



Adsorption of 2,4,6-trichlorophenol on montmorillonite surface: ONIOM study

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ABSTRACT

The wastewater contains several chemicals, organic and inorganic molecules, among themolecules, 2,4,6-trichlorophenol, which is a source of contamination. The main aim of this work is to distinguish the process of 2,4,6-trichlorophenol retention with montmorillonite using QM: MM-ONIOM approach and applying local and global reactivity parameters that are an excellent key for identifying adsorption sites. A weak hydrogen bond between the hydroxyl proton of 2,4,6-trichlorophenol molecule and oxygen atom on the montmorillonite surface, with a specific distance, $H_b = 2.66 \text{ \AA}$ using M06-2X functional) has proved the physical adsorption. Thermochemical analysis reveals the exothermic nature of adsorption process. Negative ΔH values signify heat release and negative ΔG values indicating spontaneity under standard conditions. The obtained results have proved an agreement with other experimental and theoretical data.

1. Introduction

The clay minerals are readily accessible due to their cost-effectiveness and possess essential physicochemical properties that make them valuable for deployment as adsorbents [1,2] in the purification of polluted water [3–5]. Notably, clay minerals like montmorillonite, classified as a 1:2 aluminosilicate, characterized by their high surface area and cation exchange capacity enable it to attract chemical pollutants [6]. Chlorophenols serve multiple roles, functioning as wood preservatives and finding utility in agriculture as herbicides, fungicides and insecticides. Their significance extends to diverse industries including chemicals, pharmaceuticals, paints and dyes [7]. Despite their widespread use, the chlorophenols present a significant risk to both human health and the environment. Extensive epidemiological research has consistently demonstrated the carcinogenic potential of chlorophenols [8–11].

Over the past decades, several experimental studies have demonstrated the potential for trichlorophenols to be adsorbed by clay minerals [12]. Daniset al. [13] have studied 2,4,6-trichlorophenol

adsorption on alumina-pillared montmorillonite and mesoporous alumina aluminum phosphates. While, Xu et al. [14] have used infrared spectroscopy (FTIR), X-ray diffraction (XRD) and thermogravimetric analysis (TGA) to research the adsorption of three chlorophenols to organo-montmorillonite [14]. Montmorillonite is not the only adsorbent available to evaluate its effectiveness compared to other materials with similar or different properties. Several comparative studies have been carried out to better understand the advantages and limitations of montmorillonite [15,16]. As a type of clay, montmorillonite can be compared to other types of clays such as kaolinite and illite. Among the three clay minerals, Montmorillonite has demonstrated the highest level of effectiveness taking into account several factors such as pH, concentration and temperature [17]. Each of these clays has specific characteristics that influence their adsorption capacity such as cation exchange capacity, specific surface area of clay and swelling [18]. Activated carbon and carbon nanotubes, are also widely used as adsorbents. They exhibit unique surface properties due to their porous structure, but it is expensive and difficult to recycle [19].

Theoretical study of this phenomenon can also offer an extra insights

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compared to experimental work. *Ab initio* calculations based on density-functional theory (DFT) is one of the favourable methods to attain this goal, where Fonseca et al. [20] have investigated the behavior of Na^+ during dehydration of smectites using DFT calculations. Roa et al. [21] have examined the adsorption processes of glycine on the surface of montmorillonite through computational modelling. Otherside, Wang et al. [22] have studied the interactions of interlayer guest and host of histidine-intercalated hydrotalcite-montmorillonite complex utilizing DFT. And, Yang et al. [23] have performed DFT calculations for the adsorption of 3-chloro-2-hydroxypropyl trimethylammonium chloride on montmorillonite. While, Ghezali et al. [24] have studied the adsorption of 2,4,6-trichlorophenol on kaolinite by DFT calculations. Additionally, quantum mechanics/molecular mechanics (QM/MM) method provides an essential approach to understand complex systems. The use of different levels of theory allows precision adjusted to the specific needs of the region of interest of molecular system, while maintaining overall computational efficiency such as ONIOM studies, which have been widely applied to understand the molecular mechanisms involved in adsorption processes [25] such as the adsorption process on the surfaces of clay minerals. The adsorption process on the surfaces of clay minerals is studied using ONIOM method [26] due to its low computational cost and capability to examine molecular systems of considerable size [27].

Global and local reactivity parameters provide important information about the electronic behavior of molecules and atoms, allowing the identification of preferred adsorption sites and thus the adsorption process can be understood more deeply [28,29].

