its oxygen-rich surface (O-slab) and aluminum oxide surface. Besides, vermiculite is known to have a large surface area, high cation exchange capacity, good swelling, and low cost. For adsorption processes on vermiculite, the stable configurations result from interactions between adsorbed molecule and vermiculite surface such as acid-base, hydrogen bonds, and van der Waals interactions. Most of the weak interactions play a significant role in the arrangement of large systems, and the eventual synthesis of useful compounds. Hence, a better knowledge of the nature of these interactions between antibiotic molecules and the kaolinite, vermiculite surfaces is useful for other important purposes, such as the custom design of adsorbents for controlled sorption and separation of guest molecules.

4. Investigations on material surfaces using computational chemistry

It is known that quantum chemical computations allow us to elucidate the sites of adsorption of molecules to clay minerals as well as to TiO_2 surfaces, determine the relative stability of different binding sites, and emphasize the geometrical details that occur on the adsorbed molecule and the surface upon adsorption. Although the stability of different adsorbate-surface configurations and the specific role in interactions have been investigated, a clear understanding of the existence and effect of material-surface on the stability of configurations and adsorption process was still not reported in detail. In this context, insights into surface phenomena constitute an attracting subject for theoretical studies.

PART 2. THEORETICAL BACKGROUND AND COMPUTATIONAL METHODS

1. Quantum chemical approaches

In this section, short descriptions of quantum chemical approaches are given. The simple Schrödinger equations for one-electron systems are solved efficiently, however, it is impossible to achieve an exact solution for many-body systems, like molecules. For solid-state materials, finding the solutions for Schrödinger equations becomes extremely complex. The pseudopotential and plane wave approaches are considered in calculations to obtain good results. A combination of DFT methods and plane wave approach is one of the efficient ways for evaluating characterized properties, potential applications of materials in various fields of science and life.

2. Computational methods

A detailed description of computations for investigated systems including adsorption of molecules on TiO_2 (anatase, rutile) and clay minerals (kaolinite, vermiculite) surfaces is presented in this section. The DFT methods are considered in calculations to have an insight into surface interactions and a thorough evaluation of the adsorption ability of various molecules on different surfaces. Some quantum chemical programs are used in this work to obtain reliable results. Structures of molecules, surfaces, configurations are optimized and analyzed clearly. Energetic aspects as well as the existence of intermolecular interactions upon adsorption processes are discussed thoroughly.

PART 3. RESULTS AND DISCUSSION
CHAPTER 1. ADSORPTION OF ORGANIC MOLECULES ON MATERIALS SURFACES

1.1. Adsorption of organic molecules on rutile-TiO$_2$ (110) surface

The stable configurations of adsorption of acids (formic, acetic, benzoic), phenol, and nitrobenzene on rutile-TiO$_2$ (110) surface (r-TiO$_2$) are observed. The stability of complexes is significantly contributed by both O···Ti strong interaction and O-H···O hydrogen bond. Remarkably, the additional role of C-H···O weak hydrogen bonds to the stability of stable configurations has been observed for the first time. The adsorption on r-TiO$_2$ is more favorable for >COOH group than -OH and -NO$_2$ ones and characterized as chemisorption.

1.2. Adsorption of benzene derivatives on rutile-TiO$_2$ (110) and anatase-TiO$_2$ (101) surfaces

1.2.1. Geometrical structures

r-P1CHO   **r-P2CHO**   **r-P1COOH**   **r-P2COOH**   **r-P1NH$_2$**   **r-P2NH$_2$**

r-P1OH   **r-P2OH**   **r-P1SO$_3$H**   **r-P2SO$_3$H**   **r-P3SO$_3$H**   **r-P4SO$_3$H**
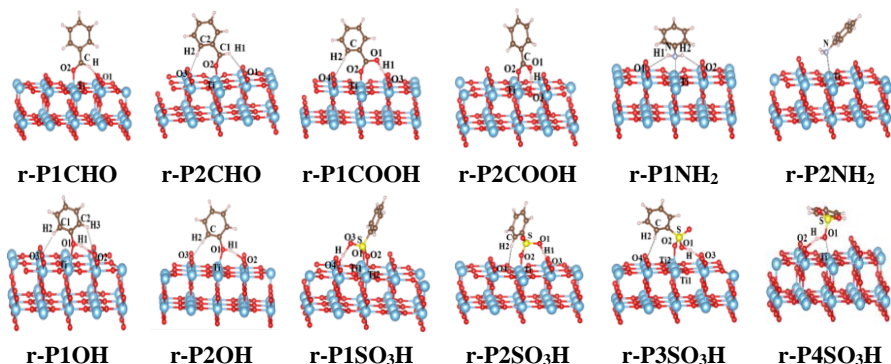
Figure 1.4. Stable complexes of adsorption of benzene derivatives on rutile-TiO$_2$ (110) surface

The stable complexes are formed favorably following the interaction between functional groups in molecules and Ti$_{5f}$, O$_b$ sites on r-TiO$_2$, and a-TiO$_2$ surfaces and contributed by Ti···O electrostatic

interactions and O/N/C-H⋯O hydrogen bonds.

