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Theoretical Study Of Triazine Structures And Their Adsorption On Montmorillonite

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Abstract. Technological development has led to a multitude of chemicals such as pesticides used in agriculture. However, pesticides can have great toxicity and present danger for humanity. Triazine is a group of six molecules considered as persistent pollutants. They are not biodegradable and can be found in surface water, groundwater and water reserves for consumption. In this paper, we are interested in studying the structure of atrazine ($C_8H_{14}ClN_5$), simazine ($C_7H_{12}ClN_5$), propazine ($C_9H_{16}ClN_5$), Desethyl-s-Atrazine ($C_6H_9ClN_5$);(DEA), Desisopropyl-s- Atrazine ($C_5H_8ClN_5$); (DIA) and Diaminochlorotriazine ($C_3H_4ClN_5$); (DACT) constituents of the triazine group. We used molecular mechanics calculations (MM) to optimize the geometry and minimize the energy of these compounds, to determine their most stable geometries. The results show that the six molecules have very stable geometries. We calculated their dimensions using molecular dynamics calculations (MD) to study the possibilities of their adsorption on montmorillonite's interlayer. Five types of montmorillonite were used; Mt (natural), Mt (Na), Mt (Ca), Mt (K) and Mt (Mg). The calculated size of the molecules revealed that the six pollutants can be adsorbed on Mt (natural), Mt (Ca) and Mt (Mg), while their adsorption on Mt (Na) and Mt(K) is not possible.

Keywords. Adsorption, Montmorillonite, Molecular Mechanics (MM), Molecular Dynamics (MD), Pesticide, Triazine.

INTRODUCTION

Pesticides have generally a low biodegradability; therefore, they are persistent, causing serious environmental risks. They are considered as pollutants even when they are used in small amounts. Their elimination is often achieved by conventional chemical treatments leading to unsatisfactory results. However, adsorption process has been crowded with success in pollutants elimination. Activated carbon has a high adsorption capacity mainly due to its large surface area, but this process is very expensive. Thereby, attention has been directed to the use

of new adsorbents based on natural materials such as clays. Indeed, clays have a high adsorption capacity, high surface area, swelling, the ability to insert and exchange of ions and molecules and can adsorb organic molecules on its surface and interlayer space (Yuan et al., 2013). Montmorillonite (Mt) is a clay, which is used as an adsorbent of several contaminants (Ma et al., 2016, Sparks, 2005). Montmorillonite is a hydrous aluminosilicate formed by octahedral alumina layer sandwiched between two tetrahedral silica layers (Mouzon et al.,2016; Dening et al., 2016) .

In this paper, we are interested in triazine which is a group of compounds classified as persistent organic pollutants (Klementova, 2015). We studied the possibility of adsorption of atrazine, simazine, propazine, Desethyl-s-Atrazine (DEA), Desisopropyl-s- Atrazine ($C_5H_8ClN_5$); (DIA) and Diaminochlorotriazine (DACT) on montmorillonite using molecular modeling calculations. At first, we performed molecular mechanics calculations to optimize the geometry and to minimize the energy of these pollutants. Then we determined the dimensions of the optimized structures by molecular dynamics calculations to study the possibility to insert these molecules in the interlayer space of the montmorillonite. we used five kinds of montmorillonite; Natural montmorillonite (Mt(Natural), modified montmorillonite with sodium Mt (Na), calcium Mt (Ca), potassium Mt (K) and magnesium Mt (Mg).

METHODS AND DISCUSSION:

Molecular Mechanics Calculations

We performed molecular mechanics calculations, using Hyperchem (Hypercube Inc. Canada), to optimize the geometry and minimize the energy of six pollutants. Calculations performed using the Steepest Descent algorithm (Henderson et al., 2000) and the MM^+ force field, converged to a finite limit with a residual gradient of energy not exceeding 0.01 $Kcal.mol^{-1}.Å^{-1}$. The low values of the steric energies obtained for all the studied molecules (Table 1) show high stability for different pollutants geometries (Fig.1-6).

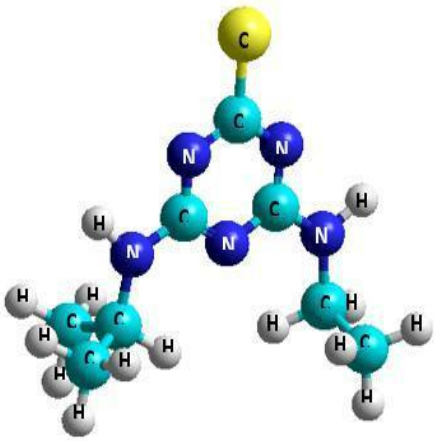

Fig.1. Optimized structure of Atrazine.

