A Quantum Chemical Evaluation of the Extraction Mechanism of Imidacloprid from Aqueous Environment by Hydrophobic Eutectic Solvent

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Abstract

In recent times, Deep Eutectic Solvents (DES) have received attention as an extractive media for separations. Promising outcomes have been obtained in the field of liquid-liquid extraction of pharmaceuticals from water media with the help of DESs. In this work, a quantum chemical analysis has been investigated where DL menthol- octanoic acid-based DES was selected for the extraction of imidacloprid (pesticide) from water. The possible sites of hydrogen bonding were confirmed by the non-bonded interactions among the molecular groups. The O…H interactions between the hydrogen bond acceptor (DL menthol) and the hydrogen bond donor (octanoic acid) were confirmed whereas multiple bonding arrangements between imidacloprid and DES components were obtained. Menthol- imidacloprid interaction occurred at ~2.896 Å. Natural Bonding Orbital (NBO) analysis suggested the direction of charge transfer (CT) in the direction of DES to pesticide. HOMO-LUMO iso-surfaces for the molecular arrangements were obtained to observe the orbitals involved in the interactions between the pesticide and the DES as well as within the DES components too. The HOMOs are filled with electrons, whereas, the LUMOs are deficient of it. So, a non-bonded interaction can be confirmed between the DES component and the pesticide molecule. The HOMO-LUMO energy gap suggested higher stability for both the arrangements which can be evident by the chemical hardness (η) values.

Keywords: DES, HBA, HBD, NBO, HOMO-LUMO etc.

Introduction

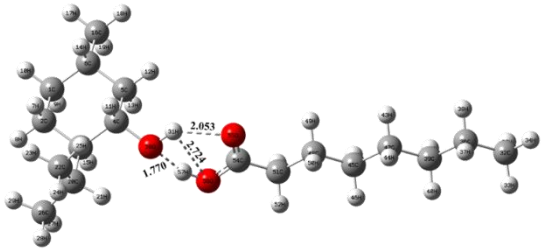
Hydrophobic deep eutectic solvents has emerged as an excellent green solvent in the removal of various pharmaceutical products from waste-water systems. DL-menthol and long-chain carboxylic acid-based DESs have been used in the extraction of pesticides from water and their excellent hydrophobicity have made them suitable for water-related treatment processes. With the proper amalgamation of the experiments and simulation, we can understand the insights into the extraction mechanism. Our present work includes quantum chemical calculation of the extraction of imidacloprid (pesticide) from an aqueous environment with DL-menthol : octanoic acid (1 :1) DES. We have studied non-bonded interactions, charge transfer process (CT), Frontier molecular orbital analysis (FMO), HOMO-LUMO studies to grasp the molecular level insights of the system. The simulated results were found to be in good agreement with the experimental findings based on the literature (Florindo et al).

Computational Methodology

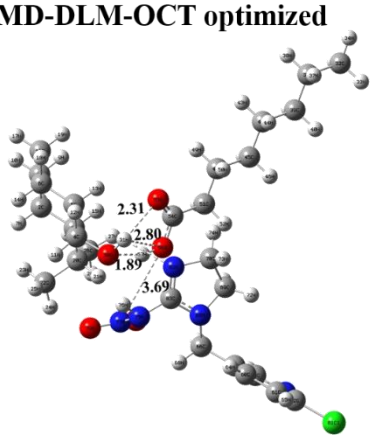
The optimized structures of imidacloprid, DES and DES- imidacloprid complex were obtained by Gaussian. The DFT studies were carried out in two basis sets i.e., B3LYP and M-062X for a comparative analysis. In our work, we have obtained two different molecular arrangements of DES and pesticide based on their mutual interactive preferences, namely ‘DES-intermolecular’ and ‘DES-intramolecular’ arrangement.

Results and Discussion

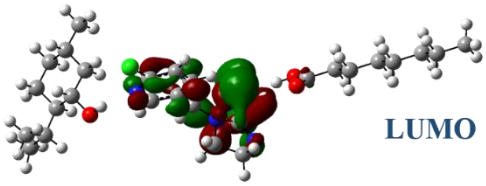
a) DLM-OCT optimized



b) IMD-DLM-OCT optimized



c) IMD-DLM-OCT complex



d) NBO charges on imidacloprid

	Imidacloprid	
	B3LYP	M062X
No DES	0	0
DLM-OCT (DES)	−0.0042	−0.0109

Figure 1. (a) Optimized structure of DL menthol- octanoic acid-based DES, (b) Optimized structure of DL menthol- octanoic acid- imidacloprid complex, (c) HOMO-LUMO orbitals of DL menthol- octanoic acid- imidacloprid complex, and (d) NBO charges on imidacloprid.

The results obtained from the QC calculation of the imidacloprid-DES systems are shown in Figure 1, where Figure 1 (a) displays the optimized structure of DL menthol- octanoic acid-based DES. The optimized structure of DL menthol- octanoic acid- imidacloprid complex is shown in Figure 1 (b), where the possible interactions have been shown. Figure 1 (c) displays the HOMO- LUMO orbitals for the imidacloprid- menthol-octanoic acid complex. Figure 1 (d) shows the NBO charges on imidacloprid with and without DES in B3LYP and M062X methods.

Conclusions

In summary, we have carried out QC simulation of imidacloprid extraction from water with menthol-octanoic acid-based hydrophobic DES. Menthol- imidacloprid interaction occurred at ~2.896 Å. Natural Bonding Orbital (NBO) analysis suggested the direction of charge transfer (CT) in the direction of DES to pesticide. The NBO charges obtained by imidacloprid are −0.0042 and −0.0109 for B3LYP and M-062X basis sets, respectively. It has been found that, HOMOs predominantly come from DL menthol and the LUMOs come from octanoic acid molecules. In case of DES-pesticide complex, HOMO and LUMO come from DL menthol and imidacloprid, respectively. Overall. The QC study suggests a strong intermolecular nonbonded interactions between the pesticide and the DES components associated with charge transfer.

References

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