1.2.2. Energetic aspects of the adsorption process

The energy aspects for stable configurations are calculated and listed in Tables 1.8 and 1.9 for r-TiO$_2$ and a-TiO$_2$ systems, respectively.

Table 1.8. Adsorption, interaction, and deformation energies of adsorption of benzene derivatives on rutile-TiO$_2$ (110) surface (all in kcal.mol^{-1})

Complex	E_{ads}	E_{int}	$E_{def\text{-}surf}$	$E_{def\text{-}mol}$
r-P1CHO	-18.0	-22.8	3.8	1.0
r-P2CHO	-17.2	-21.8	3.7	0.9
r-P1COOH	-24.2	-35.0	6.4	4.4
r-P2COOH	-18.0	-25.5	5.2	2.3
r-P1NH$_2$	-19.0	-23.0	2.9	1.0
r-P2NH$_2$	-15.2	-19.7	3.3	1.2
r-P1OH	-15.3	-20.0	3.9	0.8
r-P2OH	-14.0	-18.9	4.0	0.9
r-P1SO$_3$H	-31.1	-146.7	25.2	90.3
r-P2SO$_3$H	-20.5	-33.2	5.8	6.9
r-P3SO$_3$H	-18.6	-28.8	6.7	3.5
r-P4SO$_3$H	-12.9	-16.4	3.4	0.0

The calculated results indicate that the ability of adsorption of these molecules on both r-TiO$_2$ and a-TiO$_2$ is approximate and decreases in the ordering of -SO$_3$H > -COOH > -NH$_2$ > -CHO > -OH. The distortion of molecules in their complexes decreases in going from -SO$_3$H, to -COOH, -NH$_2$, -CHO, and finally to -OH.

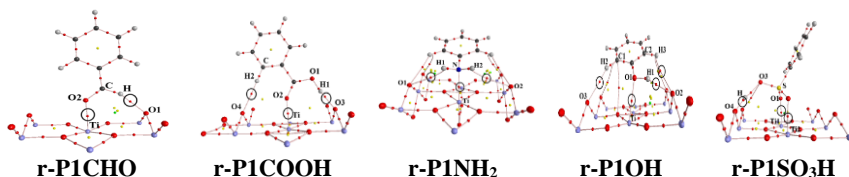*1.2.3. Formation and role of intermolecular interactions*

Figure 1.7. Topological geometry of the first-layered structures of the most
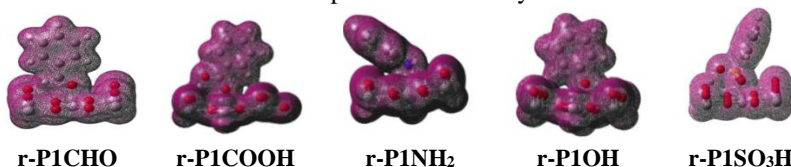stable complexes for rutile systems

Figure 1.9. EDT maps of investigated structures for rutile systems

AIM analysis shows that the $Ti\cdots O$ and $O\text{-}H\cdots O$ intermolecular contacts are significantly strong in complexes of $-SO_3H$ derivatives and reduced following the order: $-SO_3H \gg -COOH > -CHO \approx -NH_2 \approx -OH$. Hence, the stability of configurations decreases in the same order. Furthermore, the overlaps of electron density at atoms involved in interactions are found following formations of $Ti\cdots O$ and $H\cdots O$ contacts.

1.2.4. Summary

Twenty-four stable structures are obtained of the adsorption of organic molecules containing benzene rings on the rutile-TiO_2 (110) and anatase-TiO_2 (101) surfaces of TiO_2. The adsorption energy values are in the range of -12.9 to -31.1 kcal.mol^{-1} and -3.4 to -29.1 kcal.mol^{-1} for rutile and anatase systems, respectively. These processes are determined as chemical adsorptions. Besides, the interaction between functional groups of molecules and surface is considerably strong with associated energy in the range of -16.4 to -146.7 kcal.mol^{-1} for rutile's complexes and of -3.9 to -151.5 kcal.mol^{-}

[1] for anatase ones. The quantum chemical analyses indicate the stability of the complexes is significantly contributed by Ti···O/N and O/C/N-H···O intermolecular interactions. Overall, the adsorptive ability of derivatives on the surfaces of TiO_2 decreases in the ordering of $-SO_3H > -COOH > -NH_2 > -CHO > -OH$.

