Removal of pyraclostrobin, pinoxaden, gammacyhalothrin pesticides from groundwater by DFT method

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Today, there is a shortage of food due to the increase in the world population. For this reason, pesticides are used to remove plant pests in order not to cause product loss in agriculture. Especially in agriculture, synthetic pesticides created to achieve high efficiency are increasing day by day. The pesticides used get into the soil and then into the groundwater. In this study, ways of decomposition of the pesticides pyraclostrobin from the fungicide variety, pinoxaden from the herbicide variety, and gammacyhalothrin from the insecticide variety in groundwater were theoretically investigated. Optimized geometries were drawn with Gauss View 5.0, and then geometric optimization was carried out by the Gaussian 09W program using functional density theory (DFT) and Hartree-Fock methods. The geometrical structure (bond angles and bond lengths) of all three molecules and their possible degradation products were calculated at the level of B3LYP theory within the Hartre-Fock (HF) method and DFT in the basic set of 6-31G(d). Thus, the possible degradation mechanisms of these three pesticide molecules in water were determined. These results will guide experimental studies.

Keywords: Gaussian09, DFT, Pesticides, Pinoxaden

INTRODUCTION

Environmental pollution is increasing with industrialization and future developments. Pesticides, which are indispensable for modern agriculture, are used in many areas. Pesticides are substances used for the purpose of destroying, removing and reducing the damage of the pests that cause product deterioration during the production, orientation and maintenance of various agricultural products [1].

The usage areas of pesticides are quite wide. They are used in agricultural production, fish breeding, places where decorations such as parks and gardens are made, industry, storage, animal food, insect control and many other areas [2]. The concentration of synthetic pesticides and the use of these pesticides occur throughout the day in order to achieve higher yields in agriculture. Pesticides can reach groundwater or surface waters depending on the soil structure, vegetation, slope, by leaking from the soil or by currents from the soil. Pesticides reaching groundwater are decomposed at a lower rate due to the lack of light, temperature and oxygen [3, 4].

The use of pesticides, especially their ratio to water bodies, is an event that must be regularly examined. If the inspections are not done at certain intervals, the harms of pesticides may increase.

Fertilizers, which are used more than necessary, reach groundwater resources with rain water. In agricultural areas, pesticides should not be diluted and filled into containers; pesticide containers should not be placed near water sources. Also, pesticide containers should not be left in nature [2]. The treatment of contaminated groundwater is very difficult and expensive. Therefore, the best protection is not to pollute the groundwater at all. Pesticides can be released into the air by spraying or misting. Depending on the prospects of the particles and the weather conditions, pesticides may spread elsewhere. For this reason, if spraying will be done by air, attention should be paid to weather conditions and should be well evaluated.

Pesticides can reach quite a distance by being dragged by air. They can interact with other substances in the air and cause more effects on living things [2]. To prevent pesticides from being dragged along, the flour Henry Act constant, which better shows the evaporation temperatures of pests in many cases, should be considered, agents that controls drift while protecting the fillers, enlarging the droplet diameter, reducing the pressure (vapor pressure detecting the evaporation of pure pesticides) should be used. Provided facilities to detect, while choosing the nozzle, it is necessary to pay attention to its requirements.

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When removing it, it should be towards the air flow, and spraying should be done in suitable weather conditions [5, 6].

In this study, firstly, the initial geometries of the molecules were determined, and their geometric optimization was made on the basis of the DFT/B3LYP/6-31G(d) (Becke(B) 3 Lee-Yang-Parr (LYP)) method of density functional theory (DFT). For each molecule, possible disintegration reactions were proposed by using the calculated energy values. All calculations were performed both in the gas phase and in the water phase by modeling the solvent effect.

