INDIAN INSTITUTE OF TECHNOLOGY GUWAHATI
SHORT ABSTRACT OF THESIS

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Thesis Title: Molecular Modeling and Experimental Insights in the Application of Hydrophobic Deep Eutectic Solvents for Remediation of Micropollutant from Aqueous Systems

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SHORT ABSTRACT

Micropollutants have emerged as a new class of pollutants due to their harmful effects on humans and livestock, even at low concentrations. Even if present in low quantities, micropollutants have been associated with a range of detrimental impacts on humans and livestock, including poisoning, neurotoxicity, endocrine-disrupting effects, and microorganism antibiotic resistance. Green solvents, especially hydrophobic DESs (HDESs) through liquid-liquid extraction and microextraction (LLE/LLME) can have a revolutionary impact in achieving the efficient pharmaceutical removal pathway.

The formation mechanism and stability of HDESs in aqueous environment were studied through molecular dynamics (MD) simulation and quantum chemical (QC) calculations. The DES integrity and the disruption through water penetration, the structural arrangements at the microscopic level, compactness of the hydrogen bond acceptor (HBA) and hydrogen bond donor (HBD) within the DES, interaction energies (IE), relative stability, structural properties, hydrogen bonding (H-bonds) and transport properties (diffusivity), and the characteristics of the non-bonded interactions were thoroughly evaluated with solvation studies employing both explicit as well as implicit solvation models. MD and QC studies for two pesticide extraction (acetamiprid & imidacloprid) from an aqueous environment via HDES. Higher interaction was witnessed between pesticide and DESs to form hydrogen bonding between the molecules. The extraction efficiency of 75% and 69% by the MD simulation was close enough to that of the experiments. Charge transfer (CT) occurred in the direction of DES to the pesticide molecule in each system as per the natural bonding orbital (NBO) analysis. Frontier molecular orbital (FMO) study indicated a relatively stronger DES-pesticide complex with higher band-gap energy.

The experimental batch-type extraction of enoxacin from the aqueous environment with three hydrophobic DESs achieved 82.6%, 79.6% and 69.1% extraction efficiency three DESs. Different recycling schemes have been implemented to assess the reuse and recovery of DESs to achieve higher net extraction efficiency (NEE) ensuring a sustainable and circular approach to solvent regeneration via adsorption on activated carbon (AC). The QC calculation elucidated the strength of the DES-enoxacin interaction and provided insights regarding the interaction mechanism with structural arrangement combined with charge transfer behaviour. Non-covalent interaction (NCI) with atoms-in molecules calculation (AIM) highlighted the multiple interacting components in the formation of the DES-enoxacin complex.

PDMS (Polydimethylsiloxane) microchannel-based continuous extraction of ciprofloxacin (antibiotic) and fluconazole (antifungal) from an aqueous environment by liquid-liquid extraction using two HDESs was carried out. The influence of flow rate, residence time and DES/water mass ratio on extraction efficiency (%EE) have been evaluated through experiments. QC calculation and MD simulation results generated atomistic and molecular-level insights into the drug-DES complexes. CT, FMO, non-bonded interaction energy, and hydrogen bonding analysis explained the stability and interactive nature of the components. Non-covalent interaction (NCI) associated with reduced density gradient (RDG) analysis was incorporated to understand the noncovalent interactions such as hydrogen bonding and dispersion interactions (van der Waals) that prevailed within the drug-DES complexes.