1.3. Adsorption of benzene derivatives on kaolinite (001) surface
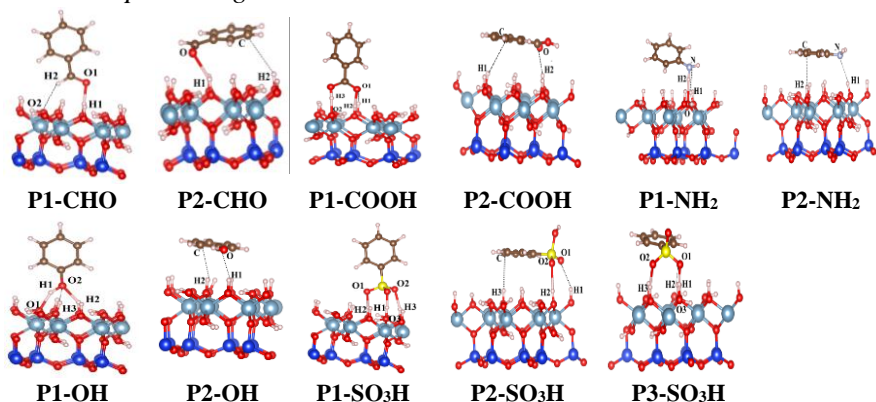
1.3.1. Optimized geometries

P1-CHO **P2-CHO** **P1-COOH** **P2-COOH** **P1-NH₂** **P2-NH₂**

P1-OH **P2-OH** **P1-SO₃H** **P2-SO₃H** **P3-SO₃H**

Figure 1.11. Stable structures of adsorption of derivatives on H-slab

The optimized structures are formed following two trends: interactions between molecules and surface at functional groups (**P1**) or benzene ring (**P2**).

1.3.2. Energetic aspects of the adsorption process

Calculated results indicate that the **P1** complexes are more stable than **P2**. The strength of complexes formed between molecules and H-slab of kaolinite decreases in the sequence: $-SO_3H > -COOH > -OH > -CHO > -NH_2$. Besides, the structural changes for molecules and surface in complexes of $-SO_3H$ derivative are considerably strong, whereas these changes are slightly small, for other derivatives' complexes.

Table 1.15. Energetic parameters of complexes, molecules and surface upon adsorption processes (in kcal.mol^{-1})

Complex	E_{ads}	E_{int}	$E_{def-surf}$	$E_{def-mol}$
P1-CHO	-7.7	-9.3	0.9	0.8
P2-CHO	-5.5	-6.9	0.8	0.6
P1-COOH	-16.2	-23.4	2.9	4.3
P2-COOH	-3.5	-4.6	0.6	0.5
P1-NH$_2$	-5.4	-6.8	0.8	0.6
P2-NH$_2$	-4.8	-5.9	0.8	0.3
P1-OH	-11.0	-15.1	1.7	2.4
P2-OH	-3.0	-3.6	0.5	0.1
P1-SO$_3$H	-24.8	-99.2	14.6	59.8
P2-SO$_3$H	-6.0	-7.6	1.4	0.2
P3-SO$_3$H	-19.6	-94.2	16.7	58.0

1.3.3. Formation and role of intermolecular interactions
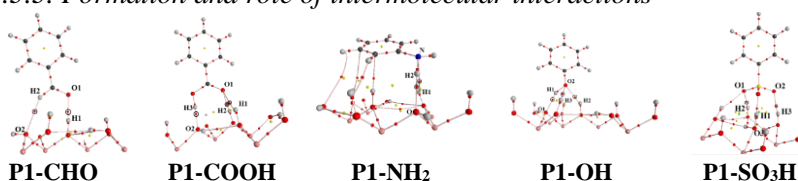

| P1-CHO | P1-COOH | P1-NH$_2$ | P1-OH | P1-SO$_3$H |

Figure 1.12. Topological geometry of the most stable complexes for adsorption of organic molecules on H-slab

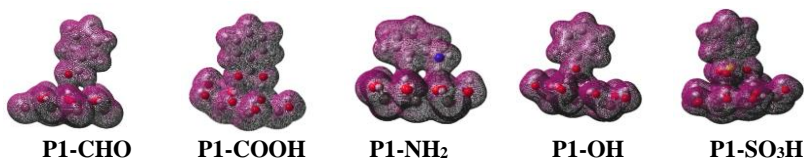| P1-CHO | P1-COOH | P1-NH$_2$ | P1-OH | P1-SO$_3$H |

Figure 1.13. Schematic of total electron density of complexes at the B3LYP/6-31+G(d,p) level

The results imply the strength of the interactions reduces at the sequence of derivatives: -SO₃H > -COOH > -OH > -CHO > -NH₂. Therefore, the stability of configurations tends to decrease in the same order.

