



Research paper

Insight into the adsorption of chloramphenicol on a vermiculite surface

Nguyen Ngoc Tri^a, A.J.P. Carvalho^{b,c}, A.V. Dordio^{b,d}, Minh Tho Nguyen^e, Nguyen Tien Trung^{a,*}^a Laboratory of Computational Chemistry and Modeling, Department of Chemistry, Quy Nhon University, Quy Nhon, Viet Nam^b Department of Chemistry, School of Sciences and Technology, University of Évora, Evora, Portugal^c Évora Chemistry Center, IIFA, University of Évora, Evora, Portugal^d MARE – Marine and Environmental Sciences Centre, IIFA, University of Évora, Evora, Portugal^e Department of Chemistry, University of Leuven, Celestijnenlaan 200F, B-3001 Leuven, Belgium

ARTICLE INFO

Article history:

Received 1 February 2018

In final form 20 March 2018

Available online 21 March 2018

Keywords:

Vermiculite

Chloramphenicol

Chemisorption

Interaction

Material surface

ABSTRACT

Four stable configurations were found upon adsorption of the chloramphenicol on a period slab model of the vermiculite surface, using the PBE and C09-vdW functionals in a projector-augmented wave (PAW) method approach. The adsorption is a strong chemisorption process, characterized by an adsorption energy of $-106.5 \text{ kcal mol}^{-1}$ at the most stable configuration. Stability of configurations contributed mainly by $\text{Mg} \cdots \text{O}/\text{Cl}$ attractive electrostatic interactions and $\text{C}/\text{O}-\text{H} \cdots \text{O}$ hydrogen bonds. It is remarkable that the vermiculite is found to be a solid material with good potential to be used for adsorption and consequent removal of this type of antibiotic drugs.

© 2018 Elsevier B.V. All rights reserved.

1. Introduction

Antibiotics were and still are proven to be powerful and effective drugs to treat various bacterial infections [1]. The popular use of antibiotics has extensively been reviewed in the literature [2,3]. Of the current antibiotics, chloramphenicol is produced in large quantities and commonly used to treat several different diseases of animals, especially in shrimp farming [4,5]. It turns out to be one of the many chemical compounds that actually contaminate water resources.

In recent years, the treatment of organic pollutants in solution has become an important concern of environmental science as it is affecting our daily life [6]. The removal of antibiotics in wastewater treatment plants is currently not given a special focus, thus being performed mostly by the conventional wastewater treatment technologies, which are, however, typically inefficient for this type of pollutants. Remarkably, clay minerals, which are important components of most types of soil, have been applied as adsorbents for wastewater treatment due to their relevant properties such as the high cation exchange capacity, swelling properties and high specific surface areas [7–9]. Clay minerals have a layered structure that may consist of various combinations of tetrahedral and octahedral sheets such as in kaolinite (a tetrahedral sheet intercalated by an octahedral sheet, i.e. 1:1), montmorillonite (two tetrahedral

sheets sandwiching a central octahedral sheet, or 2:1) or vermiculite (also 2:1). Among these minerals, vermiculite has been suggested as an adsorbent with good potential for removal of organic pollutants owing to its hydrophilicity, high charge density on surface, and its layered crystalline structure [10].

Adsorption of organic molecules on vermiculite surfaces has been investigated on both experimental and theoretical studies [7,10]. Some reports indicated that the adsorption capacity of materials mainly depends on the cation exchange and surface complexation (e.g. hydrogen bonds) between functional groups of organic compounds and the charged sites of adsorbents [11,12]. 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 weak interactions have a significant role in determining the nature of intermolecular forces, arrangement of large systems, and eventual synthesis of useful compounds in which the hydrogen bond is of prominent importance. The hydrogen bonding formed between organic compounds has extensively been investigated in various works [13–16], as it significantly contributes to the stability and property of the complexes obtained. In this context, a better knowledge of the nature of interactions between antibiotic molecules and the vermiculite surface is primordial for a better prediction of the environmental fate of these organic pollutants. In addition, this understanding is useful for other important purposes such as the custom design of adsorbents for controlled sorption and separation of guest molecules.