The objective of this work is to elucidate the adsorption mechanism of 2,4,6-trichlorophenol (TCP) on montmorillonite (MMT) surfaces, thereby contributing to the development of effective methods for purifying polluted water. This study employs the ONIOM approach and integrating both local and global reactivity descriptors to provide a comprehensive analysis. Furthermore, it is aimed to minimize the computational expenses by utilizing a cost-effective methodology, ensuring the practicality and efficiency of the process. This work is divided as the following; sections two and three are devoted to theoretical, and materials and method, respectively. Followed by elaborated results and discussion in section four. The conclusions are outlined in section five.

2. Theoretical background

2.1. Global and local reactivity parameters

Density Functional Theory (DFT) and the ONIOM method, enable a thorough investigation of the electronic structure and properties of molecules. Concurrently, ONIOM method, a specialized technique in quantum chemistry, serves to refine and deepen our understanding of molecular reactivity.

ONIOM is often integrated with DFT for quantum mechanical calculations for attaining high precision at a minimal cost [30]. The combination of ONIOM and DFT extends the applicability of both methods, allowing for a more comprehensive understanding of electronic structures and optical properties.

Quantum chemical calculations based on E_{HOMO} and E_{LUMO} energies [31] are to analyze the reactivity and electronic properties of molecules. These energy values are used to derive critical reactivity parameters [32,33].

In this context, E_{LUMO} , E_{HOMO} and ΔE represent the energy of the highest occupied molecular orbital, the energy of the lowest unoccupied molecular orbital, and energy gap, in that order and symbols I, A, χ and S correspond to the following parameters; ionization potential, electron affinity, electronegativity and global softness, respectively.

$$\Delta E = E_{\text{HOMO}} - E_{\text{LUMO}} \quad (1)$$

Ionization potential (I) and electron affinity (A) have been proposed

by Koopmans' theorem [34] for using the energies of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), respectively. The theorem states that the negative of HOMO energy ($-E_{\text{HOMO}}$) approximates the ionization potential (I), and negative of LUMO energy ($-E_{\text{LUMO}}$) approximates the electron affinity (A). It can be expressed as:

$$I = -E_{\text{HOMO}} \quad (2)$$

$$A = -E_{\text{LUMO}} \quad (3)$$

Electronegativity is a fundamental concept in chemistry that quantifies the tendency of an atom to attract electrons in a chemical bond. There are different methods to define and calculate electronegativity, and two commonly used scales are those developed by Pauling [35,36] and Mulliken.

$$\chi = -\left(\frac{\partial E}{\partial N}\right)_{v(r)} = -\frac{E_{\text{HOMO}} + E_{\text{LUMO}}}{2} = \frac{I + A}{2} \quad (4)$$

Chemical potential is defined as negative electronegativity [37]:

$$\mu = -\chi = \left(\frac{\partial E}{\partial N}\right)_{v(r)} = -\left(\frac{I + A}{2}\right) \quad (5)$$

Global hardness (η) [38] is a concept in theoretical chemistry that measures the resistance of a molecule to changes in electron density. The global hardness is defined as half of energy difference between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO):

$$\eta = \left(\frac{\partial^2 E}{\partial N^2}\right)_{v(r)} = \left(\frac{\partial \mu}{\partial N}\right)_{v(r)} = \left(\frac{I - A}{2}\right) \quad (6)$$

The global softness (S) is also a relevant parameter. It is defined as the inverse of global hardness (η) [39]:

$$s = \left(\frac{\partial^2 N}{\partial \mu}\right)_v = \frac{1}{2\eta} \quad (7)$$

The global electrophilicity (ω) is the measure of electrophilic reactivity of a molecule. The expression for global electrophilicity is given by [40]:

$$\omega = \frac{\mu^2}{2\eta} \quad (8)$$

In another hand, the local reactivity concentrates on specific atomic sites within a molecule or a surface. It seeks to identify regions that are particularly susceptible to nucleophilic (electron-donating) or electrophilic (electron-accepting) interactions. The local reactivity is often assessed through the Fukui function analysis [41–43], which quantifies the changes in electron density at individual atomic sites upon the addition or removal of electrons. By pinpointing nucleophilic and electrophilic sites, the Fukui function is characterized by the change in electron density in terms of the change in the number of electrons:

$$(r) = (r)/(\partial N)(r) \quad (9)$$

For nucleophilic attack:

$$f^+(r) = \rho(N+1)(r) - \rho(N)(r) = q(N+1) - q(N) \quad (10)$$

For electrophilic attack:

$$f^-(r) = \rho(N)(r) - \rho(N-1)(r) = q(N) - q(N-1) \quad (11)$$

For radical attack:

$$f^0(r) = \hat{A}^{1/2}(\rho(N)(r) - \rho(N-1)(r)) = \hat{A}^{1/2}(q(N+1) - q(N-1)) \quad (12)$$

where ρ , $q(N+1)$, $q(N)$ and $q(N-1)$ are the electronic density and atom charges for systems containing $N+1$, N , and $N-1$ electrons, respectively.