1.3.4. Summary

Eleven stable complexes are obtained corresponding to two special structures: i) vertical arrangement with forming interactions between functional groups and surface (**P1** type) and ii) parallel arrangement with the existence of interactions at benzene ring (**P2** type). The adsorption energy of complexes ranges from -3.0 to -24.8 kcal.mol^{-1} in which the values are more negative for **P1** than for **P2**. Remarkable, strong intermolecular contacts are found in complexes of -SO₃H derivatives. The adsorption ability of molecules on H-slab decreases in the order of -SO₃H > -COOH > -OH > -CHO > -NH₂.

1.4. Adsorption of benzene derivatives on a K⁺-supported kaolinite (001) surface

Two trends are found following the adsorption processes to form stable configurations: i) interactions locate at functional groups (**P1** type) and ii) interactions focus at benzene ring (**P2** type). The adsorptions of these organic molecules are evaluated weak chemisorption processes. The stability of configurations is contributed by interactions between K⁺ site on surface and O/N atoms high negative charge regions of molecules or benzene ring. AIM analysis shows these intermolecular contacts have non-covalent in nature. Besides, the electron density transfer is favorable from molecules to K⁺-slab.

CHAPTER 2. ADSORPTION OF ANTIBIOTICS MOLECULES
ON TiO_2 AND VERMICULITE SURFACES

2.1. Adsorption of enrofloxacin molecule on rutile-TiO_2 (110) surface

Two stable complexes (**ER1**, **ER2**) formed by the interaction between ER and r-TiO_2 were observed. The adhesion of ER molecule onto the r-TiO_2 is chemical adsorption with associated energies of -35 kcal.mol^{-1}. The stability of the complexes significantly depends on the strong $O \cdots Ti_{5f}$ electrostatic interactions. The $O-H \cdots O_b$ hydrogen bond found in **ER1** plays an important role in stabilizing this adsorbate-adsorbent system. Besides, the $O \cdots O$ chalcogen interaction examined in **ER1** slightly contributes to the complex's strength.

2.2. Adsorption of ampicillin, amoxicillin, and tetracycline molecules on rutile-TiO_2 (110) surface
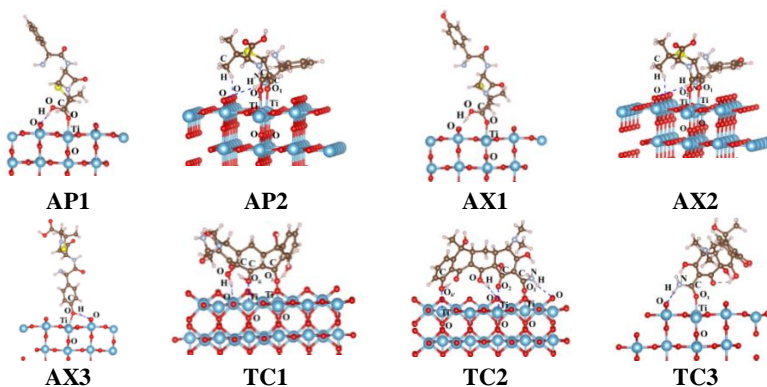
3.2.1. Stable complexes

Figure 2.3. Stable complexes for adsorption of antibiotic molecules on rutile-TiO_2 (110) surface

The optimized structures are formed in a horizontal arrangement and stabilized by $Ti \cdots O$ and $H \cdots O$ intermolecular interactions.

2.2.2. Energetic aspects of the adsorption process

Calculated results show the adsorption ability of these molecules on the r-TiO$_2$ is quite strong and similar to each other.

Table 2.5. Energies for adsorption processes using both PBE and optPBE-vdW functionals (kcal.mol^{-1})

	AP1	AP2	AX1	AX2	AX3	TC1	TC2	TC3
E$_{ads}$	-23.0	-25.3	-26.1	-26.6	-15.4	-19.1	-24.1	-21.7
	-42.7	*-64.9*	*-42.9*	*-66.5*	*-28.4*	*-58.9*	*-66.6*	*-45.1*
E$_{int}$	-37.5	-43.6	-37.6	-44.7	-22.1	-42.5	-50.0	-40.6
E$_{def-surf}$	7.4	11.5	5.9	11.7	4.4	13.5	13.0	12.1
E$_{def-mol}$	7.1	6.9	5.5	6.5	2.2	9.9	12.9	6.8