METHODOLOGY

The reaction model used in the computational part of this study is the reaction between the pyraclostrobin, pinoxaden, gammacyhalothrin molecules and the photo-generated •OH radicals [7]. Therefore, all the calculations were based on hydroxyl radical chemistry. Hydroxyl radicals can react with organic compounds by (i) hydrogen abstraction from single bonds, (ii) addition to double bonds, and (iii) one-electron oxidation, which is mostly loss of water from hydroxyl radical adducts. The reaction system under consideration consists of •OH radicals, in other words, of open-shell species. It is well known that open-shell molecules pose severe problems in quantum mechanical calculations. Hartree–Fock (HF) methods suffer from spin contamination, because they are wave function-based. In contrast to the HF methods, density functional theory (DFT) methods use the exact electron density instead of the wave function to calculate molecular properties and energies. Electron correlation, whose absence is the main drawback of HF methods, is accounted for in DFT methods. They suffer from spin contamination less than HF methods and this feature makes them suitable for calculations involving open-shell systems. Therefore, geometry optimizations of the reactants were performed with the DFT method. The

DFT calculations were carried out as implemented in GAUSSIAN 09 code [8], using the exchange-correlation functional B3LYP which combines HF and Becke exchange terms with the Lee–Yang–Parr correlation functional, together with the 6-31G* basis set. Vibrational frequencies were calculated for the determination of the structures as stationary points and true minima on the potential energy surfaces. All the possible stationary geometries located as minima were generated by free rotation around single bonds [9-11].

RESULTS AND DISCUSSION

In the search for a plausible mechanism for the photocatalytic degradation reaction of pyraclostrobin, pinoxaden, gammacyhalothrin molecules DFT reactivity descriptors were employed to have information about the most susceptible sites for hydroxyl radical attack. Fig. 1 shows the optimized structures of pyraclostrobin, pinoxaden, gammacyhalothrin molecules and the numbering system that is used throughout the calculations. Three main competing reaction pathways shown in Fig. 2 were determined by selecting the specific sites of pyraclostrobin molecule, on the basis of their softness values being close to that of the •OH radical.

Three main competing reaction pathways shown in Figs. 2-4 were determined by selecting the specific sites of pyraclostrobin, pinoxaden, gammacyhalothrin molecules, on the basis of their softness values being close to that of the •OH radical. The predicted mechanism was confirmed by comparison with the experimental results on simple structures reported in the literature, as explained below. The lowest-energy structure is the most stable structure. Statements in this fragmentation took place both experimentally and theoretically, as seen from the Gibbs free energy values of Tables 1-3 and support it.
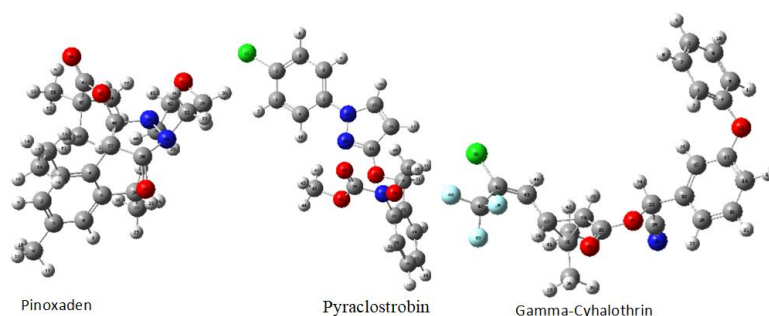