In addition to Fukui functions and global softness, the reaction sites can also be predicted by local softness that is defined as follows [44]:

$$S^+ = S.f^+ \quad (13)$$

$$S^- = S.f^- \quad (14)$$

$$S^0 = S.f^0 \quad (15)$$

The dual descriptor $\Delta f(r)$ is calculated as [44]:

$$\Delta f(r) = f^+(r) - f^-(r) \quad (16)$$

And so,

$$\Delta S^x = S.\Delta f(r) \quad (17)$$

where $x = 1$ or -1 . If $\Delta f(r) > 0$, indicates a nucleophilic character and $\Delta f(r) < 0$ indicates an electrophilic character of atom in a molecule, S^+/S^- and S^+/S^+ are relative electrophilicity and relative nucleophilicity, respectively.

2.2. Hard-Soft acid-base (HSAB) principle

The hard-soft acid-base approach, suggested by Pearson [45–47] is a fundamental concept in chemistry utilised to categorize chemical species into “hard” or “soft” acids and bases according to the absolute hardness:

Hard Acids: These species consist of acceptor atoms with a high positive charge and small size that are not polarisable.

Hard Bases: Characterized by donor atoms with low polarizability.

Soft Acids: Species with a low positive charge and a larger size.

Soft Bases: Consists of donor atoms with high polarizability and low electronegativity.

As a results, the hard acids tend to form complexes with hard bases, while soft acids have an affinity for soft bases.

3. Materials and method

3.1. Model

Montmorillonite consists of two layers of tetrahedral silicon and a central aluminum octahedron. They have been arranged in such a way that the oxygen atom vertices of each silicon tetrahedron and one of hydroxyl planes of octahedral layer are in the same plane. The vertices of tetrahedra are formed by four oxygen atoms connected to central silicon atom. The octahedra, on another hand, have their vertices occupied by four oxygen atoms and two hydroxyls of octahedral layer [48]. A $4 \times 3 \times 1$ supercell composed of 390 atoms (Fig. 1) is used to perform calculations. We chose two unit cells in the middle of cluster with a depth of four atomic mono-layer, and a total of 58 atoms in the higher level to calculate it by DFT method, since the rest of the system is calculated with the Universal Forcefield (UFF) method.

3.2. Computational details

The studied geometries are optimized by the two-layer ONIOM hybrid method [49], and both local and global reactivity descriptors are computed to pinpoint the interaction position corresponding to the lowest energy level. With two DFT functionals B3LYP [50], M06-2X [51], applying the 6-31G (d) basis set in the high layer and UFF method in the low layer, all calculations are performed using the Gaussian 09 software [52]. Adsorption energies are calculated by the following equation:

$$E_{ads} = E_{Tot}(TCP + MMT) - E_{Tot}(TCP) + E_{Tot}(MMT) \quad (18)$$

where E_{ads} , $E_{Tot}(TCP+MMT)$, $E_{Tot}(TCP)$ and $E_{Tot}(MMT)$ are the adsorption energy, total energies of complex (2,4,6-trichlorophenol and

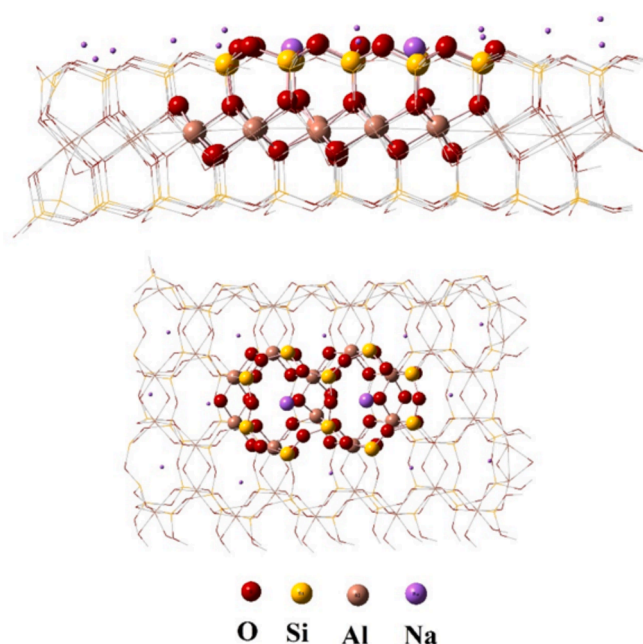


Fig. 1. Schematic representation of a montmorillonite model.

montmorillonite) adsorbate (2,4,6-trichlorophenol) and adsorbent (montmorillonite), respectively.