2.2.3. Characteristic properties of intermolecular interactions

AP2 (a)   AX2 (a)   TC2 (a)
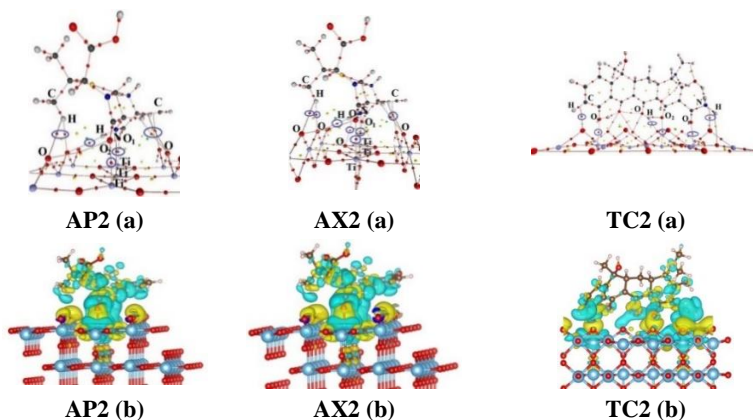
AP2 (b)   AX2 (b)   TC2 (b)

Figure 2.5. a) Topological critical points and b) electronic charge density transfer of the most stable complexes

The quantum chemical analyses imply that the Ti⋯O interactions and O/N-H⋯O hydrogen bonds are highly stable and play an important role in the stability of complexes.

The adsorption energies of the antibiotic-surface systems are calculated to be in the range of -15 to -27 kcal.mol^{-1} (PBE functional). These processes are regarded as chemical adsorptions. The ability of interactions between functional groups of antibiotic molecules and the rutile-TiO$_2$ (110) surface is regarded approximately for AP, AX, and TC. The complexes are stabilized by the significant contribution of O⋯Ti$_{5f}$ electrostatic attractions and the additional role of the O/N-H⋯O$_b$ hydrogen bonds. Adhesion of these molecules on the TiO$_2$ surface occurs favorably in a horizontal arrangement with predominant interactions of >C=O or -COOH groups of the molecules and Ti$_{5f}$ sites of the surface.

2.3. Adsorption of ampicillin and amoxicillin molecules on anatase-TiO$_2$ (101) surface
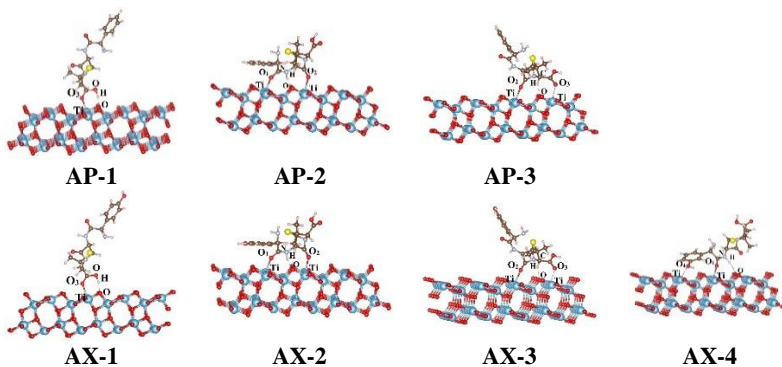
2.3.1. Stable structures

Figure 2.7. The optimized structures of ampicillin, amoxicillin adsorbed on anatase-TiO$_2$ (101) surface

The AP, AX molecules tend to arrange in horizontal sequence onto a-TiO$_2$ to form various intermolecular contacts including Ti⋯O and H⋯O, similar to rutile-TiO$_2$ systems.

2.3.2. Adsorption energy

The E_{ads} values for AP and AX systems range from -17.7 to -31.1 kcal.mol^{-1}. The adsorption processes are evaluated as chemical adsorptions.

Table 2.7. Adsorption energy (E_{ads}, kcal.mol^{-1}) of stable complexes

i	1	2	3	4
AP-i	-22.9	-31.1	-18.6	
AX-i	-21.0	-29.3	-17.7	-25.5

2.3.3. AIM and NBO analyses
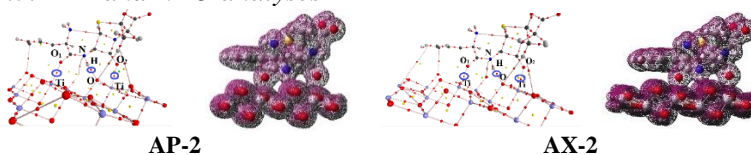
Figure 2.8. The topological geometries and EDT maps of the first-layered structures

The results show that the Ti···O and N-H···O intermolecular contacts are noncovalent interactions. The stability of these interactions in these configurations is nearly equal.

2.3.4. Summary

Obtained results show that the adsorption of ampicillin and amoxicillin molecules on the anatase-TiO$_2$ (101) surface (a-TiO$_2$) is regarded as chemical adsorption. The stable configurations are contributed significantly by Ti···O electrostatic interactions along with O/N/C-H···O hydrogen bonds. The adsorption of ampicillin onto the a-TiO$_2$ is slightly stronger than that of amoxicillin. Similar to rutile-TiO$_2$ systems, the arrangement of molecules on the a-TiO$_2$ tends to be

preferable in a horizontal sequence and occurs on a large surface area to form stable interactions.