* Corresponding author.

E-mail address: nguyentienrung@qnu.edu.vn (N.T. Trung).

It is well known that quantum chemical computations allow us to elucidate the sites of adsorption of a molecule to a clay surface, the relative stability of different binding sites, and geometrical details that take place on the adsorbed molecule and on the surface upon adsorption. In the present work, we perform a theoretical investigation into the chloramphenicol molecule adsorbed on the vermiculite surface making use of density functional theory (DFT) computations. Stability of different adsorbate-surface configurations, the presence and specific role of interactions are thoroughly investigated quantitatively. The atom in molecule (AIM) method and molecular electrostatic potential (MEP) maps are also employed to emphasize the nature of the intermolecular interactions involved.

2. Computational details

Geometrical structures of the systems considered were optimized using the GPAW package [17], a software that uses the projector-augmented wave (PAW) method and describes wave functions in real-space orthorhombic grids, following a finite-difference approach. The Perdew-Burke-Ernzerhof (PBE) generalized-gradient approximation (GGA) of the exchange correlation functional was employed [18–20]. To model the vermiculite surface, a periodic slab was constructed from crystallographic data available in American Mineralogist Crystal Structure Database [21]. Its structure normally contains some Al^{3+} , Mg^{2+} and Fe^{2+} octahedral ions and Si^{4+} or Al^{3+} tetrahedral ions in which the ratio of tetrahedral and octahedral sheets is 2:1. In this study, the vermiculite surface model that was used contains exclusively Mg^{2+} as the octahedral ions and some of the Si^{4+} cations in tetrahedral sheets are substituted by Al^{3+} cations in a 1:3 ratio. To perform calculations for the large size of the adsorbed molecule, a single unit cell of the structure was expanded by replication into a 2×1 super-cell defined by $a = 10.698 \text{ \AA}$, $b = 18.510 \text{ \AA}$, $c = 46.638 \text{ \AA}$ and $\alpha = 90.00^\circ$, $\beta = 97.12^\circ$, $\gamma = 90.00^\circ$ lattice parameters (monoclinic structure). Additionally, periodic boundary conditions were applied in all directions. The vacuum thickness in this cell in the direction normal to the surface is large enough for calculation of interactions between molecule and surface and relaxation without significant perturbation from periodic images in that direction.

Considering a simplified model, the water molecules hydrating the Mg^{2+} cations external to the surface were removed and the obtained surface was used as such for all DFT calculations. In the present study both the PBE and the C09-vdW-DF functionals [22] were selected for geometry optimizations, and calculation of energies. As shown in these previous studies, these functionals yield comparable results for the adsorption capacity and interactions of organic molecules with surfaces. Adsorption energy (ΔE_{ads}) and interaction energy (ΔE_{int}) are thus calculated using both PBE and C09-vdW-DF functionals. For both energies calculated by the C09-vdW-DF functional, the structures optimized with the PBE functional were utilized for single point energy calculations. These energies are simply defined by the following expressions:

$$\Delta E_{\text{Ads}} = E_{\text{surf-mol}} - (E_{\text{surf}} + E_{\text{mol}});$$

$$\Delta E_{\text{Int}} = E_{\text{surf-mol}} - (E_{\text{surf}}^* + E_{\text{mol}}^*)$$

where $E_{\text{surf-mol}}$, E_{surf} and E_{mol} are the energies of the surface-adsorbate system, surface and molecule, respectively, all three in their optimal separate geometries. E_{surf}^* and E_{mol}^* are single point energies of the surface and molecule while keeping the same geometries as in the surface-adsorbate optimized structure. In addition, the deformation energies of the adsorbate molecule ($\Delta E_{\text{D-mol}}$) and of vermiculite surface ($\Delta E_{\text{D-surf}}$) upon the adsorption process

are computed by the differences between E_{mol}^* and E_{mol} and between E_{surf}^* and E_{surf} , respectively.