Frequency calculations are performed for the most stable models according to the values of adsorption energies to extract the thermodynamic parameters, specifically the Gibbs free energy change (ΔG) and the enthalpy change (ΔH). Following this, we have embarked on the computation of entropy changes (ΔS) and adsorption constants. These calculations are conducted by the following fundamental equations;

$$\Delta G = \Delta H - T\Delta S \quad (19)$$

$$\ln K = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (20)$$

where $T=298.15$ K and $R=1:987$ kcal/mol.K (the gas is constant).

4. Results and discussion

The local reactivity parameter Table 1 are computed for Na-montmorillonite and 2,4,6-trichlorophenol separately to identify the chemical behavior of each atom within the molecules. First five atoms of Na-montmorillonite in addition to the 2,4,6-trichlorophenol hydroxyl group ($-OH$) are selected and listed in descending order, while the local reactivity parameters allow the identification of sites that have nucleophilic or electrophilic tendencies, as an important key to determine potential adsorption sites. In addition to a sixth atom that has the lowest Fukui and Local Softness values. Global reactivity parameters Table 2 provides an overview of adsorption process, including the stability and reactivity of molecules. The structural parameters in Table 3 display the different bond lengths and angles formed between the atoms in a single molecule, well as distances (Fig. 2) between the sodium ion, montmorillonite and 2,4,6-trichlorophenol atoms helping in understanding how the geometry of molecules changes during the adsorption process. The structural changes occur before and after adsorption that can be observed. Energies and thermodynamic parameters are presented in Table 4. These values provide an important information about the adsorption process and possibility of knowing whether the adsorption is exothermic or endothermic.

Table 1

Local reactivity properties using B3LYP:UFF and M06-2X:UFF.

Molecule/method	Atom	F ⁺	F [−]	Δ f	S ⁺	S [−]	ΔS	S ⁺ /S [−]	S ^{−8} /S ⁺
<i>B3LYP:UFF</i>									
Na-MMt	Na 22	0.0795	0.0258	0.0537	9.0138	2.9271	6.0866	3.0793	0.3247
	Na 23	0.0730	0.0362	0.0368	8.2769	4.1069	4.1699	2.0153	0.4961
	O 17	0.0177	0.0074	0.0103	2.0098	0.8406	1.1691	2.3907	0.4182
	O 9	0.0161	0.0065	0.0095	1.8319	0.7454	1.0864	2.4573	0.4069
	O 21	0.0162	0.0066	0.0095	1.8427	0.7589	1.0837	2.4278	0.4118
	O18	0.0004	0.0021	−0.0017	0.0522	0.2487	−0.1964	0.2100	4.7613
2.4.6-TCP	O	0.1082	0.0380	0.0702	1.0682	0.3748	0.6933	2.8493	0.3509
	H	0.0423	0.0303	0.0120	0.4177	0.2989	0.1187	1.3971	0.7157
<i>M06-2X:UFF</i>									
Na-MMt	Na 22	0.0423	0.0159	0.0263	1.8159	0.6858	1.1301	2.6479	0.3776
	Na 23	0.0391	0.0240	0.0151	1.6824	1.0342	0.6482	1.6267	0.6147
	O 16	0.0122	0.0022	0.0099	0.5260	0.0981	0.4278	5.3581	0.1866
	O 20	0.0118	0.0059	0.0059	0.5086	0.2543	0.2543	1.9998	0.5000
	O 18	0.0066	0.0014	0.0052	0.2858	0.0625	0.2232	4.5665	0.2189
	O 15	0.0044	0.0054	−0.001	0.1896	0.2359	−0.0463	0.8035	1.2445
2.4.6-TCP	O	0.1148	0.0371	0.0777	0.7984	0.2578	0.5405	3.0958	0.3230
	H	0.0433	0.0291	0.0141	0.3009	0.2023	0.0985	1.4868	0.6725

Table 2

Global reactivity parameters of Na-Montmorillonite, 2.4.6-TrichloroPhenol calculated by and Na-Montmorillonite/2.4.6-TrichloroPhenol complex (M1 and M2) calculated by B3LYP:UFF and M06-2X:UFF.