2.4. Adsorption of chloramphenicol molecule on a vermiculite surface

Four minima on the potential energy surface denoted as **CP1**, **CP2**, **CP3**, and **CP4**, are characterized as stable configurations upon interaction with the surface. Adsorption energies for these stable configurations are significantly negative and increase in the sequence **CP1** < **CP4** < **CP3** < **CP2**. The adsorption process of chloramphenicol on the vermiculite surface is characterized as chemical adsorption, and largely favorable in the **CP1** configuration. The adherence of molecule to the surface is attained due to the effect of stabilizing interactions between Mg^{2+}, O^{2-} ions of vermiculite surface and O, Cl, H atoms at the high charge density regions of chloramphenicol. Remarkably, the O-H⋯O hydrogen bonds and Mg⋯O electrostatic interactions play an important role in the stability of adsorbate – surface complexes. The AIM analysis results suggest that O-H⋯O hydrogen bonds in **CP1** and **CP4** have a part of covalent nature. The weaker C-H⋯O hydrogen bonds bring in also an important contribution to complex stability.

2.5. Adsorption of β-lactam antibiotics on vermiculite surface

2.5.1. Stable structures

The minima on the potential energy surface located upon optimization are illustrated in Figure 2.13. The adhesion of these antibiotics molecules onto a vermiculite surface is favorable to form C-O/S⋯Mg or Mg⋯π and O-H⋯O interactions between functional groups (eg. –COOH, -NH$_2$, -OH in most the complexes) and surface, especially in the horizontal arrangement of molecules.
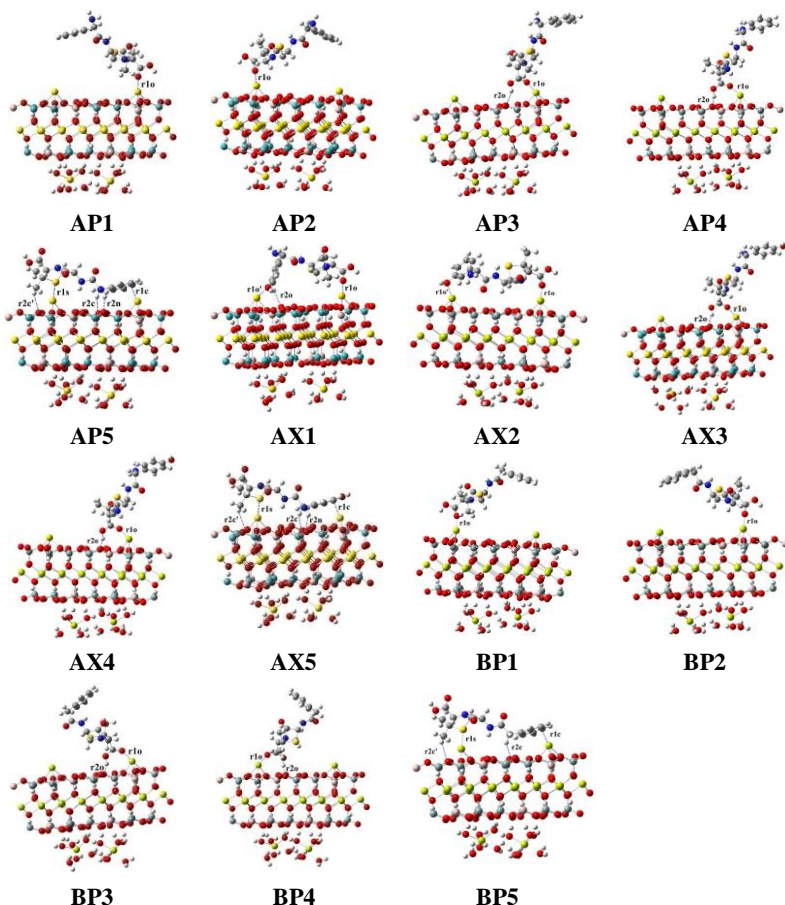
Figure 2.13. Stable complexes of adsorption of AP, AX, and BP on a vermiculite surface

2.5.2. Energetic aspects of the adsorption process

Adsorption of an antibiotic molecule on the surface is evaluated, per convention, as a strong process with a highly negative adsorption energy E_{ads}. The amount is in the range of -34.7 to -77.6 kcal.mol^{-1}; -42.6 to -71.7 kcal.mol^{-1} and -35.2 to -72.5 kcal.mol^{-1} for AP, AX and BP systems, respectively (Table 2.13). Hence, these processes can be

assigned as strong chemical adsorptions. There is only a small difference in the adsorption ability of antibiotics molecules on the vermiculite surface, which marginally decreases in going from AP to BP and then to AX.