Pinoxaden   Pyraclostrobin   Gamma-Cyhalothrin

Fig. 1. The optimized geometric structure of pyraclostrobin, pinoxaden, gammacyhalothrin molecules *via* DFT method (grey: C; white: H; red: O; blue: N; green: Cl; light blue: F).
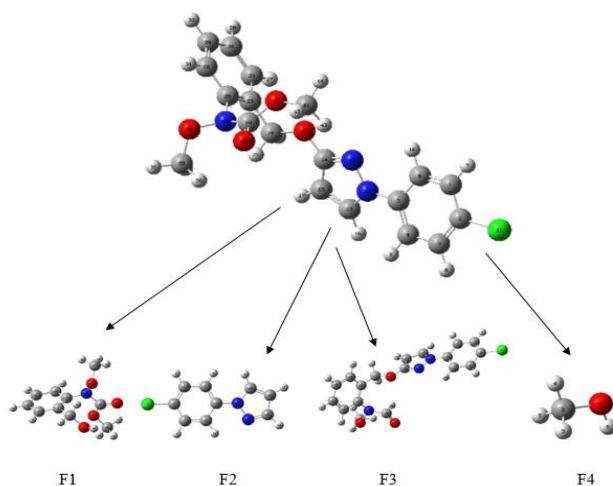
Fig. 2. Possible pathways for the photocatalytic degradation of pyraclostrobin (grey: C; white: H; red: O; blue: N; green: Cl).
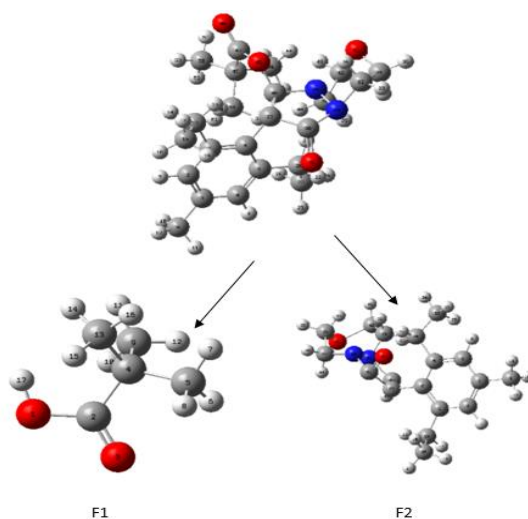

Fig. 3. Possible pathways for the photocatalytic degradation of pinoxaden (grey: C; white: H; red: O; blue: N).
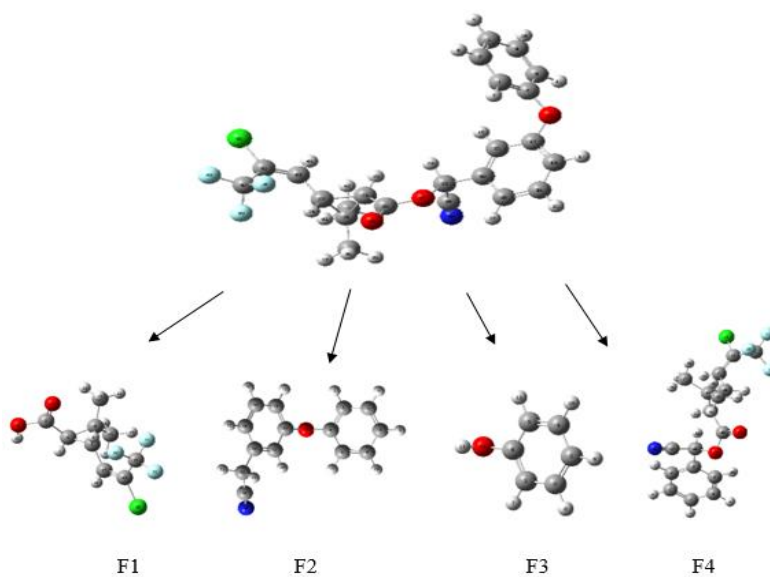

Fig. 4. Possible pathways for the photocatalytic degradation of gammacyhalothrin (grey: C; white: H; red; O; blue: N; green: Cl; light blue: F).

Table 1. Constant energy, enthalpy and Gibbs free energy values according to the DFT method.