Method	E _{LUMO}	E _{HOMO}	ΔE	I	A	χ	μ	η	S	ω
<i>B3LYP:UFF</i>										
Na-MMt	−0.20238	−0.22003	0.01765	0.22003	0.20238	0.21	−0.21	0.00883	113.31	1.96 × 10 ⁴
2.4.6-TCP	−0.03863	−0.24124	0.20261	0.24124	0.03863	0.13	−0.13	0.10131	9.87	9.18 × 10 ⁴
M1	−0.20214	−0.21975	0.01761	0.21975	0.20214	0.21	−0.21	0.00881	113.57	1.95 × 10 ⁴
<i>M06-2X:UFF</i>										
Na-MMt	−0.19905	−0.24564	0.04659	0.24564	0.19905	0.22	−0.22	0.0233	42.92	5.75 × 10 ⁴
2.4.6-TCP	−0.0039	−0.29148	0.28758	0.29148	0.0039	0.14	−0.14	0.14379	6.95	1.56 × 10 ⁴
M3	−0.19319	−0.23966	0.04647	0.23966	0.19319	0.21	−0.21	0.02324	43.03	5.44 × 10 ⁴

Table 3

Bonds length and angles of adsorption of 2.4.6-TrichloroPhenol by Na-Montmorillonite.

Bond	This work				Theoretical	Experimental
	Before adsorption		After adsorption			
	B3LYP: UFF	M06-2X: UFF	B3LYP: UFF	M06-2X: UFF		
<u>Na-Montmorillonite</u>						
Si-O	1.65	1.64	1.66	1.65	1.63 ⁴¹ --1.64 ^{40 - 41}	1.63 ³³
Si-O	1.67	1.66	1.67	1.66		
Al-O	1.88	1.88	1.88	1.88	1.93 ⁴¹ --1.96 ^{40 - 41}	1.96 ³³
Al-O	1.83	1.83	1.83	1.83		
<u>2.4.6-TrichloroPhenol</u>						
O—H	0.97	0.97	0.97	0.97	0.96 ³⁹	0.82 ³⁹
C—O	1.35	1.34	1.37	1.36	1.34 ³⁹	1.34 ³⁹
C—C	1.40	1.40	1.40	1.39	1.39 ³⁹	1.37 ³⁹
C-Cl	1.75	1.74	1.75	1.73	1.74 ³⁹	1.72 ³⁹
C—H	1.08	1.08	1.08	1.08	1.08 ³⁹	0.93 ³⁹
Angle						
<u>Na-Montmorillonite</u>						
Si-O-Si	121.96	122.78	120.70	121.67	133.3 ⁴¹	130.51–140.71 ³³
O-Si-O	107.61	107.80	107.56	107.34		
<u>2.4.6-TrichloroPhenol</u>						
H—O—C	108.84	109.35	107.86	108.77	—	119.6 ³⁹
O—C—C	123.75	123.83	122.92	122.93	—	123.5 ³⁹

4.1. Local reactivity analysis

We have observed that the sodium ions found on the surface of

montmorillonite rank highest as potential adsorption sites due to having the most substantial positive values Δf and ΔS values, in addition to considering the relative electrophilicity (S⁺/S[−]) and relative

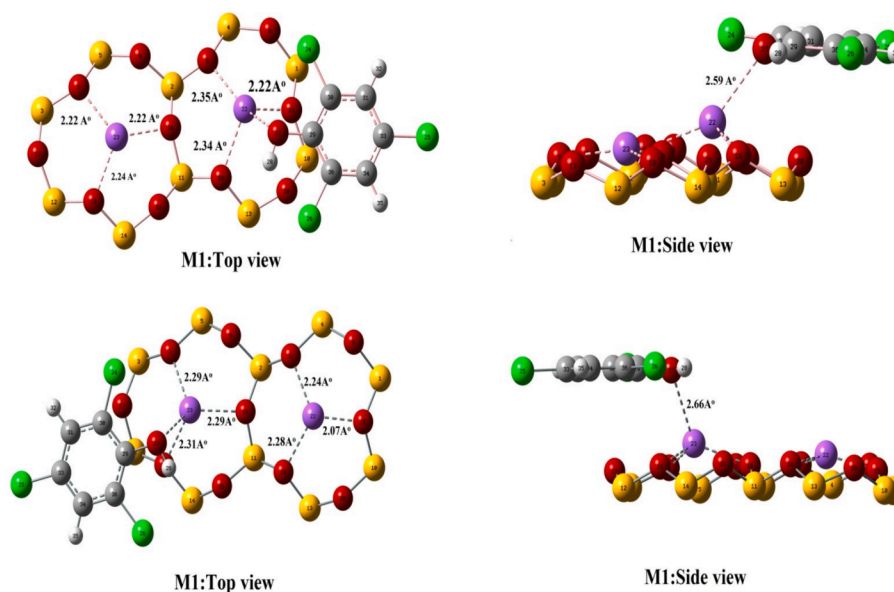


Fig. 2. Visualization of 2,4,6-TCP in Montmorillonite using B3LYP/6-31G(d):UFF.