Table 2.13. Adsorption energies (E_{ads}), interaction energies (E_{int}), and deformation energies for antibiotics and vermiculite surface ($E_{def\text{-}mol}$, $E_{def\text{-}surf}$) (all values in kcal.mol^{-1} obtained from DFT computations)

Complexes	E_{ads}	E_{int}	$E_{def\text{-}mol}$	$E_{def\text{-}surf}$
AP1	-34.7	-47.0	4.5	7.8
AP2	-37.8	-50.7	5.5	7.4
AP3	-35.6	-54.7	10.7	8.4
AP4	-47.2	-77.7	19.4	11.2
AP5	-77.6	-100.2	13.1	9.5
AX1	-67.2	-97.4	14.5	15.8
AX2	-71.7	-94.7	15.4	7.6
AX3	-57.2	-79.8	14.2	8.5
AX4	-42.6	-77.7	23.9	11.2
AX5	-67.9	-99.2	20.4	10.9
BP1	-35.2	-46.9	4.0	7.7
BP2	-38.5	-50.7	4.9	7.3
BP3	-46.9	-70.3	8.8	14.6
BP4	-58.3	-83.8	12.0	13.5
BP5	-72.5	-91.5	10.5	8.6

2.5.3. *Existence and role of different interactions upon complexation*

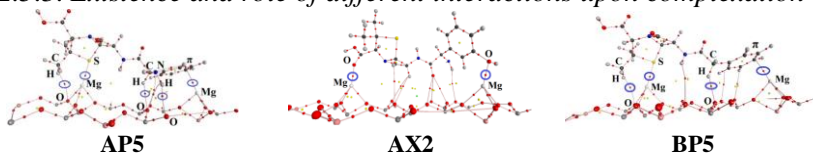AP5   AX2   BP5

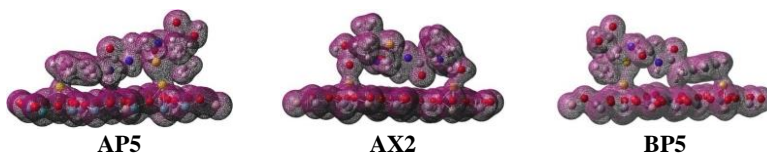**Figure 2.15.** Topological features for the most stable adsorption configurations

Figure 2.16. Total electron density maps of most stable complexes

The quantum chemical analyses suggest that the stability of investigated complexes arises considerably from Mg···O/S/π, O-H···O strong interactions, and cooperative addition from N/C-H···O, C/O···O weak interactions.

2.5.4. Summary

A horizontal trend of antibiotic molecules is geometrically preferred when ampicillin (AP), amoxicillin (AX), and benzylpenicillin (BP) antibiotic molecules are adsorbed on the vermiculite surface. Adsorption energies for these stable complexes are large, in the range of -35 to -78 kcal.mol^{-1}, and slightly increase in the sequence of AP < BP < AX. Such stabilizing quantities confer these processes as strong chemical adsorption. It is found that the Mg···O/S/π electrostatic interactions and O-H···O hydrogen bonds determine the stability of complexes, in which the Mg···π interaction has been detected for the first time, and plays an important role in the complexes stabilization. The AIM analysis indicates that most of these interactions have a non-covalent nature. NBO results also show the transfers of electron density occur favorably from π(C=O/C), σ(C-S/C) and LP(O/S) orbitals in the molecules to the LP*(Mg) orbital to form Mg···O/S/π intermolecular interactions.

CONCLUSIONS AND OUTLOOK

The most important results emerge as follows:

1. Concerning the mechanism of the adsorption of organic molecules including benzene derivatives and formic, acetic acids on rutile-TiO_2 (110) and anatase-TiO_2 (101) surfaces (r-TiO_2 and a-TiO_2), the adsorption processes are determined as chemisorptions characterized by high adsorption energies in the range of -10 to -31 kcal.mol^{-1}. Stability of the adsorptive configurations is mainly contributed by Ti···O/N electrostatic interactions with addition of O-H···O hydrogen bonds. Computed results indicate that the adsorption ability of these molecules on both r-TiO_2 and a-TiO_2 surfaces decreases in the order of -SO_3H > -COOH > -NH_2 > -NO_2 > -CHO > -OH. Besides, the adsorption of these molecules on r-TiO_2 is slightly stronger than that on a-TiO_2.

2. For kaolinite, calculated results on the adsorption of benzene derivatives on H-slab and K$^+$-slab surfaces show that adsorption energies of the resulting complexes range from -3 to -25 kcal.mol^{-1} (PBE functional) for H-slab and from -5 to -21 (PBE), -9 to -23 (vdW) kcal.mol^{-1} for K$^+$-slab. The stability of the configurations is mainly governed by O/N-H···O intermolecular contacts for H-slab and by O/N-H···O and K···O/N/C(π) for K$^+$-slab. The adsorption ability of these molecules on kaolinite decreases in the order of -SO_3H > -COOH > -OH > -CHO > -NH_2 (H-slab) and -COOH ≥ -CHO > -NH_2 > -OH (K$^+$-slab).