Molecules	Phase	ΔE Energy (kcal mol⁻¹)	ΔH Enthalpy (kcal mol⁻¹)	ΔG Gibbs free energy (kcal mol⁻¹)
Pyraclostrobin	Gas	-1041505.427	-1041504.800	-1041558.326
	COSMO	*-1041517.036*	*-1041516.471*	*-1041570.123*
F1	Gas	-467005.689	-467005.124	-467043.277
	COSMO	*-467015.792*	*-467015.164*	*-467052.940*
F2	Gas	-575235.743	-575235.178	-575264.169
	COSMO	*-575237.374*	*-575236.810*	*-575264.671*
F3	Gas	-969651.128	-969650.563	-969699.948
	COSMO	*-969662.172*	*-969661.545*	*-969711.181*
F4	Gas	-72577.439	-72576.812	-72593.755
	COSMO	*-72580.64*	*-72580.075*	*-72597.018*

Table 2. Constant energy, enthalpy and Gibbs free energy values according to the DFT method.

Molecules	Phase	ΔE Energy (kcal mol⁻¹)	ΔH Enthalpy (kcal mol⁻¹)	ΔG Gibbs free energy (kcal mol⁻¹)
Pinoxaden	Gas	-819249.395	-819248.830	-819308.506
	COSMO	*-819260.250*	*-819259.623*	*-819319.362*
F1	Gas	-217656.767	-217656.203	-217682.432
	COSMO	*-217752.257*	*-217752.101*	*-217752.198*
F2	Gas	-602330.640	-602330.075	-602376.637
	COSMO	*-602340.053*	*-602339.488*	*-602386.237*

Table 3. Constant energy, enthalpy and Gibbs free energy values according to the DFT method.

Molecules	Phase	ΔE Energy (kcal mol⁻¹)	ΔH Enthalpy (kcal mol⁻¹)	ΔG Gibbs free energy (kcal mol⁻¹)
Gamma-cyhalothrin	Gas	-1209558.550	-1209557.922	-1209618.414
	COSMO	*-1209569.155*	*-1209568.590*	*-1209630.023*
F1	Gas	-789978.735	-789978.108	-790017.139
	COSMO	*-789987.332*	*-789986.705*	*-790025.171*
F2	Gas	-420330.503	-420329.938	-420366.145
	COSMO	*-420337.405*	*-420336.840*	*-420372.859*
F3	Gas	-192867.777	-192867.150	-192889.364
	COSMO	*-192871.856*	*-192871.291*	*-192893.505*
F4	Gas	-1017432.174	-1017431.546	-1017483.818
	COSMO	*-1017441.649*	*-1017441.085*	*-1017492.540*

CONCLUSIONS

The degradation system was determined for these three effective molecules. The energy values caused by the fragmentation and the electronegative atoms in it, bond lengths and angles were examined and explained. In the study, possible reaction routes were used in the reaction between pesticide active ingredients and water. It functions as an energy for a reaction to disintegration. So, the OH radicals in water break down these chemicals. The most focal structure of a group is its lowest energy state. Accordingly, when we rank the pesticide agents from the most stable to the most unstable, the order is: gammacyhalostrobin -1209558.550 kcal/mol, pyraclostrobin -1041505.427 kcal/mol, pinoxaden -819249.395 kcal/mol. Pesticide agents' purpose was to break down products down to the smallest harmless substances. As a result, when we list the 4 fragments which are the degradation products of the 1st molecule, the pyraclostrobin fragment, as the most unstable, the order is: F3 - 969651.129 kcal/mol, F2 -575235.743 kcal/mol, F1 -467005.689 kcal/mol, F4 -72577.439 kcal/mol. When we order the 2 fragments, which are the fragmentation products of the 2nd molecule pinoxaden, from the most stable to unstable, F2 is -602330.640 kcal/mol, F1 is -217656.767 kcal/mol. When we rank the 4 fragments, degradation products of the 3rd molecule, gammacyhalothrin, from the most unstable, F4 -1017441.649 kcal/mol, F1 -789978.735 kcal/mol, F2 -420330.503 kcal/mol, F3 -192867.777 kcal/mol. As can be seen from the results, the fragmentation occurred theoretically. These results will guide experimental workers and determine the fragmentation mechanism.

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