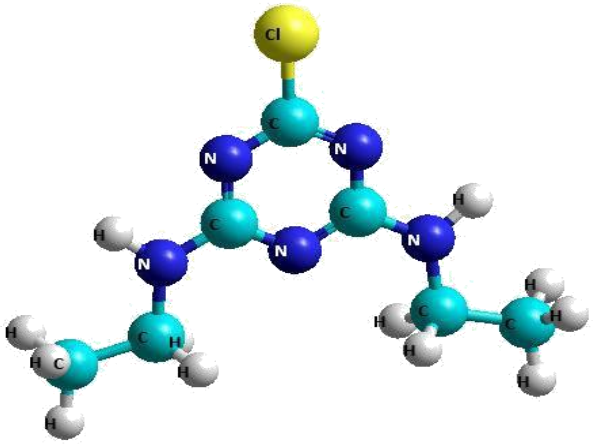

Fig.2. Optimized Structure of Simazine.

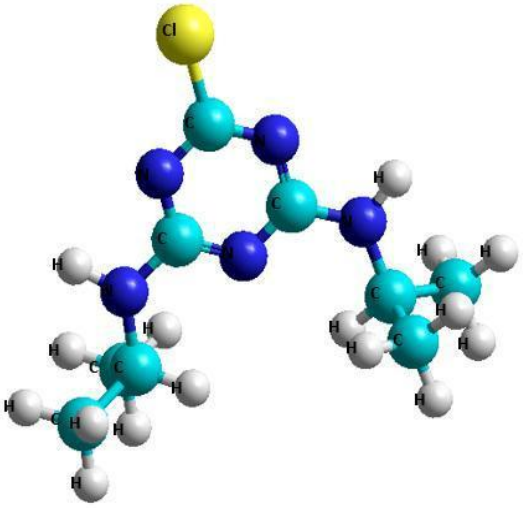

Fig.3. Optimized structure of Propazine.

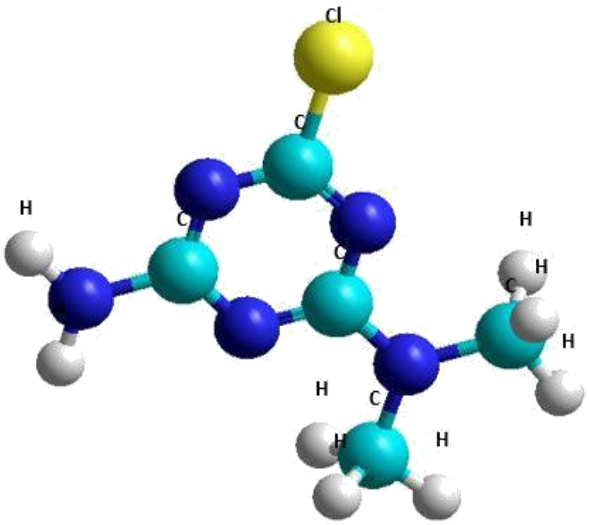

Fig.4. Optimized structure of Desethyl-s-Atrazine (DEA).

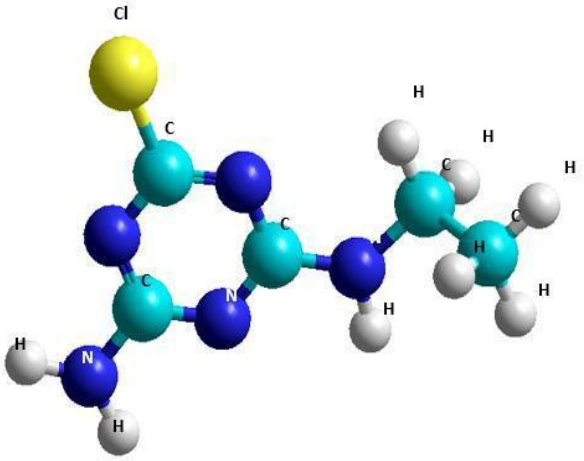

Fig.5. Optimized structure of Desisopropyl-s- Atrazine (DIA).

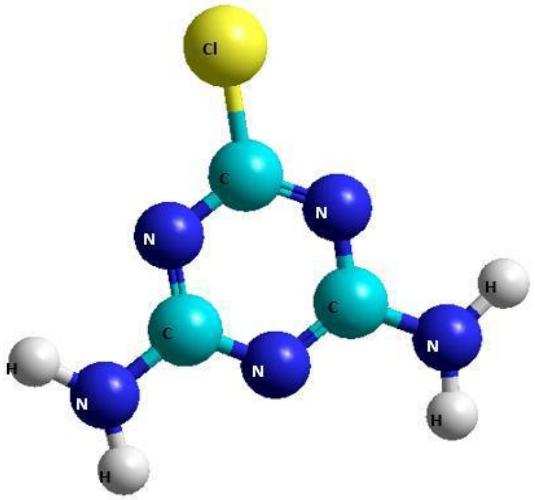

Fig.6. Optimized structure of Diaminochlorotriazine (DACT).