3. Regarding the adsorption of antibiotics molecules, including ampicillin (AP), amoxicillin (AX), enrofloxacin (ER), and tetracycline (TC) on r-TiO_2 and a-TiO_2, it is found that these molecules occurred onto r-TiO_2 and a-TiO_2 are characterized as chemisorption processes with associated energies of ca. -24 to -35 kcal.mol^{-1} and -29 to -31 kcal.mol^{-1} (PBE), respectively. The adsorption ability of these antibiotics on r-TiO_2 slightly decreases in the order of TC ≥ AX ≥ AP ≥ ENR, while for a-TiO_2, the adhesion of AP is slightly more favorable than that of AX. Quantum chemical

analyses further illustrate the significant contributions of Ti⋯O electrostatic interactions and O/N/C-H⋯O hydrogen bonds to the stabilization of adsorption configurations. Remarkably, the most stable complexes tend to be formed preferably in horizontal arrangement along with Ti^{4+} sites on the r-TiO_2 and a-TiO_2 to form Ti⋯O strong electrostatic interactions. Moreover, the adsorption of AP and AX antibiotics on r-TiO_2 is slightly weaker than on a-TiO_2.

4. The adsorption processes of chloramphenicol (CP) and β-lactam antibiotics, including ampicillin (AP), amoxicillin (AX), and benzylpenicillin (BP), on the vermiculite surface were thoroughly investigated. They are strong chemisorption processes characterized by large adsorption energies of ca. -72 to -107 kcal.mol^{-1}. The stability of the configurations mainly arises from Mg⋯O/Cl/S/π attractive electrostatic interactions and O/C-H⋯O hydrogen bonds. Each molecule prefers to arrange horizontally on the surface to form Mg⋯S and Mg⋯π contacts, or two Mg⋯O electrostatic interactions between S atom in -CS, π-electrons of a benzene ring or O atoms of -COOH, -OH groups in molecules and Mg^{2+} sites on the surface. Noticeably, an important role of Mg⋯π interaction in the complex stabilization has been observed in β-lactam antibiotics systems for the first time.

5. Some intermolecular contacts, including Ti⋯O, O/N-H⋯O, have slightly negative H(r) values at their BCPs and thus, they have a small covalent part. The existence of cations such as K^+, Mg^{2+} on clay minerals surfaces (kaolinite, vermiculite) plays a crucial role in the adsorption ability of organic compounds. From a methodological viewpoint, the vdW forces included in computations induce a considerable effect on geometrical structure, adsorption energy, and the nature of interactions between functional groups and surfaces. Overall, vermiculite emerges to offer an efficient adsorption surface and can be used as a suitable material to remove antibiotics from wastewaters in comparison to kaolinite and TiO_2.

List of publications used for this thesis

1. **Nguyen Ngoc Tri**, Dai Q.Ho, A.J.P. Carvalho, Minh Tho Nguyen and Nguyen Tien Trung, Insights into adsorptive interactions between antibiotic molecules and rutile-TiO_2 (110) surface, *Surface Science*, **2021**, 703, 121723(1-8).
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3. Nguyen Thi Thuy, **Nguyen Ngoc Tri**, Nguyen Tien Trung, A theoretical study on adsorption of organic molecules containing benzene ring onto kaolinite surface, *Quy Nhon University Journal of Science*, **2020**, 14(1), 5-14.
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5. **Nguyen Ngoc Tri**, Huynh Thi My Phuc, Nguyen Tien Trung, A theoretical investigation of interaction of organic molecules with anatase-TiO_2 (101) surface, *Vietnam Journal of Catalysis and Adsorption*, **2019**, 8(4), 42-48.
6. Huynh Thi My Phuc, **Nguyen Ngoc Tri**, Nguyen Tien Trung, Theoretical study on adsorption of organic molecules containing benzene ring onto rutile-TiO_2 (110) surface using density functional theory method, *Quy Nhon University Journal of Science*, **2019**, 13(5), 89-93.
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8. **Nguyen Ngoc Tri**, Ho Quoc Dai, Nguyen Tien Trung, Chemisorption of enrofloxacin on rutile-TiO_2 (110) surface: a theoretical investigation, *Vietnam Journal of Science and Technology*, **2019**, 57(4), 449-456.
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10. **Nguyen Ngoc Tri**, A.J.P. Carvalho, A.V. Dordio, Minh Tho Nguyen and Nguyen Tien Trung, Insight into the adsorption of chloramphenicol on a vermiculite surface, *Chemical Physics Letters*, **2018**, 699, 107-114.