

Comparative First-Principles Study of Ciprofloxacin Intercalation in Montmorillonite and Kaolinite

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Keywords: Ciprofloxacin; Clay minerals; Density Functional Theory (DFT-D3); *ab initio* molecular dynamics (AIMD).

The interaction of pharmaceutical contaminants with natural mineral phases is a key process controlling their environmental fate, transport, and persistence. Once released into aquatic and terrestrial environments, pharmaceutical molecules can partition between aqueous and solid phases through adsorption and incorporation into mineral structures, influencing their mobility and retention [1]. Among emerging pharmaceutical contaminants, **ciprofloxacin** (CIP), a widely used fluoroquinolone antibiotic, is of particular interest because its multifunctional and ionizable structure enables diverse interactions with mineral surfaces. **Clay minerals** are especially important because their layered structures, surface charge, interlayer environments, and hydroxylated sites provide multiple pathways for contaminant retention [2]. However, the molecular mechanisms governing CIP accommodation within structurally distinct clay minerals remain insufficiently resolved.

In this study, we present a comparative first-principles investigation of CIP incorporation into 2:1 montmorillonite (Mnt) and 1:1 kaolinite (K) using density functional theory method for solid state systems with the D3 scheme for correction of dispersion forces (**DFT-D3**), and *ab initio* molecular dynamics (AIMD) to obtain the vibrational density of states (**VDOS**) [3]. The optimized structures revealed stable CIP–clay configurations governed by strong electrostatic interactions, weaker hydrogen bonding, and the weakest dispersion forces. The expandable Mnt accommodated CIP with a basal spacing of **12.3 Å**, compared with **10.1 Å** for the less-expandable K, and intercalation was far more favorable in **Mnt** ($-1099.1 \text{ kJ mol}^{-1}$) than in **K** ($-166.08 \text{ kJ mol}^{-1}$) (Fig. 1). This reflects the combined effects of the expandable interlayer, layer charge, and Na^+ counterions in montmorillonite, whereas the confined kaolinite framework allowed only limited accommodation. **AIMD** simulations at 300 K confirmed that the principal CIP–clay interactions persist under thermal fluctuations, and VDOS analysis provided insight into the vibrational response associated with CIP incorporation.

Overall, montmorillonite provided a substantially more favorable environment for CIP accommodation and stabilization than kaolinite, driven by its expandable interlayer and stronger cumulative interactions. These findings establish a clear relationship between clay-mineral architecture, CIP adsorption and mobility, providing a mechanistic interpretation of pharmaceutical contaminant behavior in clay-rich environments and highlighting the **environmental significance** of clay–pharmaceutical interactions for predicting contaminant fate and supporting soil and water protection.

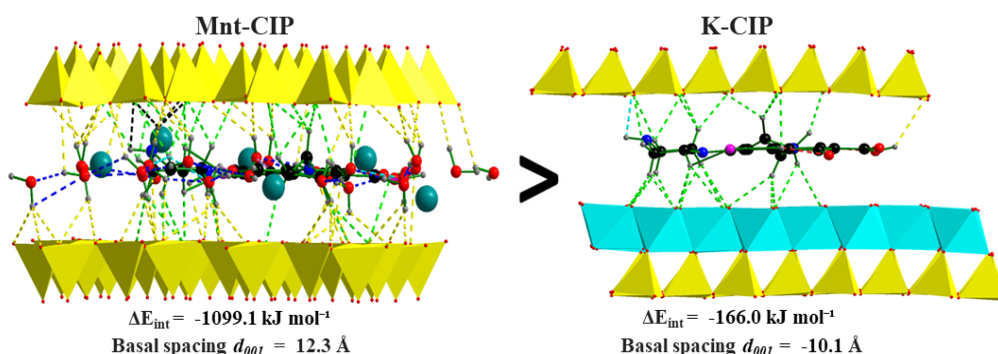


Fig. 1. Comparison of physicochemical properties after intercalation of 1:1 and 2:1 clays with ciprofloxacin.

Acknowledgments: The financial support from the Scientific Grant Agency VEGA (02/0026/23) is gratefully acknowledged. The use of computational resources from the National Competence Centre for High Performance Computing (project code: 311070AKF2), funded by the European Regional Development Fund under the EU Structural Funds program for the Informatization of Society, is also acknowledged.

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