Table 1. Steric energies of the pollutants, calculated by molecular mechanics.

Polluant	Steric Energy (Kcal/mol)
Atrazine	**-2.683835**
Simazine	**-1.628198**
Propazine	**-0.450964**
DEA	**-3.761551**
DACT	**-5.816523**
DIA	**-3.633638**

Molecular dynamics calculations

Molecular dynamics calculations were performed to determine the pollutants size (Table 2).

Table 2.Pollutants size determined by molecular dynamics.

Proprieties / Structures	Molecular Area ($Å^2$)	Critical Volume ($Å^3$)	Dimension (Å)
Atrazine	186.116	635.5	3.41
Simazine	172.615	585.5	3.39
Propazine	198.802	685.5	3.45
DEA	155.5	517.5	3.33
DACT	111.6	349.5	3.13
DIA	141.921	467.5	3.29

Montmorillonite is a clay with an octahedral layer sandwiched between two tetrahedral layers (Fig.4). The thickness of these layers is 9.6 Å (Yang et al.,2007). The d_{001} distance is the sum of the thickness and the distance of the interlayer space in which the organic pollutants will be trapped.

Table 3 shows the values of d_{001}(Assaad,2006) of five types of montmorillonite used in our work, natural Mt, Mt (Na), Mt (K), Mt (Mg) and Mt (Ca). These values allowed us to calculate the distances of the interlayer space (Table 3).

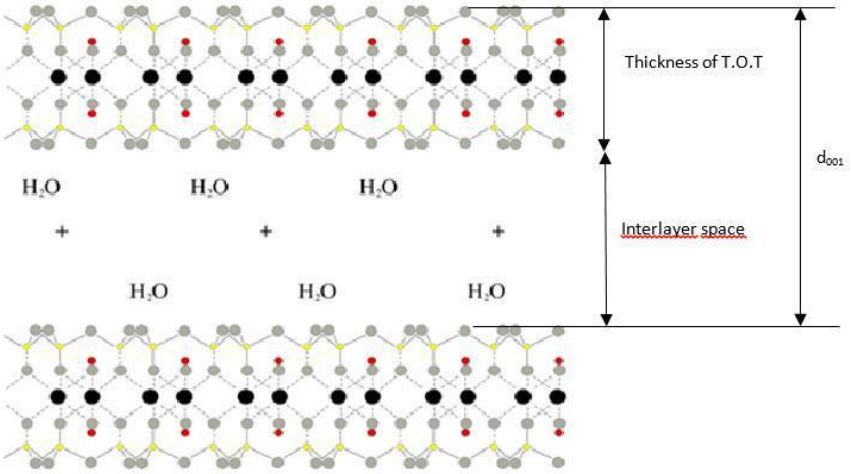

Fig.4. Montmorillonite Structure.

Table 3. Characteristics Of Natural Montmorillonite, Mt (Na), Mt (K), Mt (Mg) and Mt (Ca).

	<	Mt(Na)	Mt(K)	Mt(Ca)	Mt(Mg)
d_{001} (**Å**)	14.26	10.06	10.47	15.08	13.68
Interlayer space (**Å**)	4.66	0.46	0.87	5.48	4.08

The comparison of the different pollutants' sizes (Table 2) with the interlayer spaces of Mt (natural), Mt (Ca) and Mt (Mg) (Table 3) shows that the six pollutants could be adsorbed. Indeed, the sizes of the molecules studied are less than the interlayer space. We can then classify these pollutants according to their adsorption on montmorillonite as follows: DACT> DIA> DEA> Atrazine> Simazine> Propazine

In the case of Mt (Na) and Mt (K), the interlayer space is smaller than the sizes of the six pollutants. This leads us to assert that in both cases the adsorption could not occur.

CONCLUSION

In this study, we applied MM calculations to study the atrazine, simazine, propazine, Desethyl-s-Atrazine (DEA), Desisopropyl-s- Atrazine ($C_5H_8ClN_5$); (DIA) and Diaminochlorotriazine (DACT) structures. We optimized the geometry and determined the molecules size, and then we studied their adsorption on natural Mt, Mt (Na), Mt (K), Mt (Mg) and Mt (Ca). The energies obtained are very low, revealing stable geometries for these pollutants.

The molecular dynamics calculations showed that possibilities of pollutants' adsorption on clays vary in opposite direction with the variation of their dimensions. Pollutants' insertion into interlayer space is easier for small molecules.

Triazine group cannot be adsorbed on Mt (Na) and Mt (K), since the interlayer space is smaller than the sizes of the six pollutants. While Mt (natural), Mt (Ca) and Mt (Mg) can adsorb the six pollutants. Indeed, the sizes of the molecules are all less than the distance of the interlayer space in this kind of clays.

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