On the other hand, for a deeper understanding of the nature of interactions between molecule and surface, we also perform calculations on proton affinity (PA) and de-protonation energy (DPE) for the chloramphenicol molecule using the B3LYP functional in conjunction with the 6-311++G(d,p) basis set. For these computations, the Gaussian 09 program was used [23]. Topological analysis, electron density ($\rho(r)$) and Laplacian of the electron density ($\nabla^2(\rho(r))$) at bond critical points (BCPs) are identified using the atoms-in-molecules theory [24,25] using the AIM 2000 program [26] also at the B3LYP/6-31+G(d,p) level. The density potential energy ($V(r)$) and density kinetic energy ($G(r)$) at the BCPs are calculated by the expressions [27,28]:

$$G(r) = \frac{3}{10} (3\pi^2)^{2/3} \rho^{5/3}(r) + \frac{1}{6} \nabla^2 \rho(r); \quad V(r) = \frac{1}{4} \nabla^2 \rho(r) - 2G(r).$$

In addition, the molecular electrostatic potential (MEP) map for chloramphenicol was estimated at the B3LYP/6-31+G(d,p) level to probe the stability of interactions between charged regions in the molecule and the clay mineral surface. Natural bond orbital (NBO) analysis was performed using NBO 5.G software [29] to evaluate electron density transfer between interaction counterparts.

3. Results and discussion

3.1. Geometrical structure

Geometry optimizations of chloramphenicol and vermiculite surface were performed using the PBE functional, and their most stable configuration on the potential energy surface is presented in Fig. 1. The MEP map of chloramphenicol calculated at the B3LYP/6-31+G(d,p) level with electron density of 0.02 au and the region of -5.10^{-5} to +0.15 au is also illustrated in Fig. 1. The adsorption of chloramphenicol to the vermiculite surface was studied using the GPAW program and the results are shown in Fig. 2. Remarkably, the optimized structure of chloramphenicol in this work is in a good agreement with the experimental data in Refs. [4,5]. Thus, this chloramphenicol structure is a global minimum and the PBE functional seems suitable for investigation of this system.

Four stable configurations, denoted as **M1**, **M2**, **M3** and **M4**, arising from adsorption and interaction of chloramphenicol with the surface of vermiculite were found. In these configurations, the sites for the adsorption of chloramphenicol on vermiculite are located on either the Mg^{2+} ions external to the surface (without water molecules) or the O^{2-} ions on the surface. Conversely, the molecule attaches to these sites on the surface through its high charge density regions. The stabilizing interactions for this adsorption process are formed between the Mg^{2+} ion (surface) and O, Cl atoms at negatively charged regions (molecule); and between O atom (surface) and H atoms of positively charged regions (molecule).

As shown in Fig. 2, the distances of $\text{Mg} \cdots \text{O}$, $\text{Mg} \cdots \text{Cl}$, $\text{O} \cdots \text{H} \cdots \text{O}$ and $\text{C} \cdots \text{H} \cdots \text{O}$ intermolecular contacts are relatively short, in the range of 1.88–1.98 Å, $\sim 2.60 \text{ \AA}$, 1.60–2.05 Å and 2.52–2.58 Å, respectively. The energy of interaction in the obtained configurations decreases in going from **M1** to **M4** to **M3** and finally to **M2**. Accordingly, the stability of these configurations is in the decreasing ordering of **M1** > **M4** > **M3** > **M2**. Furthermore, these results are in agreement with previous studies on adsorption of organic compounds on clay mineral surfaces [6,9]. For adsorption of (4-chloro-2-methylphenoxy) acetic acid (MCPA) and 2-(4-chlorophenoxy)-2-methylpropionic acid (clofibrac acid, CA) on a mica surface, the complex formation is due to the contribution of $\text{O} \cdots \text{H} \cdots \text{O}$ and $\text{O} \cdots \text{K}$ intermolecular interactions. The corresponding intermolecular distances are in the range of 2.35–2.52 Å and 2.64–2.67 Å,

Download English Version:

<https://daneshyari.com/en/article/7837795>

Download Persian Version:

<https://daneshyari.com/article/7837795>

[Daneshyari.com](https://daneshyari.com)