Table 4

Adsorption energies, Thermodynamics properties and adsorption constants obtained by: B3LYP/6-31G (d): UFF and M06-2X/6-31G (d).

	Eads	ΔH°_{298} (kcal/mol)	ΔG°_{298} (k cal/mol)	ΔS°_{298} (kcal/ mol.K)	K_{298}
B3LYP: UFF	-77.93	-77.770	-256.70	346.9395	4.2918
M06-2X: UFF	-120.89	-105.520	-502.60	522.4887	4.6578

nucleophilicity (S^-/S^+) indicating the potential for sodium ions to engage in a nucleophilic attack [53]. Despite being positively charged ions, the sodium ions acquire a negative charge due to their electrostatic interaction with the oxygen atoms comprising the montmorillonite surface, effectively forming a complex with it. This is supported by the short distances observed between the sodium ions and surface oxygen atoms as illustrated in Fig. 2.

Apart from sodium ions, there is a discrepancy regarding the ranking of other adsorption sites when employing both the B3LYP:UFF and M062X:UFF methods. For instance, when using M062X:UFF, oxygen site 293 is ranked fourth, with positive values of $\Delta f = 0.0052$ and $\Delta S = 0.2232$ and an S^+/S^- ratio of 4.5665, which indicates its nucleophilic tendencies. Conversely, utilizing the B3LYP:UFF approach resulting in negative Fukui values, $\Delta f = -0.0017$ and $\Delta S = -0.1964$, along with S^-/S^+ ratio of 4.7613, indicating the atom's electrophilic tendencies due to ion-dipole interaction between the sodium ion and oxygen no18, which are approximately 2.22 Å. As for oxygen no 15, it is considered a nonnucleophilic site using M062X:UFF, with negative values for both $\Delta f = -0.001$ and $\Delta S = -0.0436$ and S^-/S^+ ratio; 1.2445, primarily due to its proximity to the sodium ion at a distance estimated to be 2.14 Å.

Regarding the trichlorophenol molecule, it is noteworthy that the hydroxyl group plays a significant role in adsorption. It exhibits favorable Fukui and local Softens values. $\Delta f = 0.0702$ and $\Delta S = 0.6933$ for B3LYP:UFF, and $\Delta f = 0.0777$ and $\Delta S = 3.0958$ for M062X:UFF. The S^+/S^- ratios are 1.3971 and 3.0958, respectively. These values suggest a propensity for adsorption at the hydroxyl function of the 2,4,6-trichlorophenol.

4.2. Structural study

A detailed analysis of bond lengths and angles Table 1 is conducted before and after the adsorption process. Notably, we have observed several significant changes. The hydroxyl bond (O—H) within the 2,4,6-trichlorophenol molecule is increased in length by approximately 0.15 Å..., while the angle containing this function is decreased by 12 degrees compared to experimental values. These alterations can be attributed to the involvement of this molecule in the adsorption process, indicating its pivotal role in the interaction.

Furthermore, we have noticed an increasing of 0.05 Å in the silicon-oxygen (Si—O) bond and 0.11 Å in the aluminum-oxygen (Al—O) bond of montmorillonite surface. Additionally, there is a contraction of approximately 12° in Si—O—Si angle due to interaction of surface oxygen Fig. 2, which forms this angle, with both the sodium ion and hydroxyl proton of 2,4,6-trichlorophenol molecule. These changes confirm that the adsorption process has occurred.

Also, Fig. 3 has illustrated an attractive interaction between 2,4,6-trichlorophenol hydroxyl oxygen atom and sodium ion located on the montmorillonite surface. This interaction occurred at a distance of 2.47 Å when employing the M062X method and 2.59 Å... with the b3LYP method.

