

Molecular Insights into the Adsorption Mechanism of Perfluorooctanoic Acid on Clay Surfaces Using Density Functional Theory

Authors : Duwage C. Perera, Ravisha N. Mudalige, Jay N. Meegoda

Abstract : Per- and polyfluoroalkyl substances (PFAS), often referred to as "forever chemicals," are a class of environmentally persistent pollutants known for their exceptional chemical stability and resistance to conventional degradation methods. Among the various PFAS compounds, perfluorooctanoic acid (PFOA) has emerged as a priority contaminant due to its widespread occurrence, bioaccumulative nature, and toxicological effects on human health and ecosystems. The need for effective remediation strategies has driven significant interest in understanding the interactions between PFOA and potential adsorbent materials such as soils and sediments at the molecular level. In this study, density functional theory (DFT) is employed to investigate the adsorption mechanisms of PFOA on kaolinite, a naturally abundant clay mineral with promising applications in PFAS remediation. The computational approach involves constructing atomistic models of the kaolinite (001) surface to capture its unique structural and chemical characteristics. Both the tetrahedral (Si-O) and octahedral (Al-O) layers of kaolinite are included in the models, with varying degrees of surface hydroxylation to simulate environmentally relevant conditions. PFOA is modeled in both protonated and deprotonated states, reflecting its behavior under different pH levels commonly encountered in natural and engineered systems. The adsorption energies are calculated to quantify the affinity of PFOA for kaolinite, while Bader charge analysis is conducted to examine charge redistribution and electrostatic interactions during the adsorption process. A detailed investigation of the molecular interactions between PFOA and kaolinite reveals the critical role of hydrogen bonding, van der Waals forces, and electrostatic interactions in PFOA adsorption. The carboxylic group of PFOA demonstrates strong binding to hydroxylated sites on the kaolinite surface, while the hydrophobic tail of PFOA interacts minimally with the mineral, reflecting its dual hydrophilic-hydrophobic nature. Vibrational frequency analysis is performed to identify shifts in the functional group vibrations, providing additional evidence of strong chemical interactions between PFOA and kaolinite. This study provides a comprehensive understanding of the molecular-level interactions governing PFOA adsorption on kaolinite. By elucidating the underlying mechanisms, it establishes a foundation for the design and optimization of clay-based remediation technologies aimed at mitigating PFAS contamination in environmental systems. Future work integrating experimental validation with the computational insights presented here will further enhance the applicability of kaolinite and other clay minerals in PFAS remediation efforts, addressing a critical global environmental challenge.

Keywords : adsorption mechanism, carbon-fluorine bond stability, density functional theory, kaolinite adsorption, perfluorooctanoic acid, PFAS, soil and water contamination

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