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Atomistic Simulations of Ciprofloxacin Adsorption to Na-Montmorillonite Under Different pH Conditions

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Ciprofloxacin (CIP) is a widely used fluoroquinolone antibiotic that is frequently detected in soils, sediments, and surface waters due to its persistence and continuous release. Because antibiotics typically exhibits strong affinity for clay minerals [1], molecular-scale insight into adsorption energetics, configurations, and hydration effects is needed to predict antibiotic retention and colloid-facilitated transport in clay-rich environments.

Here, we quantify pH-dependent CIP adsorption to Na-montmorillonite (MMT) using molecular dynamics simulations with Gromacs, comprising unbiased simulations, umbrella sampling to obtain potentials of mean force (PMFs), and alchemical free-energy perturbation (FEP) to resolve hydration free energies in distinct environments. The simulations were performed for the three environmentally relevant CIP species, cationic (CIP^+), zwitterionic ($CIP^{+/-}$), and anionic (CIP^-), interacting with basal surfaces and variably hydrated interlayers. The clay/water interactions were modeled with CLAYFF/SPC and MINFF/OPC3 forcefields and water models for comparison [2,3], using angle terms to improve the clay structural properties. CIP was described with GAFF parameters, with RESP-A1 atomic charges.

All species approach comparable center-of-mass separations from the basal surface, but exhibit distinct orientational preferences. CIP^+ adsorbs predominantly in a flat configuration, $CIP^{+/-}$ partitions between flat and side-on poses, and CIP^- samples multiple metastable configurations. The free energy estimates from PMFs show favorable adsorption for all CIP species, with adsorption strength increasing steeply in the order $CIP^- < CIP^{+/-} < CIP^+$. The corresponding standard adsorption free energies are −2.1, −11.8, and −30.0 kJ mol^{-1} (Figure 1). By integrating the PMFs from the bulk to the MMT interface [4], the corresponding sorption coefficients (K_d) from the simulations was found to be 6.4, 5.2×10^2, and 1.0×10^6 cm^3 g^{-1}, respectively. Open-system simulations further indicate that CIP^+ and $CIP^{+/-}$ can intercalate into 2W and 3W hydration states, whereas CIP^- does not intercalate below 4W.

References

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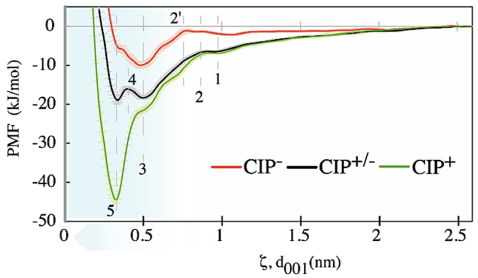


Figure 1. Potential of mean force (PMF) profiles for CIP^- (red), $CIP^{+/-}$ (black) and CIP^+ (green) adsorption to MMT along the z-direction. Error bars represent a 95 % confidence interval from 10 independent simulations. CIP^+ exhibits the deepest minimum, $CIP^{+/-}$ shows a characteristic double-minimum structure, and CIP^- displays shallow metastable states.