Furthermore, the distances between the adsorbed atoms are considerably shorter by approximately 0.1 Å, when using the M06-2X function as compared to B3LYP method. This observation strongly suggests that the 2,4,6-trichlorophenol molecule forms a strong attraction with a clay surface. Additionally, our analysis indicates the formation of a weak hydrogen bond between the hydroxyl proton of 2,4,6-trichlorophenol molecule and oxygen atom presented on the montmorillonite surface and a moderate hydrogen bond $Hb = 2.66$ Å using M06-2X functional. These findings have shed a light on the molecular interactions playing a fundamental role in the adsorption process and indicate physical adsorption. The results obtained are largely consistent with previous experimental and theoretical data [48,54–56].

The presence of the sodium ion on the surface of montmorillonite is important to neutralize the negative charge on clay surface and thus achieve its stability. We can observe the attraction of sodium ions to oxygen atoms could be present on the surface Fig. 3, this makes sodium ions a competitive with trichlorophenol molecules in the adsorption process that is an important factor in the adsorption of any chemical compound in the future. Other side, we have noticed that the sodium ion

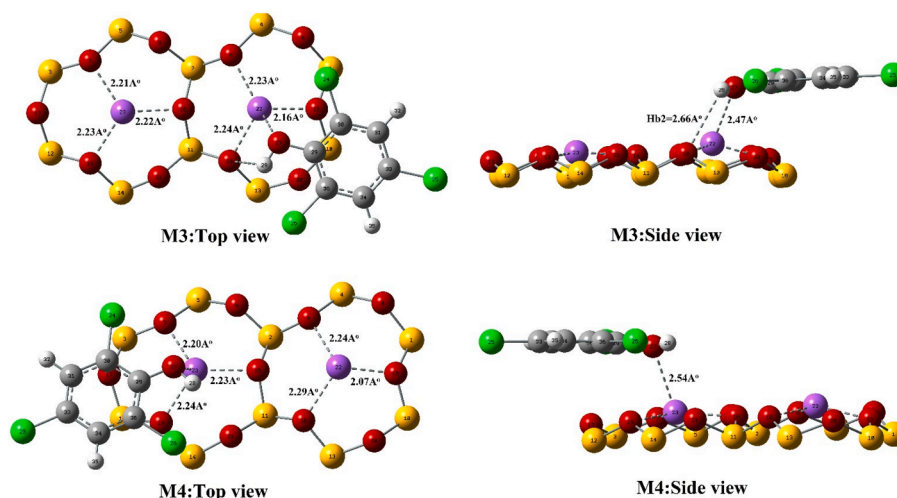


Fig. 3. Visualization of 2,4,6-TCP in Montmorillonite using M06-2X/6-31G(d):UFF.

produces both the hydroxyl oxygen of trichlorophenol and oxygen on clay surface, which leads to the formation of a complex between them.

4.3. Global reactivity descriptors and hard-soft acid-base (HSAB) principle

Global reactivity descriptors as presented in Table 2 based on HOMO and LUMO energies are a powerful key in understanding chemical reactivity and behavior of molecules in various chemical processes; hardness (η), softness (S) and nucleophilicity (ω). These descriptors help us to understand whether the molecule is more inclined to donate or accept electrons, its reactivity in nucleophilic or electrophilic processes, and its overall chemical stability.

Highest Occupied Molecular Orbital (HOMO) is the highest energy molecular orbital that contains electrons. It is often associated with electron-donating or nucleophilic properties. Molecules with lower energy HOMOs are more likely to donate electrons and participate in nucleophilic reactions. While, Lowest Unoccupied Molecular Orbital (LUMO) is the lowest energy unoccupied molecular orbital. It is related to electron-accepting or electrophilic properties. Molecules with lower energy LUMOs are more likely to accept electrons and act as electrophiles in reactions. The small gap, ΔE ; 0.01765 eV and 0.04659 eV using B3LYP:UFF and M06-2X:UFF, respectively indicates that Na-montmorillonite has a low-energy gap between the HOMO and LUMO. This suggests high reactivity, particularly in nucleophilic reactions, as it is more likely to donate electrons (due to lower EHOMO). While 2,4,6-Trichlorophenol has a larger gap, ΔE ; 0.20261 eV using B3LYP:UFF method and 0.28758 eV, employing M06-2X:UFF method indicating lower reactivity, particularly in electrophilic reactions, as it is more likely to accept electrons (due to the lower ELUMO).

In the context of Hard Acid Soft Base Theory (HSAB) principle, Na-montmorillonite is considered relatively "soft" due to its lower hardness (η) and higher softness (S). The low nucleophilicity (ω) suggests that it might preferentially react with 2,4,6-Trichlorophenol that is considered relatively "hard" due to its higher hardness (η) and lower softness (S) compared to clay softness. The nucleophilicity (ω) suggests that it might preferentially react with "soft" nucleophiles (Table 2).

The formation of hydrogen bond between TCP and MMT, the reactivity of these compounds is influenced by their electronic properties. Na-montmorillonite is more likely to act as a nucleophile, while 2,4,6-trichlorophenol is more likely to act as an electrophile, which aligns with HSAB principle. The interactions can be explained by the electron density and electrostatic potential differences between these compounds.

Another type of attraction as shown in Fig. 3 can be explained in terms of HSAB approach, which is a sodium ion, a hard acid reacts with

the montmorillonite oxygen atoms and 2,4,6-TCP hydroxyl oxygen, forming a coordination complex in which the oxygen atom donates its electron pairs to the vacant orbital of sodium cation.

4.4. Adsorption energy

The results are summarized in Table 4 of negative adsorption energy values to prove the possibility of forming a stable complex between 2,4,6-TCP and MMT. All adsorption energy values are negative, indicating an exothermic process. The adsorption energy values for geometry calculated by B3LYP(M1 model) method indicate a more favorable adsorption interaction (more negative energy) compared to M062X (M3 model) method. This suggests that M1 is more stable geometry, indicating a stronger binding interaction and noting hydrogen bonds, for B3LYP and HB for M062X. We also have noticed that the best adsorption energy values are obtained in the areas containing nucleophilic adsorption sites. These results are supported by the previous mentioned in local reactivity section.

4.5. Thermochemistry

In the case of B3LYP, the negative value of ΔH (−0.77770 kJ/mol) signs an exothermic nature of reaction, where heat is released. Furthermore, the negative ΔG value (−0.25670 kJ/mol) implies that, under standard conditions at 298.15 K and 1 bar, the reaction proceeds spontaneously, without requiring an external energy input. The positive ΔS value (346.93946 J/K) associated with B3LYP reflects an increasing in disorder within the system during the reaction, thus reinforcing the spontaneity of the process.

Regarding M062X, a negative ΔH (−0.105520 kJ/mol) indicates that the reaction is exothermic, involving the release of heat. Similarly, the negative ΔG value (−0.50260 kJ/mol) for M062X confirms the spontaneous character of reaction under standard conditions. Notably, the positive ΔS value, 522.4886802 J/K is linked to M062X that reveals a more substantial increasing in entropy compared to B3LYP. This heightened positive entropy change further bolsters the spontaneity of the reaction in this method.

The negative ΔG values signify that both reactions occur spontaneously under standard conditions. The variations in ΔH and ΔS values provide insights into the enthalpy and entropy alterations during these reactions. Specifically, the B3LYP method demonstrates a more exothermic reaction accompanied by a smaller increase in entropy, while the M062X method shows a slightly less exothermic reaction but with a notably higher positive change in entropy.

5. Conclusions

In this work, we have investigated the adsorption process of 2,4,6-trichlorophenol (TCP) on montmorillonite (MMT) using QM: MM-ONIOM approach and DFT method, and Hard and Soft Acids and Bases (HSAB) principle using both local and global reactivity parameters. The structural changes, as revealed by bond lengths and angles, have provided specific details about molecular interactions. Notably, the hydroxyl group of 2,4,6-trichlorophenol played a pivotal role in adsorption, with a considerable increasing in bond length and changes in associated angles. The attractive interaction between the hydroxyl oxygen atom of 2,4,6-trichlorophenol and sodium ion on montmorillonite surface is characterized by distances, 2.47 Å (M062X method) and 2.59 Å (B3LYP method). The low-energy gap between HOMO and LUMO indicates reactivity, particularly in nucleophilic reactions, for Na-montmorillonite with values, 0.01765 eV (B3LYP: Uff) and 0.04659 eV (M06-2X: Uff). Additionally, local softness values are determined to be 0.6933 (B3LYP: Uff) and 3.0958 (M062X: Uff) for further demonstrating the material's reactivity and potential for electron donation. The ONIOM approach is proposed as a cost-effective and efficient solution for studying adsorption on clay surfaces and opening avenues for future investigations into the effects of acidity and temperature.

CRedit authorship contribution statement

Badji Taqiyeddine: Conceptualization. **M. Ameri:** Investigation. **N. Bouzouira:** Formal analysis. **I. Ameri:** Investigation. **L.F. Blaha:** Software. **Y. Al-Douri:** Writing – review & editing, Supervision. **A. Bouhemadou:** Validation. **Riyadh A. Al-Samarai:** Validation. **Mayson F.A. Alias:** Visualization.

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

No data was used for the research described in the article.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.comptc.2024.114770>.

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